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Nanostructured Air Electrodes and Electrochemical Reaction Mechanism Studies for Sodium-Oxygen Batteries

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Abstract

Alkali metal-O\textsubscript{2} batteries, i.e. Li- and Na-O\textsubscript{2}, are considered as the next generation of energy saving technologies with potential application in electric transportation. The high theoretical energy density in these cells is related to the use of high energy alkali metals as negative and oxygen as the positive electrode materials. The performance of alkali metal-O\textsubscript{2} cells is highly dependent on the positive electrode material, where oxygen reduction and evolution reactions take place. Besides, the primary products of oxygen reduction reaction in these cells are typically metal oxides, which are insoluble in nonaqueous electrolytes, resulting in accumulation on the porous air electrode surface. Accordingly, an ideal air electrode should have a porous structure with appropriate pore volume and pore size distribution in addition to necessary characteristics such as conductivity, chemical stability, high surface area, and low cost. Several air electrode architectures are designed and developed in the studies presented in this thesis to improve the cyclability and performance of alkali metal-O\textsubscript{2} cells.

In the first part of experimental results, the correlation between the surface area and pore size of the air electrode materials with the electrochemical behavior of Na-O\textsubscript{2} cell was studied in detail. Series of specific air electrode materials with different surface area and porosity were synthesized using a heat-treatment procedure under various corrosive atmospheres using non-precious carbon black as starting materials. Then, the correlation between discharge capacity, surface area and porosity of the cathode materials was studied. The results indicate that the discharge capacity in Na-O\textsubscript{2} cells is linearly correlated with surface area while morphology of the solid discharge product strongly depends on specific surface area and pore size. In addition, studying the kinetics of electrochemical reactions in Na-O\textsubscript{2} cells revealed that different sodium oxides (peroxide and superoxide) species are produced during the discharge cycle of the cell.

To further improve the cyclability of Na-O\textsubscript{2} cells, a binder-free three dimensional (3D) air electrode was designed and synthesized in the second part of this thesis. The air electrode was composed of vertically grown nitrogen doped carbon nanotubes on carbon paper. The electrochemical tests demonstrated that 3D architecture of the air electrode results in
increased discharge capacity by optimizing the utilized area of the electrode material. Moreover, synchrotron-based X-ray absorption spectroscopy was employed to study the failure mechanism of the cell. The results revealed that formation of parasitic carbonate-based side products on the carbon surface increases the charging overpotential of the cell and results in battery failure.

Based on the results from previous parts, a combination of carbonaceous hierarchical 3D structured design with a mesoporous Mn$_3$O$_4$/Pd bifunctional catalyst was employed to prepare the air electrode in the next part. The catalyst layer in this design serves as a protective layer against the oxidation of the carbon surface by highly oxidative environment of the cell and also decreases the charging overpotential. Electrochemical studies showed a stable cycling performance as well as a synergistic catalytic effect in both Na- and Li-O$_2$ cells. Spectroscopic investigations revealed a dynamic electron exchange between Pd and Mn$_3$O$_4$ during the discharge and charge cycles of the cell which is responsible for the synergetic effect. In addition, analysis of the discharge products in both Na- and Li-O$_2$ cells demonstrated that the oxygen-bonding properties of the electrode surface may increase the oxygen-rich phase of the products by stabilizing the superoxide intermediate and hence reduce the charging overpotential of the cell.

In the final part of this study, the influence of oxygen-containing functional groups on the morphology and composition of discharge products in alkali metal-O$_2$ cell is studied. The results suggest that functional groups on the carbon surface play a significant role in choosing either the surface-mediated or the solution-mediate mechanisms for formation of the discharge products. The results presented in this study help to better understand the electrochemical mechanism governing on alkali metal-O$_2$ cells and contribute to improve the performance of the cells.

**Keywords:** Sodium-oxygen batteries; Lithium-oxygen batteries; Electrocatalysis; Reaction mechanism; Nanomaterials, Mesoporous, Nitrogen-doped carbon nanotubes; Graphene foam; Three-dimensional electrodes; hierarchical structures; Atomic layer deposition; Palladium
Co-Authorship Statement

1. Title: On rechargeability and reaction kinetics of sodium-air batteries

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# Table of Contents

Co-Authorship Statement........................................................................................................ ii
Acknowledgments....................................................................................................................... iv
Table of Contents ....................................................................................................................... v
List of tables ................................................................................................................................... ix
List of Figures .............................................................................................................................. x
List of Abbreviations .................................................................................................................. xxi

Chapter 1 .................................................................................................................................. 1

1 Literature review .................................................................................................................... 1

1.1 Introduction ......................................................................................................................... 1

1.2 Principles of Na-O\textsubscript{2} cell ....................................................................................... 5

1.2.1 Electrochemical reactions in Na-O\textsubscript{2} cell .......................................................... 5

1.2.2 Chemistry of sodium and sodium oxides ........................................................................ 9

1.2.3 Components of the Na-O\textsubscript{2} cell ........................................................................... 11

1.3 Charging overpotential in Na-O\textsubscript{2} cells .................................................................. 15

1.3.1 Theoretical calculations ................................................................................................. 15

1.3.2 Chemical composition of the discharge product in Na-O\textsubscript{2} cells ......................... 18

1.4 Cyclability in Na-O\textsubscript{2} cell ......................................................................................... 31

1.4.1 Morphology of the discharge products ......................................................................... 31

1.4.2 Side reactions ................................................................................................................. 35

1.5 Air electrode design ............................................................................................................ 50

1.5.1 Carbon based air electrodes ......................................................................................... 50

1.5.2 Catalyst .......................................................................................................................... 54

1.6 Summary and conclusion remarks ..................................................................................... 61

1.7 Thesis objectives ................................................................................................................. 62
1.8 Thesis organization ........................................................................................................ 63

References ..................................................................................................................... 65

Chapter 2 .......................................................................................................................... 72

2 Experimental methods................................................................................................. 72

2.1 Synthesis of electrode materials................................................................................ 72

2.1.1 Mesoporous carbon black with controlled porosity ........................................... 72

2.1.2 Three-dimensional nitrogen doped carbon nanotubes on carbon paper ............. 73

2.1.3 Three-dimensional nitrogen doped carbon nanotubes on graphene foam ............... 75

2.2 Characterization techniques ...................................................................................... 76

2.2.1 Morphological observation .................................................................................. 76

2.2.2 X-ray diffractometry ........................................................................................... 78

2.2.3 X-ray absorption spectroscopy ........................................................................... 79

2.2.4 Other techniques .................................................................................................. 79

2.3 Electrochemical measurements ................................................................................. 80

References ..................................................................................................................... 81

Chapter 3 .......................................................................................................................... 82

3 On Rechargeability and Reaction Kinetics of Sodium-Air Batteries ......................... 82

3.1 Introduction ............................................................................................................... 83

3.2 Experimental ............................................................................................................. 85

3.2.1 Positive electrode material preparation ............................................................ 85

3.2.2 Physical characterizations .................................................................................. 85

3.2.3 Electrochemical Measurements ......................................................................... 86

3.3 Results and discussion ............................................................................................. 87

3.4 Conclusion ................................................................................................................ 118

References ..................................................................................................................... 119
Chapter 4: Three-Dimensional Nanostructured Air Electrode for Sodium-Oxygen Batteries: A Mechanism Study toward the Cyclability of the Cell

4.1 Introduction

4.2 Experimental

4.2.1 Preparation of the air electrode

4.2.2 Physical characterizations

4.2.3 Electrochemical Measurements

4.3 Results and discussion

4.4 Conclusion

Chapter 5: Atomically Deposited Pd on Mesoporous Mn$_3$O$_4$ as Catalyst for Na and Li-O$_2$ Peroxide Cells: Revealing the Role of Catalyst

5.1 Introduction

5.2 Experimental

5.2.1 Synthesis of electrode materials

5.2.2 Physical Characterizations

5.2.3 Electrochemical Measurements

5.3 Results and Discussion

Chapter 6: Effect of solvent DN and properties of air electrode surface on the chemical composition and morphology of discharge products in Na-O$_2$ cell

6.1 Introduction

6.2 Experimental
6.2.1 Preparation of the air electrode ................................................................. 199
6.2.2 Physical characterizations ................................................................. 199
6.2.3 Electrochemical Measurements ...................................................... 200
6.3 Results and discussion ........................................................................ 201
6.4 Conclusion ................................................................................................. 210
References .................................................................................................. 211
Chapter 7 ........................................................................................................ 212
7 Conclusion and future remarks ................................................................. 212
7.1 Summary of the results ......................................................................... 212
7.2 Future perspective ................................................................................. 215
Curriculum Vitae .......................................................................................... 217
List of tables

Chapter 1

Table 1.1: A summary of the reported discharge products for Na-O2 battery system....... 2

Table 1.2: The calculated ionic and electronic conductivity values for NaO2, Na2O2
and Li2O2. Adapted from ref. 54. .................................................................................. 18

Table 1.3: An overall summary of the reported stability of polymer binders versus
superoxide and peroxide. .................................................................................................. 49

Table 1.4 A summary of physical properties, experimental conditions and
electrochemical responses of the carbonaceous air electrodes employed in Na-O2
cells. .................................................................................................................................. 57

Chapter 2

Table 2.1: BET specific surface area of heat treated carbon materials under different
atmospheres...................................................................................................................... 72

Chapter 5

Table 5.1: Comparison of BET surface area of the synthesized electrodes............. 167

Table 5.2: The structural parameters obtained from curve fitting depicted in Figure
5.17.................................................................................................................................... 172

Table 5.3: The structural parameters obtained from curve fitting depicted in Figure
5.29.................................................................................................................................... 187
List of Figures

Chapter 1

Figure 1.1: Major challenges of Na-O\textsubscript{2} cell. ................................................................. 4

Figure 1.2: Schematic diagram of Na-O\textsubscript{2} cell. ........................................................................... 6

Figure 1.3: (a) Cyclic voltammograms of a glassy carbon electrode (vs. Ag/AgCl) for the reduction of oxygen in the presence of 0.1 M TBAPF\textsubscript{6} (black), 0.1 M TBACIO\textsubscript{4} (blue), and the argon background (dotted) in MeCN solution. (b) Cyclic voltammograms of a glassy carbon electrode (vs. Ag/AgCl) for the oxygen reduction in the presence of 0.1 M LiPF\textsubscript{6} (dashed line), 0.1 M NaPF\textsubscript{6} (solid line), and KPF\textsubscript{6} (dash-dotted line) in MeCN solution. (Scan rate = 100 mV s\textsuperscript{-1}). Adapted from ref. 32................................................ 8

Scheme 1.1: The electronic structure of peroxide and superoxide ions. .................................................. 10

Figure 1.4: (a) Cross section SEM images of a pristine separator and one after cycling. (b) Application of a Na-beta-alumina solid electrolyte membrane (0.5 mm thickness) as barrier for dendrite growth.\textsuperscript{19} (c) Optical images of the Na anode surfaces and separators under different cycling conditions. The surface roughness increases upon increasing the cutoff discharge capacity as well as the cycle number due to the Na dendrit growth.\textsuperscript{22} Adapted from ref. 19 and 22. ......................... 13

Figure 1.5: (a) Phase stability map of various lithium/sodium oxides as a function of oxygen chemical potential or oxygen partial pressure. The blue region shows the oxygen chemical potential range under nonequilibrium conditions that can result from fast consumption of O\textsubscript{2} in the electrolyte during discharge.\textsuperscript{27} (b) Phase diagram of Na-O as function of temperature and O\textsubscript{2} partial pressure.\textsuperscript{28} (c) Phase diagram of Na\textsubscript{2}O\textsubscript{2} (red) and NaO\textsubscript{2} (green) at 300 K as a function of particle size and P\textsubscript{O2} at the O\textsubscript{2} gas limit.\textsuperscript{28} Adapted from ref. 27 and 28. ......................... 16

Figure 1.6: (a) Discharge/charge cycles of Na-O\textsubscript{2} cells at various current densities.\textsuperscript{4} (b) Galvanostatic discharge/charge of a Na-O\textsubscript{2} cell (top); O\textsubscript{2} consumption, n\textsubscript{O2,d}, and NaO\textsubscript{2} formation, n\textsubscript{d}, during discharge (middle); O\textsubscript{2} evolution, n\textsubscript{O2,c}, and NaO\textsubscript{2} oxidation, n\textsubscript{c}, during charge (bottom) (the dashed black line is a 1 e\textsuperscript{-} process). 0.2 N NaOTf in DME were used as electrolytes and the cell was discharged and charged at 0.5 mA.\textsuperscript{21} (c) The thermodynamic data of Na-O\textsubscript{2} cell.\textsuperscript{40} Adapted from ref. 4, 21 and 40................................................................. 20

Figure 1.7: (a) Limited discharge and charge curves of the Na-O\textsubscript{2} cell at current densities of 75 and 40 mA g\textsuperscript{-1}, respectively.\textsuperscript{26} (b) Limited discharge and charge curves of Na-O\textsubscript{2} cells at different discharge current densities of 75, 150 and 300 mA g\textsuperscript{-1} and a constant charge current density of 40 mA g\textsuperscript{-1}.\textsuperscript{26} (c) Oxygen 1s spectra
of reference sodium peroxide and discharge products resulted at current densities of 75 and 300 mA g\(^{-1}\). (d) Restricted discharge and charge curves of Na-O\(_2\) cell at different discharge current densities of 0.1, 0.5, and 1.0 mA cm\(^{-2}\) and a constant charge current density of 0.1 mA cm\(^{-2}\) (top); normalized O K-edge XANES spectra recorded under the TEY and FLY modes for the air electrodes discharged under different current densities of 0.1, 0.5, and 1.0 mA cm\(^{-2}\) (left) and for the air electrodes charged to the various cutoff potentials of 2.75, 3.5, and 4.3 V (color coded) as well as the discharged air electrode and the standard Na\(_2\)O\(_2\) sample (right).\(^{30}\) Adapted from ref. 26 and 30.

Figure 1.8: (a and b) Cyclic voltammogram of a gold electrode in (a) CH\(_3\)CN and (b) Me-Im with various ratios of [Li\(^+\)]:[TBA\(^+\)]. The Li\(^+\) concentration is depicted on the plots, where the remaining concentrations to 100 mM are TBA\(^+\). The scan rate was 100mV s\(^{-1}\) and the anion was ClO\(_4\)\(^-\). (c) Schematic of the O\(_2\) reduction mechanism in an aprotic solvent containing Li\(^+\) showing the surface pathway followed when \(\Delta G^0 > 0\) (low DN) and the solution pathway followed when \(\Delta G^0 < 0\) (high DN). Plot at right corner shows the dominant pathway as a function of DN and potential. Adapted from ref. 75.

Figure 1.9: SEM micrographs of the discharge products of Na-O\(_2\) cell using (a and b) carbon fiber;\(^{19, 40}\) (c) vertically aligned carbon nanotubes;\(^{22}\) (d) nitrogen-doped graphene nanosheets;\(^{16}\) (e) carbon nanotube paper;\(^{18}\) (f) NiCo\(_2\)O\(_4\) nanosheets;\(^{83}\) (g) prous CaMnO\(_3\);\(^{23}\) (h) nitrogen-doped carbon nanotubes;\(^{84}\) (i) nitrogen-doped carbon nanotubes on carbon paper\(^{30}\) air electrodes. (j-l) Change in morphology of the discharge products of Na-O\(_2\) cell using heat-treated carbon black with different specific surface area values of (j) 155.3 (k) 1053.5 (l) 1390.1 m\(^2\) g\(^{-1}\) as the air electrode.\(^{26}\) (m-o) Change in morphology of the discharge products of Li-O\(_2\) cell using Vulcan XC72 carbon black air electrode discharge under different current densities of (m) 5; (n) 25; and (o) 100 \(\mu\)A cm\(^{-2}\).\(^{67}\) Adapted from ref. 16, 18, 19, 22, 23, 26, 30, 37, 67, 83 and 84.

Figure 1.10: (a) Galvanostatic discharge-charge curves of Li- and Na-O\(_2\) cells, and total Li\(_2\)CO\(_3\) and Na\(_2\)CO\(_3\) formed as measured by CO\(_2\) evolution from discharged and partially charged cathodes immersed in 3 M H\(_2\)SO\(_4\). The labels of the black arrows in are the charge-normalized Li\(_2\)CO\(_3\) or Na\(_2\)CO\(_3\) (in \(\mu\)mol Li\(_2\)CO\(_3\) or Na\(_2\)CO\(_3\)/mAh) over the corresponding regions.\(^{21}\) (b) Gradual increase of the charging overpotential during consecutive discharge and charge curves of Na-O\(_2\) cell using NCNT-CP air electrode cycled between 1.8 and 4.3 V at a current density of 0.1 mA cm\(^{-2}\).\(^{30}\) (c) Normalized O K-edge XANES spectra recorded under the TEY mode for the cycled air electrode as well as the standard Na\(_2\)O\(_2\) and Na\(_2\)CO\(_3\) samples.\(^{30}\) Adapted from ref. 21 and 30.

Figure 1.11: Effect of CO\(_2\) on the electrochemical behavior of Na-O\(_2\) batteries. (a) Schematic graph of OER reaction pathways of a Li-O\(_2\) battery in the presence of CO\(_2\) with DME and DMSO electrolytes summarized from theoretical calculation and experimental evidence.\(^{87}\) (b) Comparison of discharge profiles of Na-CO\(_2\), Na-O\(_2\), and Na-CO\(_2\)/O\(_2\) cells with tetraglyme electrolyte.\(^{94}\) (c) GITT discharge profile
of Na-CO$_2$/O$_2$ cell with propylene carbonate electrolyte with the dotted lines indicating the theoretical potentials.\textsuperscript{95} Adapted from ref. 87, 94 and 95. .................. 40

Figure 1.12: Effect of water on the electrochemical response of Na-O$_2$ batteries. (a) Discharge curves of Na-air batteries under dry and humid air ambience with relative humidity of 10\% to 60\%.\textsuperscript{96} (b) Calculated theoretical redox potentials of the possible reactions in Na-air batteries with and without the participation of water.\textsuperscript{104} (c) First discharge curves of Na-O$_2$ cells using water-free and water-containing NaOTf salts and (inset) evolution of cell capacity toward water contents ranging from 0 to 14 ppm.\textsuperscript{105} (d) XRD patterns of the discharged cathodes: black for dry pure NaOTf, blue for with 8 ppm water added, red for pure NaOTf with 14 ppm water, magenta for with 10 ppm anhydrous benzoic acid added, green for with 10 ppm anhydrous acetic acid added.\textsuperscript{105} (e) Schematic graphs of the role of proton playing in ORR and OER processes of Na-O$_2$ cells as phase-transfer catalyst.\textsuperscript{105} Adapted from ref. 104 and 105. .............................................. 46

Figure 1.13: Application of carbonaceous air electrode with various architectures in Na-O$_2$ cells: (a) diamond-like carbon (DLC) thin film discharged at 1/60C-3C in 1M NaPF$_6$/1:1 EC/DMC;\textsuperscript{6} (b) pristin and nitrogen-doped graphene nanosheets (GNS and N-GNS) discharged at 75-300 mA g$^{-1}$ in 0.5 M NaSO$_3$CF$_2$/DEGDME;\textsuperscript{16} (c) heat-treated carbon black with different specific surface area discharged at 75 mA g$^{-1}$ in 0.5 M NaSO$_3$CF$_2$/DEGDME;\textsuperscript{26} (d) ordered mesoporous carbon (OMC) discharged at 100 mA g$^{-1}$ in 0.5 M NaSO$_3$CF$_2$/PC;\textsuperscript{25} (e) carbon nanotube paper discharged at 500 mA g$^{-1}$ in 0.5 M NaTFSI/TEGDME;\textsuperscript{18} (f) vertically aligned carbon nanotubes (VACNTs) grown on stainless steel discharged at 67 mA g$^{-1}$ in 0.5 M NaSO$_3$CF$_2$/TEGDME;\textsuperscript{25} (g) carbon nanotubes with added carbon nanofibers (CF-CNT) and carbon nanotubes with added carbon black (CB-CNT) discharged at 200 $\mu$A cm$^{-2}$ in 0.5 M NaOTf/DEGDME;\textsuperscript{111} (h) nitrogen-doped carbon nanotubes on carbon paper (NCNT-CP) discharged at 0.1-0.5 mA cm$^{-2}$ in 0.5 M NaSO$_3$CF$_2$/DEGDME.\textsuperscript{30} Adapted from ref. 6, 16, 18, 22, 25, 26, 30 and 111. ............................................................................ 52

Figure 1.14: Typical catalysts adopted for Na-O$_2$ batteries. SEM and XRD patterns of (a) NiCo$_2$O$_4$,\textsuperscript{83} (b) CaMnO$_3$,\textsuperscript{23} and (c) Pt@graphene nanosheets air electrodes.\textsuperscript{24} (d) Charge and discharge curves and schematic graph of a typical Na-O$_2$ cell with soluble NaI catalyst in electrolyte.\textsuperscript{126} Adapted from ref. 23, 24, 83 and 126. ........... 58

Chapter 2

Figure 2.1: Schematic diagram of NCNT-CP preparation........................................ 74

Figure 2.2: Digital photo of SEM (Hitachi, S-4800) machine.................................. 77

Figure 2.3: Digital photo of TEM (Hitachi, H-7000) machine.................................. 77

Figure 2.4: Digital photo of Bruker D8 Advance XRD machine.............................. 78
Chapter 3

Figure 3.1: Schematic diagram of carbon black electrode material during the heat-treatment process........................................................................................................... 87

Figure 3.2: SEM micrographs of (a) N330 and NH$_3$-treated carbon black with (b) 13%, (c) 35%, (d) 50%, (e) 75% and (f) 85% mass losses. ................................................... 88

Figure 3.3: Nitrogen adsorption/desorption isotherms of different heat-treated carbon materials under (a) NH$_3$; (b) CO$_2$ and (C) CO$_2$/H$_2$ atmospheres with various mass losses. ................................................................................................................................. 90

Figure 3.4: Pore size distribution plots for (a) NH$_3$-; (b) CO$_2$- and (c) CO$_2$/H$_2$-treated carbon materials with different mass losses from 0 to 90%. ................................................... 91

Figure 3.5: (a) Discharge curves of Na-air cells using NH$_3$-treated carbon materials with different mass losses from 0 to 85% as cathode electrode recorded at a current density of 75 mA g$^{-1}$; (b) Plot of specific capacitance and specific surface area of the cathode electrode materials of the cells depicted at Fig. 3.5a as a function of mass loss; (c) Area-normalized specific capacity of the cells depicted at Fig. 3.5a as a function of mass loss................................................... 93

Figure 3.6: Plots of specific capacitance and specific surface area of the cathode electrode materials of the cells using (a) CO$_2$- and (b) CO$_2$/H$_2$-treated carbon materials as a function of mass loss. ........................................................................................................... 94

Figure 3.7: Total pore volume of different heat-treated carbon materials under NH$_3$; CO$_2$ and CO$_2$/H$_2$ atmospheres plotted versus mass losses. ................................................................. 95

Figure 3.8: Morphology of discharge products of the Na-air cells using different NH$_3$-treated carbon materials with 0 (a), 13 (b), 35 (c), 50 (d), 75 (e) and 85% (f) mass losses as cathode electrode (Discharge current density: 75 mA g$^{-1}$). ................................................... 96

Figure 3.9: Morphology of discharge products of the Na-O$_2$ cells using different CO$_2$-treated carbon materials with 10 (a), 30 (b), 50 (c), 75 (d) and 90% (e) mass losses as cathode electrode. ........................................................................................................... 97

Figure 3.10: Morphology of discharge products of the Na-O$_2$ cells using different CO$_2$/H$_2$-treated carbon materials with 10 (a), 30 (b), 50 (c), 75 (d) and 90% (e) mass losses as cathode electrode. ........................................................................................................... 98
Figure 3.11: SEM micrographs of carbon (NH₃-heat treated with 85% mass loss) electrode before discharge (a-c) and after charge (d-f) with different magnifications. ................................................................. 99

Figure 3.12: Morphology of discharge products of the Na-air cell using NH₃-treated carbon material with 85% mass loss as cathode electrode after (a) 8, (b) 16, (c) 24 and (d) 36 hours of discharge (Discharge current density: 75 mA g⁻¹). ...................... 100

Figure 3.13: SEM micrographs with different magnifications of discharge products of the Na-O₂ cell using NH₃-treated carbon material with 85% mass loss as cathode electrode after (a, b) 8, (c, d) 16, (e, f) 24 and (g, h) 36 hours of discharge. ................. 101

Figure 3.14: Schematic diagram of Na-air cell using different heat-treated carbon materials as cathode electrode................................................................. 103

Figure 3.15: Limited discharge/charge curves of Na-air cell using NH₃-treated carbon with 85% mass loss at current densities of 75 and 40 mA g⁻¹, respectively. ............... 104

Figure 3.16: Limited discharge/charge curves of Na-O₂ cells using CO₂- and CO₂/H₂-treated carbon materials with 90% mass loss as cathode electrode. ..................... 104

Figure 3.17: XRD patterns of positive electrode, electrolyte salt and discharge products of Na-air cell................................................................................................. 105

Figure 3.18: XRD patterns of positive electrode after discharge of the Na-air cell to 1.8 V and also after charge to 2.75, 3.60 and 4.0 V .................................................... 107

Figure 3.19: Raman spectra of positive electrode after discharge and first charge step shown in Fig. 3.15, the peak marked with asterisk refers to NaO₂ phase ................. 107

Figure 3.20: FTIR spectra of positive electrode after discharge and charge to the various regions shown in Fig. 3.15 ................................................................. 108

Figure 3.21: Discharge curves of Na-air cells using NH₃-treated carbon material with 85% mass loss as cathode electrode recorded at different current densities of 75, 150 and 300 mA g⁻¹................................................................. 109

Figure 3.22: (a) Oxygen 1s spectra of reference sodium peroxide; and discharged products resulted at current densities of (b) 75 and (c) 300 mA g⁻¹ .................... 111

Figure 3.23: Sodium 1s spectra of reference sodium peroxide as well as discharged products resulted at current densities of 75 and 300 mA g⁻¹............................... 112

Figure 3.24: XRD patterns of positive electrode materials after discharge of the cell to 1.8 at different current densities of 75 and 300 mA g⁻¹ ...................................... 113

Figure 3.25: Limited discharge and charge curves of Na-air cells using NH₃-treated carbon material with 85% mass loss as cathode electrode recorded at different
discharge current densities of 75, 150 and 300 mA g\(^{-1}\) and a constant charge current density of 40 mA g\(^{-1}\). ................................................................. 114

Figure 3.26: Limited discharge (from 250 to 1000 mAh g\(^{-1}\)) and charge curves of Na-air cells using NH\(_3\)-treated carbon material with 85% mass loss as cathode electrode recorded at constant discharge and charge current densities of 300 and 75 mA g\(^{-1}\), respectively. ................................................................. 115

Figure 3.27: Cyclic voltammogram of Na-air cell recorded at a potential sweep rate of 10 mV s\(^{-1}\) in a potential range of 1.8 to 4.0 V. The CV recording was started by the cathodic sweep from 2.5 to 1.8 V followed by the anodic sweep from 1.8 to 4.0 V and terminated to the start point. ................................. 116

Figure 3.28: First three limited discharge and charge curves of Na-air cell recorded at current density of 150 mA g\(^{-1}\)............................................................. 117

Chapter 4

Figure 4.1: SEM (a-e) and TEM (f) micrographs of pristine CP (a) and NCNT-CP (b-f) air electrode synthesized via SPCVD method for 3 minutes. ....................... 126

Figure 4.2: High resolution TEM micrographs of NCNTs synthesized using SPCVD method (scale bar = 100 nm). ................................................................. 127

Figure 4.3: SEM micrographs of NCNT-CP air electrode synthesized via SPCVD method for prolonged synthesis times of 5 (a-c) and 10 (d-f) minutes. .................. 128

Figure 4.4: (a) Nitrogen adsorption/desorption isotherm of the synthesized NCNT-CP air electrode; (b) Pore size distribution plot of the NCNT-CP air electrode.......... 129

Figure 4.5: XPS survey scan of NCNTs prepared using the spray pyrolysis CVD method; inset: high resolution N1s spectrum......................................................... 129

Figure 4.6: Raman spectra of NCNT-CP air electrode. .......................................................... 130

Figure 4.7: Discharge curves of pristine CP and NCNT-CP air electrodes (NCNT length of 10 µm) at a current density of 0.1 mA cm\(^{-2}\) (a); Discharge curves of NCNT-CP air electrodes obtained at different current densities of 0.1, 0.2, 0.5 mA cm\(^{-2}\) (b); the specific capacities are calculated based on the geometric surface area (mAh cm\(^{-2}\)) and also based on the total weights of CP and NCNT-CP electrodes (mAh g\(^{-1}\))......................................................................................... 131

Figure 4.8: The discharge/charge curves of the NCNT-CP air electrode under various current densities and full discharge depth........................................ 132
Figure 4.9: Thermogravimetric analysis (TGA) of the pristine CP, NCNT and NCNT-CP electrodes with 10 and 25 µm length of NCNT .................................................. 133

Figure 4.10: The specific capacity for NCNT-CP and other CNTs containing air electrodes with different architectures including powder-based, CNTs paper and vertically aligned CNTs from the literature........................................ 134

Figure 4.11: Discharge curves of Na-O₂ cell using NCNT-CP air electrodes prepared through the prolonged synthesis times .......................................................... 134

Figure 4.12: Restricted discharge and charge curves of Na-O₂ cell using NCNT-CP air electrode recorded at different discharge current densities of 0.1, 0.5 and 1.0 mA cm⁻² and a constant charge current density of 0.1 mA cm⁻² (a); Normalized O (b and d) and Na (c and e) K-edge XANES spectra recorded under the TEY (b and c) and FLY (d and e) modes for the NCNT-CP air electrodes discharged under different current densities of 0.1, 0.5 and 1.0 mA cm⁻² as well as standard Na₂O₂ sample ................................................ 136

Figure 4.13: The normalized O K-edge spectra recorded in the TEY mode for potassium superoxide (KO₂), sodium peroxide (Na₂O₂) and lithium peroxide (Li₂O₂) standard samples ........................................................................................................ 137

Figure 4.14: The normalized O K-edge spectra recorded in both TEY and FLY modes for Na₂O₂ standard sample ................................................................................................................. 139

Figure 4.15: XRD patterns of the pristine NCNT-CP air electrode as well as the air electrodes discharged at lower and higher current densities of 0.1 and 0.5 mA cm⁻¹ in Na-O₂ cell ................................................................................................................................. 139

Figure 4.16: (a) Restricted discharge and charge curves of Na-O₂ cell using NCNT-CP air electrode recorded at discharge and charge current density of 1.0 and 0.1 mA cm⁻², respectively; Normalized O (b and d) and Na (c and e) K-edge XANES spectra recorded under the TEY (b and c) and FLY (d and e) modes for the NCNT-CP air electrodes charged to the various cut-off potentials of 2.75, 3.5 and 4.3 V as well as the discharged air electrode and the standard Na₂O₂ sample.................. 140

Figure 4.17: The normalized O K-edge spectra recorded in the TEY mode for NCNT-CP air electrode charged to 4.3 V as well as standard samples of Na₂O₂, Na₂CO₃ and NaSO₃CF₃ as the references .............................................................. 141

Figure 4.18: The normalized Na K-edge spectra recorded in the TEY mode for NCNT-CP air electrode charged to 4.3 V as well as standard samples of Na₂O₂, Na₂CO₃ and NaSO₃CF₃ as the references .............................................................. 142

Figure 4.19: (a) Cycling profiles of Na-O₂ cells using NCNT-CP air electrode restricted to the different discharge capacities of 0.14, 0.28, 0.5 and 1.0 mAh cm⁻²; (b) Consecutive restricted discharge and charge curves of Na-O₂ cell using NCNT-CP air electrode cycled between 1.8 and 4.3 V at a current density of 0.1 mA cm⁻². 143
Figure 4.20: Normalized O (a), and Na (b) K-edge XANES spectra recorded under the TEY mode for the cycled air electrode as well as the standard Na$_2$O$_2$ and Na$_2$CO$_3$ samples................................................................. 144

Figure 4.21: FTIR spectra of Na$_2$CO$_3$ (a); Na$_2$O$_2$ (b); as-prepared NCNT-CP air electrode (c); and NCNT-CP air electrode cycled in Na-O$_2$ cell restricted to different discharge capacities of 0.5 (d) and 1.0 mAh cm$^{-1}$ (e)................................. 145

Figure 4.22: Schematic illustration of the Na-O$_2$ cell operational mechanism........ 146

Chapter 5

Figure 5.1: SEM micrographs of Gr foam before and after Ni removal.................. 158

Figure 5.2: SEM micrographs of Gr/NCNT (a-c) and Gr/NCNT/MnO (d-f) electrodes with different magnifications................................................................. 159

Figure 5.3: Raman spectra of Gr, Gr/NCNT and Gr/NCNT/MnO electrodes......... 160

Figure 5.4: Thermogravimetric analysis (TGA) of Gr foam, Gr/NCNT and Gr/NCNT/MnO electrodes................................................................. 161

Figure 5.5: SEM micrographs of Gr/NCNT/MnO/Pd and Gr/NCNT/Pd with various ALD cycles................................................................. 162

Figure 5.6: TEM, HAADF and HRTEM micrographs of Gr/NCNT/MnO electrode before and after 100 cycles of Pd deposition by ALD ......................... 163

Figure 5.7: TGA results of NCNT/MnO/Pd electrode materials before and after various number of Pd ALD cycles................................................................. 164

Figure 5.8: Nitrogen adsorption/desorption isotherms of Gr/NCNT, Gr/NCNT/MnO and Gr/NCNT/MnO/Pd-100C electrodes................................................................. 165

Figure 5.9: Nitrogen adsorption/desorption isotherms of Gr/NCNT/MnO/Pd-100C electrodes with various number of Pd ALD cycles................................................................. 166

Figure 5.10: Pore volume distribution of Gr/NCNT/MnO in comparison with that of Gr/NCNT/MnO/Pd electrodes with various cycles of Pd deposition by ALD .... 166

Figure 5.11: XRD pattern of Gr/NCNT, Gr/NCNT/MnO and Gr/NCNT/MnO/Pd-100C electrodes................................................................. 167

Figure 5.12: XRD pattern of Gr/NCNT and Gr/NCNT/Pd-100C electrodes.............. 168

Figure 5.13: Normalized Mn (a) and TEY O (b) K-edge XANES spectra of standard Mn$_3$O$_4$, Gr/NCNT/MnO and Gr/NCNT/MnO/Pd electrodes................................................................. 169
Figure 5.14: Normalized O k-edge XANES spectra of MnO$_2$ and Mn$_2$O$_3$ and Mn$_3$O$_4$
standard samples recorded under TEY mode............................................................... 170

Figure 5.15: Normalized O k-edge XANES spectra of standard Mn$_3$O$_4$, Gr/NCNT/MnO and Gr/NCNT/MnO/Pd electrodes recorded under FLY mode. .... 170

Figure 5.16: (a) normalized Pd K-edge XANES spectra of standard Pd foil, Gr/NCNT/Pd and Gr/NCNT/MnO/Pd electrodes; (b) Fourier transform $K^3$-weighted EXAFS spectra of standard Pd foil, Gr/NCNT/Pd and Gr/NCNT/MnO/Pd electrodes alongside with simulated results for Pd and PdO crystals............................................................................................................ 172

Figure 5.17: Fourier transform signal $\chi(R)$ of the experimental (circles) and calculated (solid line) Pd K-edge EXAFS $\chi(k)$ for standard Pd foil, Gr/NCNT/Pd and Gr/NCNT/MnO/Pd electrodes. The crystal structures of Pd/O used as fitting model are also given........................................................................................................ 173

Figure 5.18: The schematic diagram for Pd ALD growth mechanisms on NCNT and Mn$_3$O$_4$ surfaces.................................................................................................................. 174

Figure 5.19: Discharge/charge curves for Gr/NCNT, Gr/NCNT/MnO, Gr/NCNT/Pd-150C and Gr/NCNT/MnO/Pd-150C electrodes in Na- (a) and Li-O$_2$ (b) cells; the cycling performance of Gr/NCNT/MnO/Pd-150C electrode in Na- (c) and Li-O$_2$ (d) cells................................................................. 175

Figure 5.20: The discharge and charge curves of Gr/NCNT/Pd electrodes with various number of Pd ALD cycles for both Na- (a) and Li-O$_2$ (b) cells........................................ 176

Figure 5.21: Discharge and charge curves of Gr/NCNT/MnO/Pd electrodes with various number of Pd ALD cycles in both Na- (a) and Li-O$_2$ (b) cells. ................. 178

Figure 5.22: The chronopotentiogram curves of the consecutive discharge and charge test of Gr/NCNT/MnO/Pd-150C electrode in bor Na- and Li-O$_2$ cells for the data shown in Figure 5.19c and d................................................................. 179

Figure 5.23: The cycling performance of Gr/NCNT/Pd and Gr/NCNT/MnO/Pd electrodes with various cycles of Pd deposition by ALD in Na-O$_2$ cell. .................. 180

Figure 5.24: The cycling performance of Gr/NCNT/Pd and Gr/NCNT/MnO/Pd electrodes with various cycles of Pd deposition by ALD in Li-O$_2$ cell. ............... 181

Figure 5.25: Normalized O K-edge XANES spectra of the discharged electrodes on Gr/NCNT, Gr/NCNT/MnO, Gr/NCNT/Pd-150C and Gr/NCNT/MnO/Pd-150C electrodes recorded under the both surface sensitive TEY (a and c) and bulk sensitive FLY (b and d) modes for both Na- (a and b) and Li-O$_2$ (c and d) cells...... 183
Figure 5.26: Normalized Mn (a) and Pd (b) K-edge XANES spectra of Gr/NCNT/MnO/Pd-150C electrode at the end of 1st discharge and 1st discharge and charge cycle in a Na-O₂ cell ................................................................. 184

Figure 5.27: The Pd K-edge XANES spectra of Gr/NCNT/Pd electrode before 1st discharge, after 1st discharge and after 1st discharge/charge cycle............................ . 185

Figure 5.28: (a) normalized Pd K-edge XANES spectra of Gr/NCNT/MnO/Pd-150C electrode before and after 100 discharge/charge cycles in Na-O₂ cell (terminated after charge cycle); (b) Fourier transform K³-weighted EXAFS spectra of Gr/NCNT/MnO/Pd-150C electrode before and after 100 discharge/charge cycles in Na-O₂ cell............................................ ................................................... 186

Figure 5.29: Fourier transform signal χ(R) of the experimental (circles) and calculated (solid line) Pd K-edge EXAFS χ(k) for Gr/NCNT/MnO/Pd electrode before and after 100 cycles in a Na-O₂ cell.............................................. .................................... 187

Figure 5.30: Morphology of the discharge products in Li-O₂ cell using various air electrodes after discharge to 1.0 mAh cm⁻² under a current density of 0.2 mA cm⁻². 188

Figure 5.31: Morphology of the discharge products in Na-O₂ cell using various air electrodes after discharge to 1.0 mAh cm⁻² under a current density of 0.2 mA cm⁻². 189

Figure 5.32: Schematic diagram of catalytic mediated discharge and charge reaction mechanisms on Mn₃O₄/Pd surface. .................................................................................. 191

Chapter 6

Figure 6.1: Full discharge curves of Na-O₂ cells using plain CC air electrode with different electrolytes.......................................................... 201

Figure 6.2: Limited discharge and charge cycles of Na-O₂ cell using a plain CC air electrode with different electrolytes.................................................. 202

Figure 6.3: XRD pattern of discharged air electrodes in Na-O₂ cells using different electrolyte with various DN. ................................................................. 203

Figure 6.4: Normalized O K-edge XANES spectra of discharged air electrode in Na-O₂ cells using different electrolytes. ................................................................. 204

Figure 6.5: Normalized O K-edge XANES spectra of the air electrodes after cycling along with a standard Na₂CO₃ sample. ................................................................. 205

Figure 6.6: Discharge curves of Na-O₂ cells using DEGDME electrolyte and CC air electrode with different hydrophobic and hydrophilic surfaces................. 206
Figure 6.7: Morphology of the discharge product of Na-O₂ cells using DEGDME electrolyte and CC air electrodes with different hydrophobic and hydrophilic surfaces ................................................................. 207

Figure 6.8: Morphology of the discharge product of Na-O₂ cells using MeIm electrolyte and CC air electrodes with different hydrophobic and hydrophilic surfaces .......................................................................................................................... 208

Figure 6.9: Electrochemical discharge/charge curves of Na-O₂ cells using DEGDME electrolyte and CC air electrodes with hydrophobic and hydrophilic surfaces .......... 209
## List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>3D</td>
<td>three dimensional</td>
</tr>
<tr>
<td>ALD</td>
<td>atomic layer deposition</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
</tr>
<tr>
<td>BJH</td>
<td>Barrett-Joyner-Halenda</td>
</tr>
<tr>
<td>CLS</td>
<td>Canadian Light Source</td>
</tr>
<tr>
<td>CNTs</td>
<td>carbon nanotubes</td>
</tr>
<tr>
<td>CV</td>
<td>cyclic voltammetry</td>
</tr>
<tr>
<td>CVD</td>
<td>chemical vapor deposition</td>
</tr>
<tr>
<td>DEGDME</td>
<td>diethylene glycol dimethyl ether</td>
</tr>
<tr>
<td>DFT</td>
<td>density functional theory</td>
</tr>
<tr>
<td>EXAFS</td>
<td>extended X-ray absorption fine structure</td>
</tr>
<tr>
<td>EVs</td>
<td>electric vehicles</td>
</tr>
<tr>
<td>FCCVD</td>
<td>floating catalyst chemical vapor deposition</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared</td>
</tr>
<tr>
<td>FLY</td>
<td>fluorescence yield</td>
</tr>
<tr>
<td>Gr</td>
<td>graphene</td>
</tr>
<tr>
<td>HRTEM</td>
<td>high-resolution transmission electron microscope</td>
</tr>
<tr>
<td>HXMA</td>
<td>hard X-ray micro-analysis</td>
</tr>
<tr>
<td>Acronym</td>
<td>Full Form</td>
</tr>
<tr>
<td>----------</td>
<td>-----------------------------------------</td>
</tr>
<tr>
<td>OER</td>
<td>oxygen evolution reaction</td>
</tr>
<tr>
<td>ORR</td>
<td>oxygen reduction reaction</td>
</tr>
<tr>
<td>PVDF</td>
<td>poly(vinylidene fluoride)</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscope</td>
</tr>
<tr>
<td>SGM</td>
<td>spherical grating monochromator</td>
</tr>
<tr>
<td>SPCVD</td>
<td>spray pyrolysis chemical vapor deposition</td>
</tr>
<tr>
<td>STEM</td>
<td>scanning transmission electron microscope</td>
</tr>
<tr>
<td>TEGDME</td>
<td>tetraethylene glycol dimethyl ether</td>
</tr>
<tr>
<td>TEY</td>
<td>total electron yield</td>
</tr>
<tr>
<td>TGA</td>
<td>thermogravimetric analysis</td>
</tr>
<tr>
<td>XANEs</td>
<td>X-ray absorption near edge structure</td>
</tr>
<tr>
<td>XAS</td>
<td>X-ray absorption spectroscopy</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
</tbody>
</table>
Chapter 1

1 Literature review

1.1 Introduction

Lithium-ion (Li-ion) batteries have been considered as a state of the art technology for energy storage applications ranging from use in portable electronic devices all the way to electrical vehicles (EVs). However, Li-ion battery systems cannot adequately meet the growing demand required for energy storage in extended range EVs. Metal-O\textsubscript{2} batteries on the other hand are among the limited number of battery systems that can appropriately compete with gasoline in terms of theoretical energy density. As a result, metal-O\textsubscript{2} batteries are considered as the next generation energy storage system with potential applications in electrical transportation. The high energy density of metal-O\textsubscript{2} cells is a product of coupling a high energy metal as the negative electrode with an air electrode that utilizes oxygen as the positive electrode material. Among the various metal-O\textsubscript{2} systems, Li- and Na-O\textsubscript{2} (alkali metal-O\textsubscript{2}) batteries exhibit the highest theoretical specific energies of 11430 and 3451 Wh/kg, respectively (based on only the weight of negative electrode materials). The accumulation of oxygen during the discharge reaction considerably increases the weight of electrode material. Considering the weight of positive electrode material in the theoretical energy density calculation of alkali metal-O\textsubscript{2} cells give a more realistic value of 3505 and 1602 (1105) Wh/kg for Li- and Na-O\textsubscript{2} cells (based on the discharge products of Li\textsubscript{2}O\textsubscript{2} and Na\textsubscript{2}O\textsubscript{2} (NaO\textsubscript{2})), respectively.

Studies on Na-O\textsubscript{2} batteries was triggered by Peled et al. who reported a battery system working at temperatures above the melting point of sodium metal (98°C) as an alternative battery system to Li-O\textsubscript{2}. Their initial work was followed by Sun et al. who introduced the first rechargeable Na-O\textsubscript{2} cell at room temperature. However, further development of alkali metal-O\textsubscript{2} cells is generally restricted by their poor cycling capability and high charging overpotential which results in decreased energy efficiency. In addition, major components of the cells such as the electrolyte and carbonaceous air electrode have been shown to undergo chemical and electrochemical decomposition reactions, especially at higher potentials. Chemical composition of the discharge products is among the major
contributing factors that results in a high charging overpotential. Although lithium peroxide (Li$_2$O$_2$) is well accepted to be the major discharge product of Li-O$_2$ in the presence of stable electrolytes, the chemical composition of Na-O$_2$ cell product is still a point of controversy. Both sodium peroxide (Na$_2$O$_2$) and superoxide (NaO$_2$) are almost evenly identified as the major discharge product.

**Table 1.1: A summary of the reported discharge products for Na-O$_2$ battery system.**

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Discharge product</th>
<th>Charge potential</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 M NaSO$_3$CF$_3$ in PC</td>
<td>Na$_2$CO$_3$</td>
<td>3.5-4.25 V</td>
<td>[25]</td>
</tr>
<tr>
<td>1 M NaClO$_4$ in PC</td>
<td>Na$_2$CO$_3$</td>
<td>&gt; 4 V</td>
<td>[17]</td>
</tr>
<tr>
<td>1 M NaPF$_6$ in 1:1 EC/DMC</td>
<td>Na$_2$O$_2$ + Na$_2$CO$_3$</td>
<td>3.5-4 V</td>
<td>[6]</td>
</tr>
<tr>
<td>1 M NaClO$_4$ in DME</td>
<td>Na$_2$O$_2$ + Na$_2$CO$_3$</td>
<td>3-4 V</td>
<td>[83]</td>
</tr>
<tr>
<td>1 M NaClO$_4$ in PC</td>
<td>Na$_2$O$_2$ + Na$_2$CO$_3$</td>
<td>3-4 V</td>
<td>[24]</td>
</tr>
<tr>
<td>0.5 M NaSO$_3$CF$_3$ in DEGDME</td>
<td>Na$_2$O$_2$</td>
<td>3-3.5 V</td>
<td>[16]</td>
</tr>
<tr>
<td>0.25 M NaPF$_6$ in DME</td>
<td>Na$_2$O$_2$</td>
<td>~ 4 V</td>
<td>[15]</td>
</tr>
<tr>
<td>0.1 M NaClO$_4$ (+ 0.001 M NaI) in DME</td>
<td>Na$_2$O$_2$</td>
<td>2.3-3.2 V</td>
<td>[126]</td>
</tr>
<tr>
<td>1 M NaClO$_4$ in TEGDME</td>
<td>Na$_2$O$_2$.2H$_2$O</td>
<td>2.5-4 V</td>
<td>[17]</td>
</tr>
<tr>
<td>0.5 M NaSO$_3$CF$_3$ in DEGDME</td>
<td>Na$_2$O$_2$.2H$_2$O</td>
<td>2.5-4 V</td>
<td>[18]</td>
</tr>
<tr>
<td>0.5 M NaSO$_3$CF$_3$ in DEGDME</td>
<td>Na$_2$O$_2$.2H$_2$O + NaO$_2$</td>
<td>2.3-4 V</td>
<td>[26]</td>
</tr>
<tr>
<td>0.5 M NaSO$_3$CF$_3$ in TEGDME</td>
<td>Na$_2$O$_2$.2H$_2$O/NaO$_2$</td>
<td>2.5-3.5 V</td>
<td>[22]</td>
</tr>
<tr>
<td>1 M NaSO$_3$CF$_3$ in TEGDME</td>
<td>Na$_2$O$_2$ + NaO$_2$</td>
<td>2.5-4 V</td>
<td>[23]</td>
</tr>
<tr>
<td>0.5 M NaSO$_3$CF$_3$ in DEGDME</td>
<td>Na$_2$O$_2$ + NaO$_2$</td>
<td>2.4-4.5 V</td>
<td>[84]</td>
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<tr>
<td>0.5 M NaSO$_3$CF$_3$ in DEGDME</td>
<td>Na$_2$O$_2$ + NaO$_2$</td>
<td>2.3-4.2 V</td>
<td>[30]</td>
</tr>
<tr>
<td>0.5 M NaSO$_3$CF$_3$ in DEGDME</td>
<td>NaO$_2$</td>
<td>~ 2.3 V</td>
<td>[4], [19], [40]</td>
</tr>
<tr>
<td>0.2 N NaSO$_3$CF$_3$ in DME</td>
<td>NaO$_2$</td>
<td>~ 2.5 V</td>
<td>[21]</td>
</tr>
<tr>
<td>0.1 M NaClO$_4$ in DME</td>
<td>NaO$_2$</td>
<td>~ 2.3 V</td>
<td>[31]</td>
</tr>
<tr>
<td>0.1 M NaSO$_3$CF$_3$ in DEGDME</td>
<td>NaO$_2$</td>
<td>2.5 V</td>
<td>[105]</td>
</tr>
</tbody>
</table>
Liu et al. and Li et al. reported the formation of Na$_2$O$_2$ in Na-O$_2$ cell using an ether-based electrolyte with a charging overpotential of ~1.5 V.$^{15,16}$ A hydrated form of sodium peroxide (Na$_2$O$_2$.2H$_2$O) has also been found in other studies.$^{17,18}$ Hartmann et al. found unique micrometer structures of cubic NaO$_2$ as the major discharge product of Na-O$_2$ cells which were decomposed below 2.5 V vs. Na/Na$^+$ (charging overpotential of ~0.2 V).$^4,19,20$ Furthermore, using differential electrochemical mass spectrometry (DEMS) analysis, McCloskey et al. showed that the discharge product of a Na-O$_2$ cell is predominantly NaO$_2$. More recently, Zhao et al. disclosed that NaO$_2$ is the main product under static oxygen atmosphere, while Na$_2$O$_2$.2H$_2$O was obtained under flowing oxygen gas.$^{22}$ A combination of NaO$_2$ and Na$_2$O$_2$ and/or Na$_2$CO$_3$ is also reported in other studies.$^{23-26}$ A summary of the reported discharge products for Na-O$_2$ battery system is presented in Table 1.1. Theoretical calculations have also been applied to predict the discharge product of Na-O$_2$ cell. NaO$_2$ has been suggested by first-principle DFT calculations to be stable discharge product of Na-O$_2$ cells under the standard conditions (300 K and 1 atm).$^{27}$ In an interesting study conducted by Cedar et al., calculation on the surface energies of various sodium oxide crystals with energy of bulk compounds, demonstrated that bulk Na$_2$O$_2$ is a more stable phase under standard operating conditions and NaO$_2$ is more stable at the nanoscale and/or under elevated oxygen partial pressures.$^{28}$

Although Na-O$_2$ batteries have demonstrated lower charging overpotentials compared to Li-O$_2$, the cycling life of the cell is still limited to a few tens of cycles. The poor cycling life of Na-O$_2$ cell is a result of multiple challenges associated with the main components of the cell, i.e. negative and positive electrodes and electrolyte. The major challenges facing Na-O$_2$ cells are summarized in Figure 1.1. Some of these challenges are in common with Li-O$_2$ cells and are related to the negative electrode and electrolyte. Dendrite formation on the negative sodium metal electrode during consecutive dissolution and deposition of sodium is even more severe than that found for lithium metal electrodes.$^{19,22}$ Formation of the dendrite structure results in destruction of the sodium metal electrode via corrosion/passivation as well as consumption of the cell electrolyte due to continuous SEI formation on high surface area dendritic structures. In addition, sodium metal exhibits greater sensitivity toward trace amounts of moisture and dissolved oxygen into the cell electrolyte compared to metallic lithium. Therefore, sodium protection is a major challenge
that should be addressed to enhance the cycling life of the Na-O\textsubscript{2} cells. In addition, instability of available organic electrolytes against oxidation and decomposition by superoxide intermediates and/or discharge products of the cell is another major challenge facing both Li- and Na-O\textsubscript{2} cells.\textsuperscript{29} Decomposition of the organic electrolyte within cells results in the production of insulating carbonate-based parasitic products which ultimately contributes in raising the charging overpotential of the cell. Higher charging potential also results in increased electrolyte decomposition.\textsuperscript{8, 12, 30} Finding an appropriate electrolyte with adequate chemical stability and wide electrochemical window will greatly improve the cyclability of both cells. Furthermore, instability of the polymeric binders and electrolyte salts in the highly oxidative environment of the alkali metal-O\textsubscript{2} cells are among other challenges that need to be addressed.

![Figure 1.1: Major challenges of Na-O\textsubscript{2} cell.](image)

In addition to the common challenges facing of Li- and Na-O\textsubscript{2} cells, there are contradictory findings over the chemical composition of discharge products produced in Na-O\textsubscript{2} cell.
While the cells with NaO₂ discharge product exhibit a very low charging potential, the overpotential in the case of cells with Na₂O₂ as the product is comparable with that of Li-O₂. Since lower charging overpotential of Na-O₂ cells is a principle advantage over Li-O₂, controlling the composition of the discharge product will play a vital role here. Moreover, chemical instability of produced NaO₂ discharge products is also reported by some researchers. Therefore, a deep understanding pertaining to the composition and stability of the discharge products in Na-O₂ cell is critical for further improvement. In the present review, the effect of various physicochemical parameters on the composition and morphology of the discharge product of non-aqueous Na-O₂ cells is discussed. The chemical and electrochemical reaction mechanisms of the cell from various perspectives including kinetic parameters, humidity effect, air electrode, binders, electrolyte, and catalysts are summarized and discussed in detail. Furthermore, several potential research directions toward enhanced alkali metal-O₂ batteries based on the comparison of Na-O₂ with Li-O₂ battery systems are proposed. We try to clarify the behavior of Na-O₂ cell from chemical and electrochemical points of view.

1.2 Principles of Na-O₂ cell

1.2.1 Electrochemical reactions in Na-O₂ cell

Metal-O₂ cells employ a dissolution/precipitation during the electrochemical process rather than intercalation mechanism. In contrast to the intercalation reaction, a dissolution/precipitation reaction involves an evolution in the crystal structure of the electrode material. The working mechanism of Na-O₂ cells is schematically illustrated in Figure 1.2. Briefly, Na metal is oxidized to form Na⁺ ions during the discharge cycle of the cell. Na⁺ ions then move through the electrolyte toward the cathode electrode, where oxygen molecules become reduced and combine with Na⁺ ions to form sodium oxide discharge products. Following cell discharge, the metal anode will be thoroughly converted to metal oxides which are insoluble in the aprotic electrolyte of the cell and accumulate on the surface of the air electrode. In order to accommodate the extra discharge product, the air electrode must possess appropriate porosity with large void volume.
Figure 1.2: Schematic diagram of Na-O\(_2\) cell.

The electrochemical reactions occurring during the discharge cycle of the Na-O\(_2\) cell can be represented in the following chemical equations:

Negative electrode: \( \text{Na} \rightarrow \text{Na}^+ + e^- \) (1.1)

Positive electrode:

\( \text{O}_2 + e^- \rightarrow \text{O}_2^- \) (1.2)

\( \text{Or} \quad \text{O}_2 + 2e^- \rightarrow \text{O}_2^{2-} \) (1.3)

Overall:

\( \text{Na} + \text{O}_2 \rightarrow \text{NaO}_2 \quad E^0 = 2.27 \text{ V} \) (1.4)

\( \text{Or} \quad 2\text{Na} + \text{O}_2 \rightarrow \text{Na}_2\text{O}_2 \quad E^0 = 2.33 \text{ V} \) (1.5)

Similar electrochemical reactions take place in the case of Li-O\(_2\) cell:

Negative electrode: \( \text{Li} \rightarrow \text{Li}^+ + e^- \) (1.6)

Positive electrode:

\( \text{O}_2 + 2e^- \rightarrow \text{O}_2^{2-} \) (1.7)

Overall:

\( 2\text{Li} + \text{O}_2 \rightarrow \text{Li}_2\text{O}_2 \quad E^0 = 2.96 \text{ V} \) (1.8)

According to Bruce et al.,\(^7, 8\) the oxygen reduction reaction (ORR) in non-aqueous electrolytes involves the formation of a superoxide (O\(_2^-\)) intermediate. The odd number of
electrons makes the superoxide ion extremely unstable resulting in rapid reaction with surrounding Li$^+$ ions to produce lithium superoxide (LiO$_2$). However, the small Li$^+$ ion is not capable of stabilizing the extremely unstable O$_2^-$. As a result, LiO$_2$ disproportionates to lithium peroxide (Li$_2$O$_2$) either chemically or electrochemically via following reaction routes:

Chemically 

$$2\text{LiO}_2 \rightarrow \text{Li}_2\text{O}_2 + \text{O}_2$$ (1.9)

Electrochemically 

$$\text{LiO}_2 + \text{Li}^+ + \text{e}^- \rightarrow \text{Li}_2\text{O}_2$$ (1.10)

Using an interesting electrochemical approach, Abraham et al.\textsuperscript{32} demonstrated that the superoxide intermediate can be stabilized in a non-aqueous solution containing tetrabutylammonium (TBA) cation. Cyclic voltammetry (CV) test for oxygen reduction and evolution (OER) reactions in acetonitrile solution containing TBA$^+$ ion with two different counter ions exhibited two pairs of redox peaks (Figure 1.3a): a reversible and a quasi-reversible pair with peak potential separations of ~0.6 and ~2 V (vs. Ag/AgCl), respectively. The peak potential separation of ~0.6 V, in the case of reversible pair (denoted as $E_{p1}$ and $E_{p3}$ in Figure 1.3a), is characteristic of a one electron transfer reaction ($\Delta E_p = 0.592/nV$ where $n =$ number of transferred electrons)\textsuperscript{33} and has been related to the O$_2$/O$_2^-$ redox coupling reaction. The $E_{p1}$ reduction peak is also followed by a second reduction peak which has been correlated to the reduction of O$_2^-$ to O$_2^{2-}$. Oxidation of O$_2^{2-}$ does not typically occur until applying a large overpotential of over 2 V. So, the quasi-reversible redox pair of $E_{p2}/E_{p4}$ can be correlated to the O$_2$/O$_2^{2-}$ redox couple. However, oxygen exhibits different electrochemical behavior in the presence of other alkali metal ions (Figure 1.3b). Only one oxygen reduction peak, corresponding to the O$_2$/O$_2^-$ redox couple, can be seen during the cathodic potential sweep of LiPF$_6$ electrolyte salt under a scan rate of 100 mV s$^{-1}$, demonstrating the rapid deterioration of O$_2^-$ in the presence of Li$^+$ via a chemical reaction. In the case of Na$^+$ cation, a shoulder-like peak related to the reduction of O$_2^-$ to O$_2^{2-}$ also appears in the voltammogram, corresponding to the elevated chemical stability of O$_2^-$ in the presence of Na$^+$. Equivalent oxidation evolution peaks also appear after applying overpotentials of more than 2 V for both of lithium and sodium. The reduction peak of O$_2^-$ to O$_2^{2-}$ is truly well-defined and distinguishable in the presence of K$^+$.
cation and two oxygen evolution peaks can also be identified during the anodic sweep. A similar comparison for oxygen electrochemical behavior in presence of TBA⁺, K⁺ and Li⁺ cations are presented elsewhere.\textsuperscript{34}

Figure 1.3: (a) Cyclic voltammograms of a glassy carbon electrode (vs. Ag/AgCl) for the reduction of oxygen in the presence of 0.1 M TBAPF₆ (black), 0.1 M TBAClO₄ (blue), and the argon background (dotted) in MeCN solution. (b) Cyclic voltammograms of a glassy carbon electrode (vs. Ag/AgCl) for the oxygen reduction in the presence of 0.1 M LiPF₆ (dashed line), 0.1 M NaPF₆ (solid line), and KPF₆ (dash-dotted line) in MeCN solution. (Scan rate = 100 mV s\textsuperscript{-1}). Adapted from ref. 32.

Abraham’s electrochemical study on the ORR and OER in non-aqueous electrolyte illustrates how the stability of the superoxide ion can be altered through the presence of cations with relatively larger radii. The increased stability of superoxide ion coupled with a large cation has been explained using hard and soft acid and base (HSAB) theory.\textsuperscript{32, 35} Larger cations, which are considered as soft Lewis acid, exhibit higher polarizability and can more effectively stabilize the superoxide ion, which is a soft Lewis base. In other words, the stability of the electrochemically produced alkali metal superoxide increases
from lithium to potassium (KO$_2$ > NaO$_2$ > LiO$_2$). While LiO$_2$ is thermodynamically unstable at standard conditions, KO$_2$ is a stable and commercially available product. These findings are also in good accordance with the detected discharge products of alkali metal-O$_2$ cells: the discharge product of Li-O$_2$ cell (in a relatively stable electrolyte and on a stable air electrode) is well-known to be Li$_2$O$_2$;$^{36-38}$ Both NaO$_2$ and Na$_2$O$_2$ are reported to be formed as the discharge products of Na-O$_2$ cell under different physicochemical conditions;$^4$,15, 17, 18, 21-23, 39, 40 and KO$_2$ is proved to be the major discharge product of K-O$_2$ cells.$^{34}$ The chemistry of discharge products in Li- and Na-O$_2$ cells will be discussed in more details in the next sections.

1.2.2 Chemistry of sodium and sodium oxides

Sodium (Na, atomic number = 11), is a highly reactive alkali metal and is the seventh most abundant element and fifth most abundant metal in the earth’s crust. The ease of sodium metal production (via electrolysis of fused sodium salts) makes it extremely inexpensive, especially compared to lithium. Another advantage of sodium over lithium for application as the anode electrode material for metal-air batteries is its stability against the formation of nitride which is important for development of Na-“air” batteries. Sodium is the second most electropositive metal after lithium ($M^+(aq) + e^- \rightarrow M(s)$; $E^0 = -3.045$ and -2.714 V for $M = Li$ and Na, respectively) which makes it a desirable candidate as an anode material.$^{41}$ However, the increased atomic weight of sodium (22.989 g mol$^{-1}$) over lithium (6.941 g mol$^{-1}$) dramatically decreases the theoretical specific capacity of the anode electrode material from 3861 mAh g$^{-1}$ for lithium to 1166 mAh g$^{-1}$ for sodium. These specific capacities correspond to a theoretical energy density value of 11757 and 3164 Wh kg$^{-1}$ for lithium and sodium, respectively.

The relatively low first ionization energy of alkali metals (ns$^1$) is responsible for the high chemical reactivity and common +1 oxidation state of these elements. Alkali metals form a variety of binary compounds with oxygen including M$_2$O, M$_4$O, M$_3$O, M$_3$O$_2$ suboxides, M$_2$O normal oxides, M$_2$O$_2$ peroxides, M$_2$O$_3$ sesquioxides, MO$_2$ superoxides (also referred to as hyperoxide) and MO$_3$ ozonides.$^{42}$ The stability of the oxygen-rich compounds
increases with atomic number and both of lithium and sodium form stable oxide and peroxide phases. Interestingly, the sodium superoxide phase is stable at STP, but lithium cannot form a stable superoxide phase above 15 K. Sodium superoxide (NaO₂) can be considered as an ionic molecular crystal which is composed of sodium and paramagnetic superoxide (O₂⁻) ions. O₂⁻ ion has nine electrons at the 2p molecular levels with the electronic configuration of \( \sigma_g^2 \pi_u^4 \pi_g^3 \) (Scheme 1.1). The remained unpaired electron is responsible for the paramagnetic properties of the superoxide phase.⁴³, ⁴⁴ This electron configuration also increases the covalent bond order between the two oxygen atoms to 1.5 (compared with bond order of 1 in \( \text{O}_2^{2-} \)). As a result, the O-O interatomic distance decreases from 1.60 in \( \text{O}_2^{2-} \) to 1.35 Å in \( \text{O}_2^- \).⁴⁵ \( \text{O}_2^- \) ion is not active in the infrared region, but has a dipole-allowed \( \pi_u - \pi_g \) transition in the visible region which is responsible for the yellow to orange color typically seen for superoxide compounds.⁴⁶ Furthermore, \( \text{O}_2^- \) is a strong oxidizing agent which can facilitate the oxidation of organic materials to carbonate species and also reacts with water and carbon dioxide in the following manner.⁴², ⁴⁷

\[
2\text{NaO}_2(\text{s}) + \text{H}_2\text{O(l)} \rightarrow 2\text{NaOH(soln)} + 3/2\text{O}_2(\text{g}) \quad (1.11)
\]

\[
4\text{NaO}_2(\text{s}) + 2\text{CO}_2(\text{g}) \rightarrow 2\text{Na}_2\text{CO}_3(\text{s}) + 3\text{O}_2(\text{g}) \quad (1.12)
\]

Scheme 1.1: The electronic structure of peroxide and superoxide ions.

Sodium peroxide on the other hand is an ionic molecular compound which is composed of sodium and peroxide (\( \text{O}_2^{2-} \)) ions. \( \text{O}_2^{2-} \) contains a single covalent bond with an electronic configuration that is isoelectronic with \( \text{F}_2 \) (see also Scheme 1.1). \( \text{Na}_2\text{O}_2 \) is stable toward
the thermal decomposition reaction in the absence of oxygen or other oxidizable compounds up to 675°C. \( \text{O}_2^{2-} \) ion does not show any absorption in the visible region and appear colorless in its compounds, however, the peroxides of the heavier alkali metals are colored. \( \text{Na}_2\text{O}_2 \) appears pale yellow in color due to the contamination by superoxide.\(^{47,48}\)

\( \text{Na}_2\text{O}_2 \) is extremely hygroscopic and tends to form peroxide hydrates in the presence of water or water vapor. Peroxide hydrates are also less thermally stable and more reactive toward reactions with carbon dioxide compared to their anhydrous counterparts. \( \text{Na}_2\text{O}_2 \) is also a strong oxidizing agent and reacts with water and carbon dioxide in the following reaction mechanism:\(^{42,47}\)

\[
\text{Na}_2\text{O}_2(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow 2\text{NaOH(\text{soln})} + \frac{1}{2}\text{O}_2(\text{g}) \quad \text{(1.13)}
\]

\[
2\text{Na}_2\text{O}_2(\text{s}) + 2\text{CO}_2(\text{g}) \rightarrow 2\text{Na}_2\text{CO}_3(\text{s}) + \text{O}_2(\text{g}) \quad \text{(1.14)}
\]

### 1.2.3 Components of the \( \text{Na-O}_2 \) cell

#### 1.2.3.1 Cathode

\( \text{Na-O}_2 \) cells employ oxygen as the positive electrode material which is being reduced and combines with \( \text{Na}^+ \) ion to form solid sodium oxide during the discharge cycle of the cell. The air electrode in \( \text{Na-O}_2 \) cells provides a three-phase zone, where oxygen reduction and evolution reactions occur. Furthermore, the air electrode also serves as a medium to accommodate the solid discharge product produced during the electrochemical process. The air electrode in \( \text{Na-O}_2 \) cells plays a similar role to the one found in \( \text{Li-O}_2 \) cells, a comprehensive discussion of this can be found in references.\(^{49-52}\) Briefly, an ideal air electrode should have adequate porosity along with appropriate pore volume and pore sizes distribution, in addition to the general characteristics of electrodes materials such as electronic conductivity, chemical stability, high surface area and low cost. The porous structure is responsible for oxygen diffusion as well as allowing for the formation and storage of discharge products and also decomposition of the produced discharge products during the charge cycle. In addition, the final performance of the metal-air systems strongly depends on the efficiency of the air electrode. Many publications have demonstrate that the
discharge capacity of the metal-O₂ cells is often limited by the air electrodes capacity to adequately store discharge product. The ability of the air electrode to accommodate the discharge products determines the discharge capacity of the electrode and hence the whole battery.⁵³

### 1.2.3.2 Anode

Despite the extremely high energy density of lithium metal as an anode material, the formation of Li dendrites during repeated charge/discharge processes severely limits its capabilities.⁵² Similar issue restricts the cyclability of sodium metal negative electrodes in Na-O₂ cells.¹⁹, ²² Dendrite formation is a result of sequential accumulation and cracking of a solid electrolyte interface (SEI) layer in the presence of incompatible organic electrolytes. Dendritic structures may ultimately penetrate into the separator; reach the positive electrode and create a short circuit within the battery, resulting in smoke or even fire, especially in presence of volatile organic electrolytes. The anode material is also destroyed from corrosion and passivation of the dendrite structures during battery cycling. In addition, continuous formation of SEI layer on high surface area dendritic structures results in consumption of the electrolyte, compromising the cycle life of the battery.⁵²

Hartmann et al. observed the growth of sodium dendritic structures penetrating into the pores of the polymer separator material during the cycling of Na-O₂ cells (Figure 1.4a).¹⁹ Energy dispersive spectroscopy (EDS) analysis revealed that the dendritic structure is composed of both sodium and oxygen. The authors also suggested that the dendrite formation in Na-O₂ cell may be physically suppressed by separating the anode and the cathode using a solid ion conducting membrane such as sodium-beta-alumina (Figure 1.4b). The formation of sodium dendritic structures is also reported by Zhao et al.²² The authors visually investigated the sodium anode electrode during the Na-O₂ cell cycling under various discharge capacity cut-off values (Figure 1.4c). It was observed that the surface of the sodium anode electrode becomes rougher with increasing discharge capacity and cycle number. Two approaches may be followed as the potential solutions for suppressing anode dendrite formation.
Figure 1.4: (a) Cross section SEM images of a pristine separator and one after cycling. (b) Application of a Na-beta-alumina solid electrolyte membrane (0.5 mm thickness) as barrier for dendrite growth. (c) Optical images of the Na anode surfaces and separators under different cycling conditions. The surface roughness increases upon increasing the cutoff discharge capacity as well as the cycle number due to the Na dendrit growth. Adapted from ref. 19 and 22.

The first involves mechanical suppression of the dendritic structure by using an interfacial or protective layer (also called ex situ or artificial SEI) comprised of Na-ion conductive polymers, ceramics or glass on the anode electrode. The softer nature of sodium metal compared to lithium might be specifically beneficial in this regard. The second approach involves the in situ formation of a stable SEI layer using various organic solvents, sodium salts and/or functional additives. Contamination of the metal negative electrode by moisture and oxygen from the positive electrode is another difficulty associated with the utilization of sodium metal in Na-O₂ cells. Replacing of sodium metal with a sodiated carbon electrode may address this issue in cost of compromising on the energy density of the cell. An appropriate protective layer, however, would undoubtedly improve the cyclability and safety of sodium metal negative electrodes for application in Na-O₂ batteries.
1.2.3.3 Electrolyte

Stability of the electrolyte is a severe challenge currently facing the development of alkali metal-O$_2$ batteries, even at the research scale. An ideal electrolyte should tolerate the highly oxidative environment of the cells for a long cycling life and facilitate the reversible formation and decomposition of the discharge product. It is well-recognized that the electrolyte not only affects the oxygen reduction and evolution reaction mechanisms, but also the chemical composition of the discharge products as well as the reversibility of the cell.\(^{29}\) Carbonates are common solvents for non-aqueous batteries due to their high stability and low volatility. Therefore, similar to the Li-O$_2$ battery system, early researches conducted on Na-O$_2$ were done using carbonate based electrolytes. In these studies sodium carbonate was reported as the major discharge products.\(^6,^{17}\) However, later studies revealed that carbonate based solvents are unstable against the nucleophilic attack by the superoxide (O$_2^-$) intermediate in Li-O$_2$ environment.\(^{55, 56}\) In addition, the superoxide anion radical reacts with the ethereal carbon atom of organic carbonates, resulting in a ring opening mechanism and the formation of peroxy anion (ROO$^-$) species, which is even more reactive than the preliminary superoxide. Accordingly, carbonate-based electrolytes decompose to form high molecular weight products including carbonates and alkyl carbonates.\(^{29}\)

Afterward, ether-based electrolytes, which are believed to be more stable than carbonates, were employed in most of the studies on Na-O$_2$ cells. Ethers are more stable than carbonates toward nucleophilic attacks by superoxide intermediates and have relatively low vapor pressure. Furthermore, ether based electrolytes display an extended oxidation potential window up to 4.5 V versus Li/Li$^+$ and hence might be considered as good candidates for Na-O$_2$ cells. Nevertheless, recent studies on Li-O$_2$ battery system revealed that Li$_2$O$_2$ produced during the first discharge of the cell using an ether-based electrolyte also contains electrolyte decomposition products, resulting in a mixture of lithium carbonate, lithium alkyl carbonates, polyethers/esters, CO$_2$, and H$_2$O.\(^{13}\) Therefore, studies toward finding a truly stable electrolyte for both Na- and Li-O$_2$ battery systems is an ongoing research subject. Besides, the hybrid electrolyte system based on two different electrolytes in the same cell, i.e. an aqueous electrolyte on the cathode side (catholyte) and...
an aprotic electrolyte on the anode side (anolyte) is also examined for Na-O₂ cell by number of researchers.\textsuperscript{57-60}

1.3 Charging overpotential in Na-O₂ cells

1.3.1 Theoretical calculations

As discussed above, the charging overpotential of Na-O₂ cell is greatly dependent on the chemical composition of the discharge product. Theoretical calculations have been employed to estimate the discharge products of Na-O₂ cell. In a comparative study, Lee et al.\textsuperscript{27} used first-principle calculations to develop a phase stability map of discharge products for Li- and Na-O₂ cells as a function of oxygen partial pressure. It was concluded that under standard experimental conditions of T = 298 K and P\textsubscript{O₂} = 1 atm, Li\textsubscript{2}O\textsubscript{2} and NaO\textsubscript{2} are the stable discharge products for Li- and Na-O₂ cells, respectively (Figure 1.5a). According to the authors, NaO\textsubscript{2} is the discharge product of the Na-O₂ cells even under the reduced oxygen partial pressure down to 10\textsuperscript{-8} atm. Na\textsubscript{2}O\textsubscript{2} and Na\textsubscript{2}O are proposed as the most stable phases under lower oxygen pressures. However, for Li-O₂ cells, Li\textsubscript{2}O\textsubscript{2} was found to be the most stable phase under standard experimental conditions and Li\textsubscript{2}O is predicted to be the product of the cell under lower oxygen partial pressure. LiO\textsubscript{2} is argued to be energetically stable only under oxygen partial pressures higher than 40 atm. The larger ionic radius of Na compared to Li is thought to contribute in the stabilization of the superoxide ion.

These results are in contrast with the finding of Ceder’s research group\textsuperscript{28} who predicted that Na\textsubscript{2}O\textsubscript{2} is the stable bulk phase for sodium oxide under standard experimental conditions. In the latter study, Ceder et al. used first principle calculations to investigate the thermodynamic stability of various sodium oxides as a function of temperature, oxygen partial pressure and particle size of the discharge product. The formation free energies of sodium oxides were calculated as a function of temperature and oxygen partial pressure by combining the phonon energy of solids with the chemical potential of oxygen at various pressures and temperatures. The results have been used to plot the equilibrium T/P\textsubscript{O₂} phase diagram for Na-O system (Figure 1.5b). Na\textsubscript{2}O\textsubscript{2} is proposed to be the stable phase under standard condition and also under higher temperatures or lower oxygen pressures.
Figure 1.5: (a) Phase stability map of various lithium/sodium oxides as a function of oxygen chemical potential or oxygen partial pressure. The blue region shows the oxygen chemical potential range under nonequilibrium conditions that can result from fast consumption of O$_2$ in the electrolyte during discharge.$^{27}$ (b) Phase diagram of Na-O as function of temperature and O$_2$ partial pressure.$^{28}$ (c) Phase diagram of Na$_2$O$_2$ (red) and NaO$_2$ (green) at 300 K as a function of particle size and P$_{O2}$ at the O$_2$ gas limit.$^{28}$ Adapted from ref. 27 and 28.

Based on the equilibrium T/P$_{O2}$ phase diagram, NaO$_2$ is only thermodynamically stable at oxygen partial pressures higher than 8.5 atm (room temperature). By entering the surface energies of the polymorphs for two competing sodium oxides into the calculations, the authors were able to calculate the phase diagram as a function of particle size and oxygen partial pressure for Na$_2$O$_2$ and NaO$_2$ (Figure 1.5c). It was concluded that the formation of NaO$_2$ is preferred when the particle size of the product decreases to nanometer scale, since the surface energies of NaO$_2$ are lower than those of Na$_2$O$_2$. The crossing point at the standard oxygen partial pressure of 1 atm points to a threshold particle size of around 6 nm for NaO$_2$ product. In addition, NaO$_2$ exhibited a lower critical nucleation energy barrier compared to Na$_2$O$_2$ suggesting that NaO$_2$ particles are more likely to nucleate. Similar to
aforementioned theoretical calculations, contradictory results over stability of NaO₂ and Na₂O₂ were also obtained in experimental studies which are discussed in the following section.

In order to determine the reason behind the lower charging overpotential for NaO₂ compared to Na₂O₂, Siegel’s research group used density functional and quasi-particle GW methods to calculate the theoretical conductivity values for these species. The calculated ionic and electronic conductivity values for NaO₂ and Na₂O₂ are listed and compared with those of Li₂O₂ in Table 1.2. The group determined that the charge transport is limited by sluggish charge hopping between O₂ dimers in all cases. The calculated conductivity values suggest that both NaO₂ and Na₂O₂ possess rather large band gaps that are greater than 5 eV, suggesting that both these species are electrically insulating. The calculated band gap for Na₂O₂ is in reasonable agreement with the value of 4.84 eV calculated by Araujo et al. While a hole polaron migration is thought to be the main route for charge diffusion in Na₂O₂, a combination of electron and hole polarons are proposed to be responsible for charge transport in NaO₂. The authors concluded that the lower charging overpotential for NaO₂ cannot be explained by the enhanced electrical conductivity of NaO₂ over Na₂O₂. On the other hand, the ionic conductivity of NaO₂ was predicted to be 10 orders of magnitude higher than Na₂O₂, mainly originating from p type conduction stemming from positive oxygen dimer vacancies as well as n type conduction from negative sodium vacancies. However, the authors discommend the contribution of ionic conductivity toward the lower charging overpotential of NaO₂ instead the authors suggest that decomposition of the electrolyte is the major contributing factor for a lower charging overpotential.

These results are in good accordance with a DFT study conducted by Arcelus et al. on the electronic structure of NaO₂. The authors studied the effect of atomic structure and morphology on the electronic properties of NaO₂ phase. Various model systems including bulk NaO₂, extended (100) surface, and small (NaO₂)ₙ clusters were investigated in this study using the Perdew-Burke-Ernzerhof (PBE) gradient-corrected functional and the Heyd-Scuseria-Ernzerhof (HSE06) hybrid density functional. The results indicate the formation of a fully occupied spin-up and half-filled spin-down antibonding states in the valence band for all systems. The empty O 2p states were calculated using hybrid HSE06
functional to appear above the Fermi level with band gaps larger than 2 eV, revealing the
insulating nature of all investigated systems. The results suggest that due to the lack of
effective electron conductive pathways along the NaO\textsubscript{2} surface, O\textsubscript{2} reduction (and
evolution) reactions take place at the air electrode/electrolyte interface rather than on the
NaO\textsubscript{2} surface. The poor electronic conductivity of NaO\textsubscript{2} may also contribute to the poor
cycling performance seen in Na-O\textsubscript{2} cells. Enhancing the charge transport characteristics of
the Na-O\textsubscript{2} discharge product by either doping or engineering the discharge products/air
electrode interface is proposed as a potential research direction to increase the efficiency
of Na-O\textsubscript{2} cells.

**Table 1.2: The calculated ionic and electronic conductivity values for NaO\textsubscript{2}, Na\textsubscript{2}O\textsubscript{2}
and Li\textsubscript{2}O\textsubscript{2}. Adapted from ref. 54.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ionic Conductivity (S cm\textsuperscript{-1})</th>
<th>Electronic conductivity (S cm\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaO\textsubscript{2}</td>
<td>4 × 10\textsuperscript{-9}/1 × 10\textsuperscript{-10}</td>
<td>1 × 10\textsuperscript{-19}</td>
</tr>
<tr>
<td>Na\textsubscript{2}O\textsubscript{2}</td>
<td>5 × 10\textsuperscript{-20}</td>
<td>1 × 10\textsuperscript{-20}</td>
</tr>
<tr>
<td>Li\textsubscript{2}O\textsubscript{2}</td>
<td>9 × 10\textsuperscript{-19}</td>
<td>5 × 10\textsuperscript{-20}</td>
</tr>
</tbody>
</table>

1.3.2 Chemical composition of the discharge product in Na-O\textsubscript{2}
cells

1.3.2.1 Effect of Kinetics on the composition of the products

The discharge product of alkali metal-O\textsubscript{2} cells has an undeniable role on the
electrochemical response of the cell.\textsuperscript{53, 65} Both the chemical composition and morphology
of the discharge products have been proven to play important roles on the charging
overpotential and discharge capacity of the cells. As mentioned earlier, Li\textsubscript{2}O\textsubscript{2} has been
detected as the discharge product of Li-O\textsubscript{2} cells.\textsuperscript{3, 66} For Na-O\textsubscript{2} cells however, there is still
no agreement on the chemical composition of the discharge product. Predictions based on the electrochemical studies conducted by Abraham determined that Na$_2$O$_2$ should be the major discharge product in Na-O$_2$ cells, however, a stable crystalline phase of NaO$_2$ with a low charging overpotential was detected as the discharge product of the cell by Hartmann et al.$^{4,39,40}$ (Figure 1.6a). Formation of a crystalline superoxide phase was also confirmed using variety of analytical techniques including SEM-EDS, XRD and Raman. McCloskey et al.$^{21}$ also measured the number of transferred electrons per consumed and evolved O$_2$ during the discharge and charge cycles of Na-O$_2$ cell using differential electrochemical mass spectrometry (DEMS) to be close to 1, indicating that the product of the cell is NaO$_2$ (Figure 1.6b). The superoxide-based products in this series of studies exhibited unprecedented low charge overpotential (~0.1 V, Figure 1.6a and b) which in turn triggered a number of other studies on Na-O$_2$ battery system. In another study by Janek and Adelhelm et al.$^{40}$ the authors compared the thermodynamics of Li- and Na-O systems. Based on standard Gibbs free energy values for Na-O$_2$ system, the formation of peroxide phase is computed to be thermodynamically more favored over superoxide phase by only 12.2 kJ mol$^{-1}$ ($\Delta G_{Na_2O_2}^0 = -449.7$ kJ mol$^{-1}$; $\Delta G_{2NaO_2}^0 = -437.5$ kJ mol$^{-1}$, see also Figure 1.6c). Therefore, kinetic parameters are thought to play an important role in determining the discharge product of Na-O$_2$ cells. In the case of Li-O$_2$ cells, however, the superoxide phase is thermodynamically unstable and cannot be stabilized by kinetic factors, resulting in formation of Li$_2$O$_2$ as the discharge product.$^{8,37,66,67}$
Further, it is argued that the superoxide is the most stable product at elevated oxygen pressures, since the corresponding free enthalpy increase at higher oxygen pressures for the starting materials (2Na + 2O₂) and the peroxide products (Na₅O₂ + O₂), while remains untouched for the superoxide (2NaO₂, see also Figure 1.6c). However, different experimental results were obtained by Zhao et al. who examined Na-O₂ cells under 100% O₂ and 80/20 vol% of Ar/O₂ atmospheres. With the use of XRD, the product of the cell...
(using an ether-based electrolyte and vertically aligned CNT air electrode) was detected to be NaO₂ under both Ar/O₂ and pure O₂ atmospheres. Moreover, a mixture of Na₂O₂·2H₂O and NaOH was found under flowing atmospheres which has been related to the introduction of humidity through the flowing oxygen atmosphere. Preferred formation of NaO₂ under reduced oxygen partial pressure reveals that oxygen pressure may play a more complex role in determining the outcome of the discharge product. It should also be noted that the aforementioned thermodynamic data was calculated based on a simplified assumption of gas phase reactions between pure reactant phases, a situation which is far from experimental conditions where the electrochemical reactions are taking place at the three-phase interface.

Other reports have indicated that Na₂O₂ is the discharge product of Na-O₂ cells. For instance, using FTIR and selected area electron diffraction (SEAD), Sun et al. found a mixture of Na₂O₂ and Na₂CO₃ as the discharge product of Na-O₂ cells using a carbonate-based electrolyte. The formation of carbonate-based complexes is likely due to the decomposition of carbonate-based electrolyte. Liu et al. also examined the product of Na-O₂ cell in 1,2-dimethoxyethane (DME)-based electrolyte by SAED and found Na₂O₂ as the major product. With the aid of the XRD data, hydrated forms of sodium peroxide (Na₂O₂·2H₂O) were discovered as a discharge product in Na-O₂ cells using ether-based electrolytes. Formation of both superoxide and peroxide phases as the product of Na-O₂ cells further highlights the impact of kinetic factors in determining the discharge product of Na-O₂ cell. We also studied the kinetics of Na-O₂ cells recently to further understand the reaction mechanism taking place. We employed a heat-treatment procedure on commercial carbon samples in presence of corrosive gasses (NH₃ or CO₂) to produce a high surface area mesoporous carbon material. The synthesized high surface area carbon was then employed as an air electrode for Na-O₂ cells and several charging plateaus were found during the charge cycle (Figure 1.7a). A variety of analytical techniques including XRD, FTIR and Raman were used to evaluate the chemical composition of the discharge product in an attempt to understand the nature of the charging plateaus. It was found that both sodium peroxide and superoxide are produced as discharge products and decomposed with different overpotentials during the charge cycle. Interestingly, the discharge current density also affected the chemical composition of the product and
consequently the charging overpotential of the cell (Figure 1.7b). XPS analysis of the discharge product formed under various discharge current densities revealed that the amount of superoxide-like product increases with increasing discharge current density (Figure 1.7c).

Figure 1.7: (a) Limited discharge and charge curves of the Na-O₂ cell at current densities of 75 and 40 mA g⁻¹, respectively.²⁶ (b) Limited discharge and charge curves of Na-O₂ cells at different discharge current densities of 75, 150 and 300 mA g⁻¹ and a constant charge current density of 40 mA g⁻¹.²⁶ (c) Oxygen 1s spectra of reference sodium peroxide and discharge products resulted at current densities of 75 and 300 mA g⁻¹.²⁶ (d) Restricted discharge and charge curves of Na-O₂ cell at different discharge current densities of 0.1, 0.5, and 1.0 mA cm⁻² and a constant charge current density of 0.1 mA cm⁻² (top); normalized O K-edge XANES spectra recorded under the TEY and FLY modes for the air electrodes discharged under different current densities of 0.1, 0.5, and 1.0 mA cm⁻² (left) and for the air electrodes charged to the various cutoff potentials of 2.75, 3.5, and 4.3 V (color coded) as well as the discharged air electrode and the standard Na₂O₂ sample (right).³⁰ Adapted from ref. 26 and 30.
Furthermore, synchrotron-based X-ray absorption spectroscopy (XAS) was used to determine the chemical reaction mechanism of Na-O₂ cells employing a binder-free 3D-structured air electrode composed of vertically grown nitrogen doped carbon nanotubes on carbon paper (NCNT-CP). Compared to our previous mechanism study, the binder-free nature of the 3D-structured air electrode in eliminates any uncertainty regarding contribution from binder decomposition. The NCNT-CP air electrode exhibited multiple charging plateaus with variable capacities under several discharge current densities (Figure 1.7d). Using XAS, two distinct absorption peaks in the O K-edge X-ray absorption near edge structure (XANES) spectra of NCNT-CP air electrodes were observed, which can be attributed to sodium superoxide and peroxide. In addition, the absorption peak related to sodium superoxide exhibited a growing trend with increasing discharge current density (Figure 1.7d), indicating the preferred formation of sodium superoxide under elevated current densities. Furthermore, the chemical composition of surface and bulk components of the discharge products was compared by collecting the total electron yield (TEY) and the fluorescence yield (FLY) during photon absorption. Looking at both the TEY and FLY signal it is clear that the bulk of the discharge product is predominantly composed of a superoxide-like phase, while the surface consists of both superoxide and peroxide (Figure 1.7d). Reduced amount of superoxide-like phase in the superficial layer of the discharge product was related to the side reaction between the highly oxidative superoxide phase of the discharge product and the electrolyte.

The finding of our studies on Na-O₂ cell can be compared with kinetic studies conducted on Li-O₂ cells by Amin and Curtiss et al. The authors provided analytical evidences toward the formation of a superoxide-like phase on a petroleum coke-based activated carbon (AC) with high surface area in an ether-based electrolyte. The Li-O₂ cell in this study showed two distinct charge plateaus at 3.2-3.5 V (for the first 40% of the charge cycle) and 4.2 (for the remaining 60% of the charge cycle). Although Li₂O₂ was detected using XRD on the discharged electrode, Raman spectroscopy showed characteristic peaks for both peroxide and superoxide-like phases. Density functional theory (DFT) calculations confirmed that the experimentally observed Raman peak is related to a superoxide-like phase absorbed on the surface of a stoichiometric Li₂O₂ phase. The authors also used magnetic measurements to trace the formation and decomposition of
superoxide-like phases during the discharge and charge cycles of the cell. A new magnetic transition was found following electrode discharge and subsequently disappears after charging the cell back to 3.7 V, confirming the formation and decomposition of a superoxide phase.

The same research group also reported on the reaction kinetics of Li-O₂ cells employing a similar high surface area air electrode. A similar two-step charging cycle was also observed, but the ratio between the lower and higher voltage plateaus decreased with increasing discharge capacity. The decrease in lower potential plateau was correlated to a decrease in the amount of superoxide due to the chemical disproportionation reaction of LiO₂ to Li₂O₂ through reaction (1-9). The authors then used the lower- and higher-potential charge plateaus as an indicator for relative amounts of LiO₂ and Li₂O₂ phases and found a first-order relation with a half-life of about 8 hours for the disproportionation of LiO₂. Another notable finding in this study is the correlation between relative amounts of superoxide phases and the discharge current density. Cells discharged at higher current densities exhibited higher charge capacity related to the lower-potential plateau. Two potential explanations are: I) lower discharge current densities provide longer time for disproportionation reaction and thus decrease the amount of superoxide phase; II) higher current densities result in higher LiO₂ nucleation due to increased rate of electron transfer. The authors also highlighted the role of the porous high surface area AC air electrode in providing an oxygen-rich environment with a large number of active sites for ORR. The dependency of charge overpotential in Li-O₂ cells on the discharge current density has also been reported by Scrosati et al. and Nazar et al. Similar plateaus at charge potentials lower than 3.5 V was observed by Nazar et al. which showed increasing trend of capacity with increase of discharge current density.

In order to have a comprehensive conclusion toward the most effective parameters in determining the reaction mechanism of alkali metal-O₂ cells, one should pay close attention to the experimental conditions affecting the electrochemical reaction occurring within the cell. A superficial comparison between studies on Na- and Li-O₂ cells reveals that a common point amongst these studies is the use of a highly porous air electrode with high surface area allowing for a large number of electrochemical active sites to be exposed. In
addition, the amount of superoxide-like phase increases with increasing discharge current density in all cases (see also figure 1.7). Elevated discharge current densities results in faster consumption of dissolved oxygen at electrochemically active sites, which accordingly leads to the oxygen depletion and decreased local oxygen concentration. Similarly, the increased surface area of the air electrode exposes a larger number of active reaction sites which can also be correlated to decreased local oxygen concentrations (since the amount of the electrolyte and hence the absolute amount of the dissolved oxygen into the electrolyte does not change grossly). As a result, it can be concluded that lower local concentrations of dissolved oxygen at electrochemically active sites results in the preferred formation of superoxide-like phases in alkali metal-O\textsubscript{2} cells. Such an interpretation on the effect of local oxygen concentration on the reaction mechanism of Na-O\textsubscript{2} cell is in accordance with the results obtained by Zhao et al.\textsuperscript{22} who found NaO\textsubscript{2} as the major product of the cell under reduced oxygen partial pressure.

The formation of cubic NaO\textsubscript{2} product on a relatively low surface area air electrode by Janek and Adelhelm\textsuperscript{4,40} can also be explained in a similar way. Due to the unique cell design containing a limited amount of oxygen employed in this series of studies, the electrochemical cells have been discharged under oxygen deficient environments. In addition, the relatively high discharge current densities used also contributed to faster consumption of dissolved oxygen, create oxygen deficient conditions. Such an explanation is in good agreement with the theoretical calculations by Lee et al.\textsuperscript{27} who employed the surface energies of sodium oxides with various crystalline structures to predict the equilibrium morphology of the discharge product in Na-O\textsubscript{2} cell. The cubic-shaped pyrite NaO\textsubscript{2} was predicted to be the preferred morphology of the cell under reducing conditions. It has been concluded therefore that the experimental conditions applied by Janek and Adelhelm\textsuperscript{4,40} was reducing and can also be obtained under oxygen deficient environments. Further, it has been mentioned that reducing conditions can also stem from higher oxygen consumption compared with its supply during the discharge cycle which can in turn be translated to higher discharge current density. The surface area of the air electrode and the amount of electrolyte employed are other experimental parameters that have been hinted by authors to contribute to the kinetics of discharge product formation. More kinetic studies are needed to truly understand the correlation between the kinetic parameters of Na-O\textsubscript{2} cell
with the chemical composition of the discharge products. Such mechanism studies are especially important to control the charge overpotential of the cell.

1.3.2.2 Effect of electrolyte on the composition of the products

A major hurdle for Li-O$_2$ batteries is electrolyte instability within the cells electrochemical window.\textsuperscript{11, 12, 29, 72} Formation of parasitic side-products as a result of oxidative decomposition of the electrolyte components is believed to hinder the cyclability of the cell. A theoretical study by Viswanathan et al.\textsuperscript{73} suggested that the HOMO level and acid dissociation constant (pK$_a$) of the solvent is critical toward determining the chemical stability of Li-O$_2$ cell. An ideal solvent should have low HOMO levels and a high pK$_a$. However, a direct correlation was obtained between the HOMO level and pK$_a$ for the most studied solvents. DME has been offered to be the most stable solvent among the available choices for Li-O$_2$ system based on its good compromise between the oxidative stability and H-abstraction. Nevertheless, McCloskey et al.\textsuperscript{72} showed that even DME is not thoroughly stable for practical applications.

The electrolyte may also alter the reaction mechanism of the cell. Abraham et al.\textsuperscript{74} initially studied the influence of the electrolyte solvent on the ORR mechanism in non-aqueous Li-O$_2$ cells. The solvents employed in this study were chosen to cover a range of donor numbers (DN), which is a quantitative measure of the Lewis basicity of cations. Using the large-diameter TBA$^+$ cation, the authors observed a reversible one-electron redox reaction involving O$_2$/O$_2^-$. In the presence of Li$^+$ counter ion, however, more reduction steps were observed for O$_2$, implying that the Li$^+$ ion has decreased ability in stabilizing O$_2$-, the initial product of ORR in non-aqueous electrolytes. Interestingly, it was found that electrolyte solvents with larger DN may influence the ORR kinetics in the presence of Li$^+$ by stabilizing the O$_2$ intermediate and hindering it from further reduction. Based on the HSAB theory, the Li$^+$-solvent bond strength increases with the solvent’s DN. As a result, the formed Li$^+$-(solvent)$_n$ complex in high-DN solvents acts as a moderately soft acid, resulting in a more effective interaction with the moderately soft O$_2$- ion. On the other side, the Li$^+$-(solvent)$_n$ complex in low-DN solvents behaves as a hard acid due to the weak Li$^+$-solvent
bond, making a more effective interaction with $O_2^{2-}$ ion which is a hard base. Consequently, high-DN solvents may stabilize the superoxide ion via making stronger Lewis acid-base complexes, while low-DN solvents facilitate the chemical or electrochemical reduction of $O_2$ to $O_2^{2-}$ ion.

More recently, Bruce et al.\textsuperscript{75} reinvestigated the role of solvents on the reaction mechanism of Li-O$_2$ cells using solvents with different DNs. Using an approach similar to the study by Abraham et al.,\textsuperscript{74} the authors examined the electrochemical response of oxygen in the presence of both TBA$^+$ and Li$^+$ ions (Figure 1.8a and b). While a single one-electrode redox process was observed in the presence of TBA$^+$ ion for all solvents, the electrochemical response of oxygen showed a strong dependency on the solvent’s DN in the presence of Li$^+$ ions. Low-DN solvents exhibited one reduction peak and one ill-defined oxidation peak at potentials over 4.0 V (Figure 1.8a). Interestingly, high-DN solvents demonstrated two consecutive reduction and two oxidation peaks at around 3.5 and 4.0 V (Figure 1.8b). The large potential separation between the reduction and oxidation peaks of oxygen has been related to the ‘EC’ reaction mechanism in low-DN solvents. The single reduction peak in low-DN solvent is correlated to the electrochemical reduction of oxygen to $O_2^-$. The produced $O_2^-$ then chemically disproportionates to $O_2^{2-}$, which correspondingly requires more positive potential for oxidation (> 4 V). In high-DN solvents, however, the produced $O_2^-$ ion is dissolved and stabilized into the solvent and is available at the electrode surface for further electrochemical reduction to $O_2^{2-}$. Two reaction mechanisms have been proposed based on the different electrochemical responses for the ORR in low- and high-DN solvents (Figure 1.8c). In low-DN solvents, according to the authors, the produced LiO$_2$ adsorbs on the electrode surface where it quickly disproportionates to Li$_2$O$_2$. In high-DN solvents, however, LiO$_2$ initially dissolves into the electrolyte and then disproportionates to Li$_2$O$_2$ via a currently undefined process. Furthermore, high-DN solvents demonstrate a considerable increase in discharge capacity compared to low-DN solvents. Higher discharge capacity in high-DN solvents has been correlated to the Li$_2$O$_2$ growth from the solution in contrast to its formation on the electrode surface in low-DN solvents.
Figure 1.8: (a and b) Cyclic voltammogram of a gold electrode in (a) CH$_3$CN and (b) Me-Im with various ratios of [Li$^+$]:[TBA$^+$]. The Li$^+$ concentration is depicted on the plots, where the remaining concentrations to 100 mM are TBA$^+$. The scan rate was 100 mV s$^{-1}$ and the anion was ClO$_4^-$.

(c) Schematic of the O$_2$ reduction mechanism in an aprotic solvent containing Li$^+$ showing the surface pathway followed when $\Delta G^\circ \gg 0$ (low DN) and the solution pathway followed when $\Delta G^\circ \ll 0$ (high DN). Plot at right corner shows the dominant pathway as a function of DN and potential.

Adapted from ref. 75.

Such a study related to the effect of the electrolyte solvent on the reaction mechanism found in Na-O$_2$ cells is still absent. However, it can be anticipated that Na-O$_2$ cells would show a more significant correlation between the electrochemical response of the cell and the electrolyte solvent, since the thermodynamic stability values of the sodium peroxide and superoxide are close (see also Figure 1.6e). It is expected that the chemical composition of the products in Na-O$_2$ cells can be precisely controlled with manipulating the kinetic parameters of the cell, including the electrolyte solvent. High-DN solvents may contribute to stabilize the superoxide phase and prevent disproportionation from occurring, which in
turn results in lower charging overpotential in Na-O₂ cells. Based on the abovementioned criteria for a desired electrolyte solvent, identifying a high-DN solvent with low HOMO level and high pKₐ may greatly enhance the cyclability of the present Li- and Na-O₂ cells. It should be noted that an appropriate solvent must display compatibility with Li or Na metal anodes, high electrolyte salt and O₂ solubility, and high ionic conductivity. Finding such a desired electrolyte solvent would be less challenging in the case of Na-O₂ cell, since the charging overpotential of the cell is lowered to less than 3.5 V. So, a chemically stable solvent, with a relatively higher HOMO level, may also be beneficial for enhancing the Na-O₂ cell cyclability.

1.3.2.3 Effects of chemical composition of discharge product on the charge overpotential of Na-O₂ cells

Amine and Curtiss et al.⁶⁸,⁶⁹ demonstrated analytical evidence regarding the presence of a lithium superoxide-like phase in Li-O₂ cells which were decomposed at a relatively low charging potential of 3.2-3.5 V. The authors attributed the low-potential charging plateau to the decomposition of a LiO₂-like discharge product formed on (Li₂O₂)ₐ clusters. Ceder et al.⁷⁶ however, argued that the initial lower-potential charging step is correlated to the off-stoichiometric delithiation of Li₂O₂ to form local superoxide ion. The authors used ab initio computations to show that the formation of non-stoichiometric Li₂₋ₓO₂ compounds out of Li₂O₂ discharge product is thermodynamically more favorable and requires only about 370 mV of overpotential. The formed off-stoichiometric states would then undergo further delithiation until finally decomposing into Li⁺ and O₂ or O₂⁻. Furthermore, the mobility of Li vacancy in Li₂O₂ is high enough to expect good electronic conductivity in off-stoichiometric Li₂₋ₓO₂ phase.⁷⁷-⁷⁹ Higher electronic conductivity of the Li₂₋ₓO₂ phase may also contribute in reducing the charging overpotential of the cell, since poor electrical conductivity of deposited Li₂O₂ at the air electrode/electrolyte interface is proposed to suppress charge transfer from occurring through the air electrode and increase the imposed potential during the charge cycle in order to overcome the charge transfer limitation.⁷⁷,⁷⁹,⁸⁰
In the case of Na-O$_2$ cells, however, an evident difference can be observed for the charging overpotential required. While a low overpotential of less than 0.2 V has been obtained in some studies in which NaO$_2$ has been detected as the discharge product (Figure 1.6), a relatively high overpotential of more than 1 V has also been reported with Na$_2$O$_2$ as the main product. Similar to the Li-O$_2$ cell, a larger charging overpotential for Na$_2$O$_2$ might be related to the different electrochemical pathways during the discharge and charge cycles. Discharge reaction in Li-O$_2$ cell results in the formation of a LiO$_2$ intermediate which subsequently disproportionates to Li$_2$O$_2$. On charging, however, Li$_2$O$_2$ directly decomposes to lithium and oxygen in a one-step electrochemical reaction. The different discharge and charge pathways reveal that the electrochemical reaction of the Li-O$_2$ cell might not involve a classic reversible redox couple. Meanwhile, other reports on Na-O$_2$ cells, exhibit more than one charge plateau with different overpotentials. In a previous study conducted by our group, we employed a variety of analytical techniques including a synchrotron-based XAS to determine the nature the discharge product at various charging plateaus. Based on this analysis, it was concluded that the superoxide-like product decomposes at a relatively lower overpotential compared to the peroxide-like product (see also Figure 1.7). In addition, a sodium deficient phase of sodium peroxide, with a general formula of Na$_{2-x}$O$_2$, was proposed to be formed as the product of Na-O$_2$ cells and can be decomposed at a middle overpotential.

Superoxide-like phases of lithium and sodium show lower charging overpotentials in both Li- and Na-O$_2$ cells. The observed lower overpotential might be related to the presence of a classic redox pair of O$_2$/O$_2$. In the case of Na-O$_2$ cell, the higher radius of sodium ion contributes to stabilize the superoxide ion and form a solid sodium superoxide phase which has been detected as the major product of the cell by researchers. In addition, higher electrical conductivity of the oxygen-rich phases of lithium and sodium oxides may also contribute toward reducing the charging overpotential. Increased electrical and ionic conductivity of the oxygen-rich lithium peroxide phase may play an important role in decreasing the charging overpotential of the Li-O$_2$ cells. Regardless of the mechanism involved in the overpotential reduction, formation of the oxygen-rich oxide phases is beneficial in decreasing the charging overpotential for both Li- and Na-O$_2$ cells. Manipulating the kinetic parameters of the cells to enrich the oxygen-rich phases in the
products of Li- and Na-O\textsubscript{2} cells can be considered as a research direction toward more energy-efficient cells. Future efforts should be devoted to truly understanding the role of kinetics parameters in the chemical composition of the discharge products of alkali metal-O\textsubscript{2} cells. However, based on literature available on Na- and Li-O\textsubscript{2} cells, it can be concluded that discharge products obtained under oxygen-deficient (reducing) conditions are more likely to be oxygen-rich.

1.4 Cyclability in Na-O\textsubscript{2} cell

1.4.1 Morphology of the discharge products

A variety of factors have been proposed to contribute in the relatively high charging overpotential and poor cycle life of the Li-O\textsubscript{2} cell. Low electrical conductivity of the deposited Li\textsubscript{2}O\textsubscript{2} at the electrode/electrolyte interface is thought to impose a large overpotential during the charging cycle in order to overcome the charge transfer limitation\textsuperscript{77, 79-81}. In addition, formation of an insulating carbonate layer at the electrolyte/Li\textsubscript{2}O\textsubscript{2} and Li\textsubscript{2}O\textsubscript{2}/carbonaceous air electrodes interfaces has been proven to contribute in high charging overpotential of the Li-O\textsubscript{2} cell, even in the relatively more stable electrolytes\textsuperscript{9, 13, 14}. However, a galvanostatic intermittent titration technique (GITT) study\textsuperscript{82} demonstrated that the equilibrium overpotential of Li-O\textsubscript{2} cells is close to zero, suggesting that the overpotential of the cell originates from a mass transfer limitation rather than the charge transfer one (at least under the low current densities). With the use of GITT, the authors were able to study the overpotential of the cell in both transient and steady-state modes. A zero open circuit voltage (OCV) hysteresis was observed between the equilibrium voltage of the discharge and charge of Li-O\textsubscript{2} cell during the GITT experiment with a 6 h relaxation time at 60°C. The findings of this study also highlight the impact of product morphology on charging overpotential of the cell. The correlation between morphology of discharge product and charging overpotential is discussed in this section.

A number of studies have identified a crystalline cubic NaO\textsubscript{2} phase as the major discharge product in Na-O\textsubscript{2} cells (Figure 1.9a-c)\textsuperscript{4, 19, 22, 40}. Micrometer-sized discharge products of the cells in these studies exhibited a low charging overpotential. However, the coulombic
efficiency was lower than 100% in all cases, resulting in poor cycling performance of the cell. Electrical isolation of the products as a result of progression in decomposition process at the product/substrate interfaces might be responsible for poor cycling performance in these studies. However, other research studies have indicated that Na$_2$O$_2$ or its hydrated form (Na$_2$O$_2$·2H$_2$O) was the major discharge products (Figure 1.9d-f).\textsuperscript{16,18,83} Depending on the cells physicochemical conditions, a number of different morphologies have been observed for sodium peroxide discharge product. Meanwhile, a combination of NaO$_2$ and Na$_2$O$_2$ was also found in other studies (Figure 1.9g-i).\textsuperscript{23,26,30,84} A mixture of crystalline (cubic-like) and amorphous products can be recognized in SEM images, in accordance with the analytical characterization of the products. Variety of different physicochemical factors affect the morphology of products in metal-O$_2$ cells. Electrode/electrolyte interactions, electrolyte concentration, surface area of the air electrode, discharge current density and oxygen partial pressure are among the most effective factors.

A correlation between the charging overpotential and the morphology of the discharge products of Li- and Na-O$_2$ cell has been investigated in a few studies. Nazar et al.\textsuperscript{67} found that the morphology of the discharge product in Li-O$_2$ cells is influenced by discharge current density. The products morphology was changed from a crystalline toroid-shaped at lower current densities to an amorphous product at higher current densities (Figure 1.9m-o). The change in crystallinity with increasing discharge current density was also confirmed by XRD. More importantly, the change in product morphology was also accompanied by a corresponding decrease in charging overpotential. Formation of an amorphous deficient phase of Li$_2$O$_2$ at higher discharge current densities has been proposed to be responsible for the reduction of charging overpotential.

A similar dependency of charging overpotential with discharge current density has also been observed for Na-O$_2$ cells (see Figure 1.7b). Further, a comparable conversion in the morphology of the discharge products was also found in our study on Na-O$_2$ cells.\textsuperscript{26} In the latter instance, the product morphology was correlated with an increase in the mesopore surface area of the electrode. While crystalline tablet-shaped particles were formed on low surface area air electrode, nanometer thick films were observed in high surface area electrodes (Figure 1.9j-l).
Figure 1.9: SEM micrographs of the discharge products of Na-O₂ cell using (a and b) carbon fiber;¹⁹,⁴⁰ (c) vertically aligned carbon nanotubes;²² (d) nitrogen-doped graphene nanosheets;¹⁶ (e) carbon nanotube paper;¹⁸ (f) NiCo₂O₄ nanosheets;⁸³ (g) porous CaMnO₃;²³ (h) nitrogen-doped carbon nanotubes;⁸⁴ (i) nitrogen-doped carbon nanotubes on carbon paper³⁰ air electrodes. (j-l) Change in morphology of the discharge products of Na-O₂ cell using heat-treated carbon black with different specific surface area values of (j) 155.3 (k) 1053.5 (l) 1390.1 m² g⁻¹ as the air electrode.²⁶ (m-o) Change in morphology of the discharge products of Li-O₂ cell using Vulcan XC72 carbon black air electrode discharge under different current densities of (m) 5; (n) 25; and (o) 100 µA cm⁻².⁶⁷ Adapted from ref. 16, 18, 19, 22, 23, 26, 30, 37, 67, 83 and 84.
The conversion trend of product morphology in these two studies may seem contradictory at first, since the local discharge current density decreases with increasing active surface area. However, the local concentration of dissolved oxygen and/or metal ions at the electrochemical active sites exhibited a similar trend. The local concentration of the electrochemical active species at the air electrode surface decreases with an increase in both discharge current density and surface area of the air electrode. Low concentration of the electrochemical active species increases the local overpotential at active sites which in turn results in an accelerated nucleation process and formation of a deficient amorphous phase. It should also be noted that there should be a significant change in either the discharge current density or the air electrode surface area in order to recognize a distinguishable change in the morphology of the products. In the abovementioned studies for instance, the morphology of the cell products is monitored while the discharge current density and the specific surface area of the air electrode are increased by 20 and 17 times, respectively.

The correlation between morphology of Li-O\textsubscript{2} cell product and the discharge overpotential has been demonstrated in a study conducted by Shao-Horn and Thompson et al.\textsuperscript{85} A similar dependency of product morphology was also observed in this study, where large and crystalline Li\textsubscript{2}O\textsubscript{2} particles were found after the discharge under a relatively low current density. However, an increased number of Li\textsubscript{2}O\textsubscript{2} particles with smaller dimensions was obtained at higher current densities. The mechanism of nucleation and growth of discharge products is compared to the electrodeposition of metals on foreign substrates. Based on the Volmer-Weber island growth theory, higher discharge overpotential caused by a higher current density, results in more energetically accessible nucleation sites. Thus, the nucleation process exceeds the growth of the nuclease, forming an increased number of smaller particles. On the other side, a lower number of nucleation sites is energetically accessible at lower discharge overpotentials or lower current densities, resulting in exceeding the growth process and the formation of larger particles. A similar dependency of the product morphology on the discharge overpotential is also expected in the case of Na-O\textsubscript{2} cell. Furthermore, a nucleation-controlled regime may also result in the formation of deficient phases of lithium and sodium peroxide which is beneficial for both battery systems in terms of reducing the charging overpotential.
1.4.2 Side reactions

1.4.2.1 Parasitic reactions

The chemistry of Na- and Li-O₂ cells was studied in a comparative study by McCloskey et al.\textsuperscript{21} Li-O₂ cells in this study exhibited an initial low charging overpotential which continually increased to more than 4.5 V vs. Li/Li⁺ in an ether-based electrolyte. Na-O₂ cells, however, displayed a low charging overpotential throughout most of the charge cycle with a sudden jump up to above 4 V vs. Na/Na⁺. To learn more about the chemistry behind Na- and Li-O₂ cells, the authors examined the galvanostatic discharge/charge of Na- and Li-O₂ cells by means of DEIMS. The number of electrons transferred per consumed and evolved O₂ during the discharge and charge cycles of Na-O₂ cell was calculated to be close to 1, illustrating that the product of the cell is NaO₂. In addition, the total parasitic side products formed during the discharge and charge cycles of the Na- and Li-O₂ cells was also measured based on the comparison of oxygen consumption and evolution to desired product formation (Li₂O₂ or NaO₂). Na-O₂ cell showed smaller deviation from the defined variables of average electrons consumed per O₂, ratio of the amount of NaO₂ formed to amount of NaO₂ expected given the Coulometry, and ratio of O₂ evolved on charge to O₂ consumed on discharge. It was concluded then that Na-O₂ cell demonstrates “cleaner” chemistry compared to Li-O₂. Furthermore, it was found that less decomposition of the electrolyte/cathode occurs in the Na-O₂ cell and also that most parasitic decomposition in Na-O₂ cells occurs during the discharge rather than charge cycle (Figure 1.10a).

In contrast, side products in Li-O₂ cell (mainly lithium carbonates) continuously form during charge cycle of the cell and leads to a continually increasing charging overpotential. Nevertheless, the origin of the sudden overpotential increase around the end of charging cycle in Na-O₂ cell is not clear yet. The same electrochemical response was also observed in Hartmann’s studies.\textsuperscript{4, 19} Either the accumulation of decomposition product on the air electrode surface or partial dissolution of NaO₂ into the electrolyte has been discussed as the potential reasons. However, a gradual increase of charging overpotential is expected to be seen in both cases. The mixed oxidation potential is expected to linearly increase with an increase in the side products/NaO₂ ratio. In addition, a diffusion-controlled electrochemical response should be seen in the latter case.
Figure 1.10: (a) Galvanostatic discharge-charge curves of Li- and Na-O₂ cells, and total Li₂CO₃ and Na₂CO₃ formed as measured by CO₂ evolution from discharged and partially charged cathodes immersed in 3 M H₂SO₄. The labels of the black arrows in are the charge-normalized Li₂CO₃ or Na₂CO₃ (in µmol Li₂CO₃ or Na₂CO₃/mAh) over the corresponding regions.²¹ (b) Gradual increase of the charging overpotential during consecutive discharge and charge curves of Na-O₂ cell using NCNT-CP air electrode cycled between 1.8 and 4.3 V at a current density of 0.1 mA cm⁻².³⁰ (c) Normalized O K-edge XANES spectra recorded under the TEY mode for the cycled air electrode as well as the standard Na₂O₂ and Na₂CO₃ samples.³⁰ Adapted from ref. 21 and 30.

A more probable scenario could be considered based on the clues from direct observation of the air electrode after several discharge and charge cycles by Hartmann et al.¹⁹ Partially
decomposed NaO₂ discharge product in deformed cubic shape could be seen on the air electrode surface after the cell cycling. It seems that progression of the decomposition process at the NaO₂/air electrode interface sites cuts off the electrical contact to the remaining discharge particles, leading to a sudden jump in charging overpotential and limited cycling performance. This explanation is in perfect accordance with theoretical calculations performed on the electronic structure of NaO₂ by Arcelus at al.⁶⁴ DFT calculations in the latter study revealed that the bulk, the extended (100) surface and (NaO₂)ₙ clusters (n = 4, 6) exhibit band gaps larger than 2 eV. As a result, O₂ reduction, and consequently evolution reactions, take place at the electrolyte/air electrode interface rather than at the NaO₂ surface, leading to loss of electrical contact between NaO₂ particles and the air electrode during the charge cycle.

Furthermore, studies conducted by our group also observed a continuous increase in the charging overpotential during consecutive discharge and charge cycles of Na-O₂ cells using NCNT-CP air electrode (Figure 1.10b).³⁰ In contrast to the abovementioned studies, a gradual increase of charging overpotential was observed in our study. Analysis of the side products on the air electrode after electrochemical cycling revealed the presence of a carbonate-like phase as well as Na₂O₂ on the electrode surface (Figure 1.10c). Based on the electrochemical and analytical data, this study conducted that a carbonate-like parasitic side product is produced on high surface area air electrodes, mainly as a result of decomposition occurring between the oxidative discharge product and the electrolyte. Accumulation of this insulating side product on the air electrode surface imposes an increasing overpotential to the cell during consecutive discharge/charge cycles and prevents complete decomposition of the discharge products. Even though Na-O₂ cells undergoes less chemical and electrochemical decomposition reactions compared to Li-O₂ counterparts during the first discharge and charge cycle according to McCloskey et al.,²¹ the formation and accumulation of carbonate-based parasitic side products on high surface area air electrodes and during consecutive discharge and charge cycles would be considerable. It is safe to say that the quantity of the parasitic products in Na-O₂ cell is lower than that of Li-O₂ due to the higher thermodynamic stability of NaO₂ phase compared to LiO₂. However, formation and accumulation of insulating side products as a
result of the decomposition reaction between highly oxidative discharge products and the electrolyte is believed to be responsible for the limited cycle life observed for both cells.

1.4.2.2 Reactions involving carbon dioxide

Formation of carbonates through parasitic reactions in Li- and Na-O2 cells is unfavourable for both cells due to the high decomposition potential of carbonate-based products. Carbonates have been known to form as a result of the reactions involving the oxidation of solvents56 and carbon cathodes13 as well as the chemical/electrochemical reactions between LiOx/NaOx with CO2. Although the influence of CO2 on the Li/Na-O2 cells with pure oxygen as the positive electrode material might be ruled out, it should be taken into consideration when ambient air is directly used as oxygen source for practical Li/Na-“air” batteries. These minor components in air may bring various side reactions, which can possibly influence the electrochemical reaction route and affect the performance of the metal air batteries.

Gowda et al.86 investigated the effect of CO2 contamination in Li-O2 cell using DME electrolyte for the first time. This study compared the electrochemical behavior of cells using pure O2, pure CO2 and 10:90 CO2/O2 mixture gas. They observed a 2 e-/O2 electrochemical process regardless of presence or absence of CO2, representing the formation of Li2O2 during the discharge cycle of the cells. In presence of CO2, however, a spontaneous chemical reaction between Li2O2 and CO2 resulted in formation of Li2CO3. Moreover, metallic Li anode was also reported to react with CO2 and O2 to form Li2CO3. The corresponding reactions are summarized as follow:86

\[
\text{Li}_2\text{O}_2 + \text{CO}_2 \rightarrow \text{Li}_2\text{CO}_3 + \frac{1}{2} \text{O}_2 \quad (1.15)
\]

\[
\text{Li}_{(s)} + \text{CO}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{Li}_2\text{CO}_3 \quad (1.16)
\]

The presence of Li2CO3 in the discharge product caused a significant increase to the overpotential required for releasing CO2 during the charging process. Accordingly, the
authors concluded it is essential to completely remove CO₂ from air to create a working rechargeable Li-air battery.

Later, Lim et al. extended the study on the effect of CO₂ to a wider range of solvents using both quantum mechanical calculations and experimental evidences. They revealed the reaction chemistry of Li-O₂ cell involving CO₂ during the initial stage of battery operation. It was found that the electrolyte solvation effect plays a critical role in alternating the reaction route at the initial complex formation (ICF) step. The proposed ICF processes involved is based on the following reaction scheme:

\[
\begin{align*}
O_2 + e^- & \rightarrow O_2^- \quad (1.17) \\
O_2^- + Li^+ & \rightarrow LiO_2 \quad (1.18) \\
O_2^- + CO_2 & \rightarrow CO_4^- \quad (1.19) \\
O_2^- + \text{electrolyte} & \rightarrow \text{decomposed electrolyte} \quad (1.20)
\end{align*}
\]

The authors stated that the potential energy surface plays a critical role in the formation of the final discharge product in the Li-air cell. Low dielectric solvents like DME were predicted to lead to the formation of Li₂O₂, while high dielectric solvents such as DMSO will result in the electrochemical activation of CO₂ to directly form Li₂CO₃ (Figure 1.11a). The authors also determined the chemical compositions of discharge products of Li-(9:1 O₂/CO₂) cell with DMSO and DME electrolytes to be only crystallized Li₂CO₃ and amorphous Li₂O₂-Li₂CO₃ mixtures, respectively, which is consistent with theoretical calculations. The GITT measurements of the Li-O₂ and Li-O₂/CO₂ batteries clearly displayed the differences between their electrochemical reaction mechanisms. Interestingly, Li-O₂/CO₂ cell with DMSO electrolyte was found to be highly reversible with Li₂CO₃ discharge products, implying the possibility of building Li-O₂/CO₂ batteries with high dielectric electrolytes.
Figure 1.11: Effect of CO$_2$ on the electrochemical behavior of Na-O$_2$ batteries. (a) Schematic graph of OER reaction pathways of a Li-O$_2$ battery in the presence of CO$_2$ with DME and DMSO electrolytes summarized from theoretical calculation and experimental evidence.$^{87}$ (b) Comparison of discharge profiles of Na-CO$_2$, Na-O$_2$, and Na-CO$_2$/O$_2$ cells with tetraglyme electrolyte.$^{94}$ (c) GITT discharge profile of Na-CO$_2$/O$_2$ cell with propylene carbonate electrolyte with the dotted lines indicating the theoretical potentials.$^{95}$ Adapted from ref. 87, 94 and 95.

The poisoning effect of CO$_2$ on (1-100) faced Li$_2$O$_2$ was investigated using DFT calculations by Mekonnen et al.$^{88}$ This facet was reported to possess suitable nucleation sites toward low overpotential growth of Li$_2$O$_2$.$^{89}$ It was found that CO$_2$ preferentially binds at step valley site at the Li$_2$O$_2$ surface and alters its growth mechanism. Even at a low concentration of 1%, CO$_2$ will severely block surface nucleation sites and result in a larger capacity as well as increased overpotential. Lu et al. carried out in-situ XPS experiments on Li-O$_2$/CO$_2$ cell and observed the formation of carbonate which was not fully decomposed during charging.$^{90}$ Nevertheless, the role of Li$_2$CO$_3$ on the rechargeability of the Li-O$_2$/air batteries can be more complicated than expected. Zhang and Zhou demonstrated a highly reversible Li-ambient air battery with multi-layer electrolytes and a gel single-walled carbon nanotubes/ionic liquid (IL) cathode. Li$_2$CO$_3$ was found to be the discharge product and believed to result from the reaction between Li$_2$O$_2$, H$_2$O and CO$_2$.$^{91}$
Also, increasing interest has been drawn toward the development of reversible Li-CO$_2$/O$_2$ batteries. It is also worth noting that a Li-pure CO$_2$ battery does not deliver negligible capacity compared to CO$_2$/O$_2$ mixture gas with EC:DEC or DME electrolytes, but the cells with mixed CO$_2$/O$_2$ gas exhibited a 1.5 to 2.9 fold increase in capacity compared to pure oxygen. However the Li-pure CO$_2$ battery is found to be highly reversible with TEGDME electrolyte as well as Li-O$_2$/CO$_2$ one. These results imply the complex role of CO$_2$ in Li-air batteries, which needs to be carefully taken into consideration.

The impact of CO$_2$ on Na-air batteries was investigated by Archer and co-workers with IL, TEGDME and PC electrolytes and its reaction mechanism was proven to be even more complicated. As shown in Figure 1.11b, Na-CO$_2$/O$_2$ batteries with TEGDME present a 2.5 fold increase in capacity compared to the battery using pure O$_2$, while the Na-pure CO$_2$ batteries displayed decreased capacity. Na$_2$CO$_3$ and Na$_2$C$_2$O$_4$ were both detected in the discharge product for TEGDME electrolyte, while Na$_2$C$_2$O$_4$ is the major product with an IL electrolyte. In contrast, NaHCO$_3$ was found to be formed in the discharge product of Na-CO$_2$/O$_2$ batteries with PC electrolytes (Figure 1.11c). Such contrast between the electrochemical behavior and discharge products of Na-CO$_2$/O$_2$ batteries with different electrolytes may be attributed to the difference between solvation effect of the electrolyte and stability of lithium/sodium salts according to HSAB theory as mentioned above. However, further theoretical calculations are still needed to address the insufficient understanding of the effect of CO$_2$ on Na-air batteries.

### 1.4.2.3 Humidity effect

Similar to CO$_2$, water is another non-negligible component in air that has underestimated influence on Li- and Na-air batteries. Unlike CO$_2$, H$_2$O mainly exists as liquid phase at STP. Its maximum concentration in gas is determined by saturation water vapor pressure under certain temperature and pressure. Therefore, the concentration of water in air is often expressed by the ratio of the actual water vapor pressure to the saturation water vapor pressure at the same condition and referred as relative humidity (RH). The saturation water concentration in air at STP is around 3%, which is around 75 times higher than that of CO$_2$.
(~0.04%), whose impact should certainly be taken into serious consideration in Li/Na-air batteries. Although one may simply assume that water will be fatal to a Li/Na-air battery, due to its chemical reactivity toward lithium and sodium (super, per)oxides, its role in these batteries has been proven to be more complex and critical than expected.

Meini et al. compared the electrochemical behavior of Li-O₂ batteries with and without water in the electrolyte with an improved cell design for the first time. It was surprising to observe that a cell with 1000 ppm of water exhibited a capacity increase 2.8 times than that of a water-free cell. When the authors purged the O₂ with water vapor into the cell, it demonstrated an overwhelming large capacity of around 14 times than that of the water-free one. A ~50 mV higher increased voltage output was also observed for the water-contaminated cell comparing to the dry one. Therefore, the authors proposed the following alternation reaction mechanism:

\[
4\text{Li} + 2\text{H}_2\text{O} + \text{O}_2 \rightarrow 4\text{LiOH} \quad E^\circ = 3.35\text{V} \quad (1.21)
\]

which is 40 mV higher than the potential corresponding to the formation of Li₂O₂ (Eqn. 8), and suggested that the capacity of Li-O₂ batteries should be carefully calibrated by taking the impact of water into consideration.

This phenomenon of trace amount of water significantly enhancing the discharge capacity of Li-O₂ batteries is also supported by studies conducted by other researchers. Guo et al. studied the influence of RH on the performance of Li-O₂ batteries in detail. They found that the cell ran under O₂ with 15% RH showed twice of the capacity than that with dry O₂. However, any efforts in further increasing the RH to 50% resulted in decreased electrochemical performance. IR and XRD analysis concluded that Li₂O₂, LiOH and Li₂CO₃ are the major discharge products formed under wet environments. Interestingly, it is worthy to note that even under wet conditions, Li-O₂ batteries were found to be reversible and maintain 30-50 cycles with a cut-off capacity of 1000 mAh g⁻¹ at a current density of 200 mA g⁻¹. This indicates that the impact of water on Li-O₂ batteries can be subtle and therefore be easily underestimated and ignored. Cho et al. focused on the influence of water vapor on the metallic Li anode and reported that water can penetrate the cell and directly
react with Li to form LiOH and release H\textsubscript{2}, which was responsible to the failure of the
cell.\textsuperscript{98}

Recently, understanding of the role of water in Li-O\textsubscript{2} batteries has been further
investigated. It was reported that the formation and growth of large Li\textsubscript{2}O\textsubscript{2} toroids can be
promoted by adding water to the electrolyte mixture.\textsuperscript{99, 100} It is reported that no LiOH was
detected in cathodes discharged in electrolytes with up to 1\% of water.\textsuperscript{100} This
unanticipated behavior of Li-O\textsubscript{2} batteries is believed to be related to the sophisticated
chemistry and stability of Li\textsubscript{2}O\textsubscript{2} against H\textsubscript{2}O. Gasteiger and co-workers proposed the
formation of Li\textsubscript{2}O\textsubscript{2} in the presence of water may involve the recrystallization reaction route
of Li\textsubscript{2}O\textsubscript{2}.\textsuperscript{100, 101}

\[ 2\text{LiOH} + \text{H}_2\text{O}_2 \rightarrow \text{Li}_2\text{O}_2 + 2\text{H}_2\text{O} \quad \text{(1.22)} \]

where H\textsubscript{2}O\textsubscript{2} may originate as a result of the following reactions:

\[ 2\text{H}^+ + \text{Li}_2\text{O}_2 \rightarrow \text{H}_2\text{O}_2 + 2\text{Li}^+ \quad \text{(1.23)} \]

\[ \text{O}_2 + e^- + \text{H}^+ \rightarrow \text{HOO}^- \quad \text{(1.24)} \]

\[ \text{O}_2^- + \text{HOO}^- \rightarrow \text{HOO}^- + \text{O}_2 \quad \text{(1.25)} \]

\[ \text{HOO}^- + \text{H}^+ \rightarrow \text{H}_2\text{O}_2 \quad \text{(1.26)} \]

Aetukuri et al. reported that the promotion effect of water on the discharge capacity of Li-
air batteries roots in the alternation of surface reaction mechanism to a solvent dissolution
of superoxide anion O\textsubscript{2} as a redox mediator.\textsuperscript{99} Water, as a high AN solvent, is believed to
contribute in the stabilization of O\textsubscript{2} as, and thus promote the dissolution for LiO\textsubscript{2}\textsuperscript{*} into Li\textsuperscript{+}
(sol) and O\textsubscript{2} (sol). The following reactions then take place:

\[ \text{O}_2^* + \text{Li}^+_{\text{(sol)}} + e^- \rightarrow \text{LiO}_2^* + \text{Li}^+_{\text{(sol)}} + e^- \rightarrow \text{Li}_2\text{O}_2(s) \quad \text{(1.27)} \]

As a result, Li\textsubscript{2}O\textsubscript{2} is formed as the final product of Li-air batteries in the presence of water.
Nonetheless, the authors suggest that water cannot be considered as a good additive, since
it will increases parasitic reactions in the cell.
A new strategy to reduce the charging overpotentials of Li-O\textsubscript{2} batteries by intentional formation and decomposition of LiOH produced in the presence of water has been recently proposed. Li et al.\textsuperscript{102} reported that adding 120 ppm of water to DMSO-based electrolyte results in significant reduction of the charge overpotential to 0.21 V in Li-O\textsubscript{2} cell with a Ru/MnO\textsubscript{2}/Super P air electrode, leading a discharge/charge potential gap of only 0.32 V and a superior cycling life of 200 cycles. The synergistic effect of Ru/MnO\textsubscript{2}/Super P catalyst during the charge cycle was proposed to undergo the following reaction:\textsuperscript{102}

\[
\text{Li}_2\text{O}_2(\text{s}) + 2\text{H}_2\text{O}(l) \rightarrow 2\text{LiOH}(s) + \text{H}_2\text{O}_2(l) \quad (1.28)
\]

\[
\text{H}_2\text{O}_2(l) \xrightarrow{\text{MnO}_2} \text{H}_2\text{O}(l) + 1/2 \text{O}_2(g) \quad (1.29)
\]

\[
\text{Li}_2\text{O}_2(s) + 2\text{H}_2\text{O}(l) \rightarrow 2\text{Li}^+ + \text{O}_2(g) + 2\text{H}_2\text{O}(l) + 2e^- \quad (1.30)
\]

The authors also noted that further increasing the amount of water (281 ppm) leads to a shortened charge plateau with increased charging potential. Higher Nernstian potential resulted from increased concentration of H\textsubscript{2}O around pre-formed LiOH is suggested as the possible reason.\textsuperscript{102}

Liu et al. also reported that dissolved LiI catalyst can also act as a soluble catalyst to promote the efficient removal of LiOH:\textsuperscript{103}

Discharge:

Electrochemical: \(4\text{Li}^+ + 4\text{O}_2 + 4e^- \rightarrow 4\text{LiO}_2\) \quad (1.31)

Chemical: \(4\text{LiO}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{LiOH} + 3\text{O}_2\) \quad (1.32)

Charge:

Electrochemical: \(6\text{I}^- \rightarrow 2\text{I}_3^- + 4e^-\) \quad (1.33)

Chemical: \(4\text{LiOH} + 2\text{I}_3^- \rightarrow 4\text{Li}^+ + 6\text{I}^- + 2\text{H}_2\text{O} + \text{O}_2\) \quad (1.34)

A low potential gap of 0.2 V between discharge and charge plateaus was reported by combining an rGO air electrode and LiI containing LiTFSI/DME electrolyte.\textsuperscript{103} Both of
these studies provide insight into the use of water as a chemical reagent for converting LiO₂/Li₂O₂ to LiOH in effort to reduce the overpotential of OER. These new findings are important in terms of both fundamental understanding and possible practical applications of Li-O₂ batteries.

Similarly, revealing the role of water in a Na-O₂ cell is expected to be equally essential. Our group has systematically investigated the composition of discharge product in Na-air batteries under different RHs recently.¹⁰⁴ We examined the electrochemical performance of the Na-air batteries under dry environments and RH ranging from 10-60% (Figure 1.12a), and identified the chemical composition of the corresponding discharge products under different RHs by their XRD patterns, FT-IR spectra and SEM images. Based on these experimental evidences, we have shown that the presence of water will alternated the reactions in Na-air batteries both chemically and electrochemically, which is also supported by thermodynamic calculations (Figure 1.12b). Na-air batteries are much more sensitive to water than Li ones. Although the cells presented increased discharge capacities under high RH, they were found to be totally irreversible and broke down during the first charge/discharge cycle. The discharge products of Na-air batteries under different RHs were found ranging from sodium superoxide and peroxide to hydroxides and carbonates, even with the same air electrode composition and cell configuration. These results might contribute toward clarifying the inconsistencies in the studies on Na-air batteries where different discharge products are observed. Besides, we also reported the releasing of liquid phase water from decomposing NaOH during the charge process, which is the reason for failure in Na-air batteries.

Nazar and co-workers investigated the critical role of protons in Na-O₂ batteries by comparing home-made water-free electrolyte salts with commercially available ones.¹⁰⁵ They showed that trace amounts of water in the electrolyte solution dramatically increases the capacities of cells (Figure 1.12c). More interestingly, they have shown that other proton donors like anhydrous acetic acid and benzoic acid could perform a similar role to promote the growth of cubic NaO₂. NaO₂ was confirmed to be the only discharge product by XRD with electrolytes containing up to 14 ppm water or acids (Figure 1.12d). Accordingly, the reaction mechanisms were proposed as follow.¹⁰⁵
Figure 1.12: Effect of water on the electrochemical response of Na-O_2 batteries. (a) Discharge curves of Na-air batteries under dry and humid air ambience with relative humidity of 10% to 60%.^96 (b) Calculated theoretical redox potentials of the possible reactions in Na-air batteries with and without the participation of water.^104 (c) First discharge curves of Na-O_2 cells using water-free and water-containing NaOTf salts and (inset) evolution of cell capacity toward water contents ranging from 0 to 14 ppm.^105 (d) XRD patterns of the discharged cathodes: black for dry pure NaOTf, blue for with 8 ppm water added, red for pure NaOTf with 14 ppm water, magenta for with 10 ppm anhydrous benzoic acid added, green for with 10 ppm anhydrous acetic acid added.^105 (e) Schematic graphs of the role of proton playing in ORR and OER processes of Na-O_2 cells as phase-transfer catalyst.^105

Adapted from ref. 104 and 105.

\[
\begin{align*}
HA + O_2^- & \leftrightarrow HO_2^- + A^- \\
HO_2^- + Na^+ & \rightarrow NaO_2 + H^+ 
\end{align*}
\] (1.35) (1.36)

where HA represents a weak acid. These weak acids play a role of phase-transfer catalyst and a low concentration of these species are proven to be essential to sufficient performance of Na-O_2 batteries (Figure 1.12e).
Ortiz-Vitoriano et al. reported that ambient exposure of discharged air electrode caused the transformation of NaO₂ in discharged electrode to Na₂O₂·2H₂O based on Raman and XRD evidences. In contrast, they stated that based on XRD results, only pure-phase NaO₂ was found to be the discharge product even at high concentrations of water electrolyte (6000 ppm). It was also noted by the authors that the actual water content in the electrolyte could be consumed by its reaction with the Na negative electrode. These results are consistent with the previous study by Zhao et al., who found that the discharge products of Na-air batteries contained NaO₂ under static oxygen environment and Na₂O₂·2H₂O under flowing oxygen gas. They also attributed the formation of Na₂O₂·2H₂O to the water content in the oxygen gas.

It can be inferred that water contamination in the gas input has a severe impact on the electrochemical performance of Na-air batteries. This can be attributed to the continuous supply of water from the flowing gas. Ortiz-Vitoriano et al. calculated the amount of water required to react with NaO₂ and produce Na₂O₂·2H₂O in a cell with a total discharge capacity of 1 mAh to be 3.73×10⁻⁵ mol. This amount of water in the typical 120 µl of electrolyte in the cell equals to around 6400 ppm. Here in this review, we can also simply estimate the content of humidity in air at STP by ideal gas law PV = nRT, where p is pressure, V is volume, n is mols of gas, R is gas constant, and T is absolute temperature in kelvin. The corresponding value of water vapor concentration in ambient air of 100% RH at room temperature (25°C) can be calculated to be approximately 1.28×10⁻⁶ mol mL⁻¹. This means that approximately 60 mL of air with RH of 50% at STP is theoretically capable of providing adequate water to decompose the same amount of NaO₂. This comparison can provide a preliminary understanding over the influence of water from gas input, considering a typical flow rate of several tens of sccm (mL min⁻¹) during the metal-air battery testing.

In summary, all the above studies strongly indicate the importance of eliminating water from both electrolyte and gas sources, which can be easily ignored but may contribute in drastically different electrochemical behaviors and rechargeability of the Li/Na-O₂ batteries. We believe that this feature should be carefully considered by the researchers moving from Li-O₂ to Na-O₂ batteries.
1.4.2.4 Binder

Binder is considered as another important component in the composition of air electrodes, which is generally a polymer and commonly used in the cathodes of Li/Na-O$_2$ batteries to integrate and hold the catalyst, carbon materials and supporting substrates together. Regardless of binder-free air electrodes, Binders are widely used for powder-based air electrodes. Polyvinylidene fluoride (PVDF) has been the most common choice adopted for metal-O$_2$ batteries, as it is also one of the most universally used binders for Li-ion batteries (LIBs). However, the role of binders in metal-O$_2$ batteries can be equally vital. Nazar and co-workers noticed the instability of PVDF binder towards superoxide species for the first time, and proposed the following decomposition route:\textsuperscript{106}

\[
\text{LiO}_2(s) + -(\text{CH}_2\text{-CF}_2)^-(s) \rightarrow \text{HO}_2 + -(\text{CH} = \text{CF})^- (s) + \text{LiF}(s)
\] (1.37)

The formed HO$_2$ subsequently disproportionates to H$_2$O$_2$ or H$_2$O together with O$_2$. This finding stimulates the urgent demand to search for an ideal binder for metal-oxygen batteries. Nasybulin et al. carried out a labour-intensive effort to screen the stability and reactivity of various binders.\textsuperscript{107} Eleven types of polymers were chosen to be dissolved in different solvents and mixed with Ketjenblack (KB) carbon black to fabricate air electrodes. Their chemical stabilities against peroxide and superoxide were examined by ball-milling the polymers with Li$_2$O$_2$ and KO$_2$, respectively, while the products were identified by XPS and XRD. A similar study was also carried out by Shao-Horn et al.\textsuperscript{108} FT-IR, UV-VIS absorption, and NMR characterizations were adopted for their study. In summary, the results and conclusion on the stability of the binders against superoxide and peroxide formation from these studies are listed in Table 1.3. It can be concluded that the functional groups on the backbone chain of the polymers are generally vulnerable to nucleophilic substitution attacking of O$_2^-$ and O$_2^{2-}$. The decomposition of binders can not only lead to the disintegration of the air electrode by losing sticking force, but also may form various side products from the decomposition reactions (e.g. H$_2$O), which could possibly participate in further side chemical/electrochemical reactions with discharge products, metal Li/Na anodes, and/or electrolytes to cause the failure of the cells.
Table 1.3: An overall summary of the reported stability of polymer binders versus superoxide and peroxide.

<table>
<thead>
<tr>
<th>Binder/Polymer</th>
<th>Stability against O$_2^-$</th>
<th>Stability against O$_2^{2-}$</th>
<th>Decompose Product</th>
<th>Reference</th>
</tr>
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<tbody>
<tr>
<td>PVDF</td>
<td>No</td>
<td>No</td>
<td>K(HF$_2$) (KO$_2$)</td>
<td>107</td>
</tr>
<tr>
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<td>No</td>
<td>-</td>
<td>HO$_2$ -(CH=CF)-; LiF (LiO$_2$)</td>
<td>106</td>
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<td>-</td>
<td>No</td>
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<td>107</td>
</tr>
<tr>
<td>PTFE</td>
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<td>Yes</td>
<td>-</td>
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<tr>
<td>Nafion</td>
<td>-</td>
<td>Yes</td>
<td>-</td>
<td>108</td>
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<tr>
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<td>No</td>
<td>-</td>
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<td>107</td>
</tr>
<tr>
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<td>Yes</td>
<td>-</td>
<td>107</td>
</tr>
<tr>
<td>PE</td>
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<td>Yes</td>
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<td>-</td>
<td>K$_2$CO$_3$ (KO$_2$)</td>
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<tr>
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<td>-</td>
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<td>-C=N; -C=C-N (Li$_2$O$_2$)</td>
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<td>-</td>
<td>LiCl</td>
<td>107</td>
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<td>-</td>
<td>No</td>
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<td>108</td>
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<td>107</td>
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<tr>
<td>PMMA</td>
<td>-</td>
<td>Yes</td>
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<tr>
<td>PIB</td>
<td>Yes</td>
<td>Yes</td>
<td>-</td>
<td>109</td>
</tr>
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</table>
Therefore, a stabilized binder toward superoxide/peroxide can be crucial toward developing long-life rechargeable Na-air batteries. As a conclusion summarized from Table 1.3, polyethylene (PE), polypropylene (PP), and fully fluorinated polymers (e.g. polytetrafluoroethylene (PTFE) and Nafion) are believed to be the most stable binders for these batteries. On one hand, novel polymer(s) have been also designed and tested for Li-O\textsubscript{2} batteries (e.g. polyisobutylene (PIB)\textsuperscript{109}). On the other hand, a binder-free design of air electrode may also be an alternative solution to this difficulty.\textsuperscript{30}

However, it should be noted that the abovementioned experiments on the stability of various polymers are generally carried out in a chemical (liquid-phase) or physical (ball-milling) environment. The effect of binder (decomposition) on a practical electrochemical cell may be more intricate than what have been suggested by their chemical reactivity. For example, it was reported that although PE was found to be the most stable polymer against superoxide/peroxide, the Li-O\textsubscript{2} battery with PE binder did not exhibited significantly prolonged cycling life compared to a cell made with PVDF binder (27 cycles versus 26 cycles).\textsuperscript{107} The authors attributed this phenomenon to an initial passivation stage of the binder by electrolyte decomposition. On the other hand, Shao-Horn and co-workers reported the decomposition of poly(ethylene oxide) (PEO) during charging to be much more severer in the presence of O\textsubscript{2} than under Ar.\textsuperscript{110} These studies suggest the necessity for the investigation of binders toward practical air cells. Nonetheless, the systematic experimental identification on the effect of binders for a practical Na-O\textsubscript{2} battery is still not presented. We have planned to address this aspect experimentally in the near future.

1.5 Air electrode design

1.5.1 Carbon based air electrodes

The gas diffusion electrode plays a fundamental role in metal-O\textsubscript{2} cells. The air electrode in these cells serves as a diffusing medium for the positive active material (oxygen) into the cell. This electrode must also provide adequate surface area for the accumulation of insoluble discharge product produced during electrochemical cycling. As a result, the final performance of the cell is strongly dependent on the efficiency of the air electrode. An ideal
air electrode should possess proper porous structure with an appropriate pore volume and pore size distribution. The porous structure is responsible for oxygen diffusion into the positive electrode material, formation and storage of the discharge products and also decomposition of the produced discharge products during the charge cycle. Carbon-based air electrodes have been used in a number of studies for Na-O₂ cells due to their unique carbonaceous properties such as excellent electrical conductivity, high surface area, light weight and controllable structure and porosity. Application of high surface area carbon materials with various porous structures and its correlation with discharge capacity and charge overpotential of the cell has been a major subject study within this field. Sun et al. demonstrated the use of diamond-like carbon (DLC) thin films air electrode as the first room-temperature Na-O₂ cell. DLC thin films in this study were deposited using r.f. sputtering using a carbon target. DLC thin film electrodes exhibited a specific discharge capacity of 1884 mAh g⁻¹ (0.56 mAh cm⁻²) at 1/10 C and 3600 mAh g⁻¹ (1.08 mAh cm⁻²) at 1/60 C in a carbonate-based electrolyte (Figure 1.13a).

Liu et al. reported the application of graphene nanosheets (GNS) air electrode in Na-O₂ cell. Thanks to the large surface area and excellent electrical conductivity of GNS, the electrode achieved a remarkable discharge capacity of 9268 mAh g⁻¹ at a current density of 200 mA g⁻¹. A nitrogen-doped graphene nanosheet (N-GNSs) analogue was also developed as an air electrode by our group and applied in Na-O₂ cells. N-GNSs air electrodes demonstrated a high discharge capacity of 8600 mAh g⁻¹ (3.6 mA cm⁻²) using a current density of 75 mA g⁻¹ (0.03 mA cm⁻²), a two fold increase in capacity compared to the pristine GNSs (Figure 1.13b). The significant high discharge capacity observed for N-GNSs air electrodes is attributed to its high surface area as well as presence of defective sites introduced by nitrogen doping in N-GNSs. On the other side, using a low surface area carbon fiber air electrode (< 1 m² g⁻¹) in Na-O₂ cell by Hartmann et al. resulted in a low discharge capacity of 300 mAh g⁻¹ (2.9 mAh cm⁻²) at a current density of 12.3 mA g⁻¹ (0.1 mA cm⁻²) along with the formation of micrometer-sized discharge products (Figure 1.9a, b). Bender et al. also employed various carbon structures for Na-O₂ cells and reported similar discharge capacities as well as electrochemical characteristics. However, no correlation was concluded between the discharge capacity values and surface area of the air electrodes, since different active material loadings were used to make the air electrodes.
In order to systematically study the correlation between the discharge capacity of the Na-O_2 cell with the surface area and porosity of the air electrode, we developed a series of engineered carbon material with controllable porosity and surface area. By applying a heat-treatment procedure to the commercial carbon black we were able to precisely control the porosity and surface area of air electrode materials. The heat-treated electrode materials were then employed as an air electrode for Na-O_2 cells. Our studies determined that the discharge capacity of the air electrode can be linearly correlated with specific surface area.
of the electrode material within the mesopores range (2-50 nm) (Figure 1.13c). More recently, Kwak et al.\textsuperscript{25} synthesized an ordered mesoporous carbon (OMC) material using hard template synthesis and evaluated it as an air electrode material for Na-O\textsubscript{2} cells. The OMC air electrode showed a specific discharge capacity of 7987 mAh g\textsuperscript{-1} which was 1.6 times larger than that of carbon black in a carbonate solution, using a current density of 100 mA g\textsuperscript{-1} (Figure 1.13d). However, sodium carbonate was detected as the major discharge product of cells, probably because of the decomposition of unstable carbonate solvent.

Carbon nanotubes (CNTs) are also widely used as the air electrode of the Na-O\textsubscript{2} cells. Jian et al.\textsuperscript{18} prepared a binder-free CNT paper as the air electrode of Na-O\textsubscript{2} cell with various electrolytes. The CNT paper exhibited the highest discharge capacity of 7530 mAh g\textsuperscript{-1} at a current density of 500 mA g\textsuperscript{-1} using 0.5 M NaSO\textsubscript{3}CF\textsubscript{3}/DEGDME electrolyte (Figure 1.13e). Zhao et al.\textsuperscript{22} also used vertically aligned carbon nanotubes (VACNTs) grown on stainless steel (SS) as the air electrode of Na-O\textsubscript{2} cell, where a discharge capacity of more than 4500 mAh g\textsuperscript{-1} was obtained under a current density of 67 mA g\textsuperscript{-1} (Figure 1.13f). In order to enhance the performance of the Na-O\textsubscript{2} cell, Bender et al.\textsuperscript{111} examined three different air electrode composed of pure CNT, CNT mixed with carbon fibers (CF), and CNT mixed with carbon black (CB). The pure CNT air electrode did not show a discharge capacity more than 1530 mAh g\textsuperscript{-1} and adding 45% of CF and CB into CNT electrode decreased the electrode discharge capacity to 800 and 530 mAh g\textsuperscript{-1}, respectively (Figure 1.13g).

Our group also designed and fabricated a 3D structured air electrode based on vertically grown nitrogen doped CNT on carbon paper (NCNT-CP) as an air electrode for Na-O\textsubscript{2} cells.\textsuperscript{30} The binder-free NCNT-CP electrode was prepared using spry pyrolysis chemical vapor deposition (SPCVD) of NCNTs directly on the 3D structure of CP. The synthesized NCNT-CP air electrode exhibited dual macro/meso-porous structure, in which large micrometer sized pores could be found between the individual carbon fibers, allowing for an increase in transportation of oxygen and sodium ions while solid state discharge products can be captured within the mesopores space provided by the NCNTs. The NCNT-CP air electrode showed a remarkable discharge capacity of 11.3 mAh cm\textsuperscript{2} (17 time larger than CP) under a current density of 0.1 mA cm\textsuperscript{2}. The elevated discharge capacity is a result
of the increased surface area provided by NCNTs allowing for discharge product to form, while the micrometer sized pores of CP structure guarantee the continuous supply of oxygen and sodium ions onto the electrode surface. The discharge capacity of the Na-O\textsubscript{2} cells using NCNT-CP air electrode decreased by 1.7 times upon 5 times increase in the discharge current density (Figure 1.13h), indicating good rate capability of the air electrode. This enhanced rate capability is a result of sufficient supply of oxygen and sodium ions into the air electrode. Summarized in Table 1.4 are the physical properties, experimental conditions and electrochemical responses of the carbonaceous air electrodes employed in Na-O\textsubscript{2} cells.

1.5.2 Catalyst

Another effective route toward improving the electrochemical performance and reversibility of Li/Na-O\textsubscript{2} batteries is through the introduction of catalysts into the air electrode. These catalytic centers are expected to promote the OER and ORR activities of the air electrode and accordingly overcome the sluggish kinetics in these batteries. The wisdom of exploring potential high performance electrocatalyst for alkali metal-O\textsubscript{2} batteries has been directionally guided by the tremendous precedential studies on OER/ORR catalyst for fuel cells. Consequently, noble metals and their alloys as well as non-noble metal oxides/nitrides/carbides have been widely applied for Li-O\textsubscript{2} batteries, which have been well-summarized in many other reviews.\textsuperscript{112-115} Although the electrocatalytic activity of these materials have been widely investigated, the mechanism responsible for the catalytic activity is still a highly debated topic.\textsuperscript{53, 65} On one side, initial formation of discharge products on the surface of the electrode during discharge is argued to rapidly reduce catalytic activity.\textsuperscript{65} For instance, McCloskey et al. demonstrated that conventional oxygen evolution electrocatalysis has no effects on Li-O\textsubscript{2} electrochemistry, but does influence the decomposition of electrolyte.\textsuperscript{116}

On the other side, there are a number of reports outlining the catalytic activity of noble and non-noble metals and metal oxides in Li-O\textsubscript{2} cells. It is believed that the ORR in non-aqueous metal-air cells is comprised of several consecutive electrochemical and non-
electrochemical stages including: initial charge transfer to dissolve oxygen, appearance of a low soluble oxygen-metal intermediate, charge transfer stage into the prepared oxygen-metal intermediate and final agglomeration into globular metal oxide precipitate. Catalyst may affect the specific reaction path taken and thus influence both appearance and structure of the oxygen-metal intermediates. Furthermore, use of catalysts may alter the size, structure, density and electronic conductivity of the metal-oxide products, since various intermediates present different mobility and diffusion rate. In such a way, it would be possible to explain the increase of the discharge capacity of metal-O\textsubscript{2} cells using an electrocatalyst as the air electrode. Formation of metal oxide products with increased conductivity in the presence of a catalyst may also result in an increase of discharge potential as well as a decrease in the charge overpotential for metal-O\textsubscript{2} cells. In a similar manner, design and application of suitable electrocatalysts for Na-O\textsubscript{2} cells may influence the discharge product composition and therefore cell overpotential. Metal oxides, which have been the most commonly choices for Li-O\textsubscript{2} batteries, are also widely examined in Na-O\textsubscript{2} batteries. Rosenberg and Hintennach reported the application of a-MnO\textsubscript{2} nanowires for Na-air batteries, which presented a large initial capacity of 2056 mAh g\textsuperscript{-1} but suffered 59\% decrease in capacity after 2 cycles. Liu et al. reported a Ni foam@NiCo\textsubscript{2}O\textsubscript{4} nanosheet electrode (Figure 1.14a), which exhibited a first discharge capacity of 1185 mAh g\textsuperscript{-1} and maintained 401 mAh g\textsuperscript{-1} after 10 cycles. Chen and co-workers developed a porous CaMnO\textsubscript{3} microspheres (Figure 1.14b), and tested it in Na-O\textsubscript{2} batteries. The CaMnO\textsubscript{3}/C electrode delivered a huge capacity of 9560 mAh g\textsuperscript{-1} at a current density of 100 mA g\textsuperscript{-1}, which was nearly 2.5 times of that of bare carbon black electrode. The Na-O\textsubscript{2} cell with CaMnO\textsubscript{3}/C electrode maintained 80 cycles with a restricted cut-off capacity of 1000 mAh g\textsuperscript{-1}. This prolonged cycle life is 8 times longer than bare carbon black (around 10 cycles). On the other hand, Zhang et al. combined Pt particles on graphene nanosheets (GNSs) to fabricate nanostructured Pt@GNSs catalyst for Na-O\textsubscript{2} batteries (Figure 1.14c). The discharge capacities of the cells increased from 5413 to 7574 mAh g\textsuperscript{-1} after introducing Pt. The cell with Pt@GNSs catalyst was cycled for around 10 cycles with a cut-off capacity of 1000 mAh g\textsuperscript{-1}. Clogging of the pores and coverage of catalytic active sites due to aggregation of discharge products results in a decrease in catalytic performance during cell discharge. Therefore, the cycling performance of the cells is
expected to improve with restricted cut-off capacities, which is consistent with afore-
mentioned reports.
Table 1.4 A summary of physical properties, experimental conditions and electrochemical responses of the carbonaceous air electrodes employed in Na-O₂ cells.

<table>
<thead>
<tr>
<th>Air electrode</th>
<th>BET Specific Surface area</th>
<th>Specific Discharge Capacity</th>
<th>Discharge Current Density</th>
<th>Electrode Loading</th>
<th>Electrolyte</th>
<th>Ref.</th>
</tr>
</thead>
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<tr>
<td>Carbon fiber</td>
<td>&lt; 1 m² g⁻¹</td>
<td>300 mAh g⁻¹ (2.9 mAh cm⁻²)</td>
<td>12.3 mA g⁻¹ (0.12 mA cm⁻²)</td>
<td>9.7 mg cm⁻²</td>
<td>0.5 M NaSO₃CF₃/DEGDME</td>
<td>4</td>
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<tr>
<td></td>
<td></td>
<td>12 mAh g⁻¹ (0.11 mAh cm⁻²)</td>
<td>51.4 mA g⁻¹ (0.50 mA cm⁻²)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diamond-like carbon (DLC)</td>
<td>-</td>
<td>3600 mAh g⁻¹ (1.08 mAh cm⁻²)</td>
<td>1/60 C</td>
<td>0.3 mg cm⁻²</td>
<td>1 M NaPF₆ EC/DMC</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1884 mAh g⁻¹ (0.56 mAh cm⁻²)</td>
<td>1/10 C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heat-treated carbon black</td>
<td>1282 m² g⁻¹</td>
<td>2783 mAh g⁻¹ (0.98 mAh cm⁻²)</td>
<td>75 mA g⁻¹ (0.03 mA cm⁻²)</td>
<td>0.25 mg cm⁻²</td>
<td>0.5 M NaSO₃CF₃/DEGDME</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1914 mAh g⁻¹ (0.67 mAh cm⁻²)</td>
<td>300 mA g⁻¹ (0.10 mA cm⁻²)</td>
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<td></td>
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<tr>
<td>ordered mesoporous carbon (OMC)</td>
<td>1544 m² g⁻¹</td>
<td>7987 mAh g⁻¹ (1.57 mAh cm⁻²)</td>
<td>100 mA g⁻¹ (0.02 mA cm⁻²)</td>
<td>-0.2 mg cm⁻²</td>
<td>0.5 M NaSO₃CF₃/PC</td>
<td>25</td>
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<tr>
<td>Graphene nanosheets (GNSs)</td>
<td>83 m² g⁻¹</td>
<td>9268 mAh g⁻¹</td>
<td>200 mA g⁻¹</td>
<td>-</td>
<td>0.25 M NaPF₆/DME</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1110 mAh g⁻¹</td>
<td>1000 mA g⁻¹</td>
<td></td>
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</tr>
<tr>
<td>Nitrogen-doped graphene nanosheets (N-GNSs)</td>
<td>-</td>
<td>8600 mAh g⁻¹ (3.6 mAh cm⁻²)</td>
<td>75 mA g⁻¹ (0.03 mA cm⁻²)</td>
<td>0.4 mg cm⁻²</td>
<td>0.5 M NaSO₃CF₃/DEGDME</td>
<td>16</td>
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<td>3980 mAh g⁻¹ (1.7 mAh cm⁻²)</td>
<td>300 mA g⁻¹ (0.12 mA cm⁻²)</td>
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<tr>
<td>Carbon nanotube (CNT) paper</td>
<td>-</td>
<td>7530 mAh g⁻¹ (~1.5 mAh cm⁻²)</td>
<td>500 mA g⁻¹ (0.1 mA cm⁻²)</td>
<td>-0.2 mg cm⁻²</td>
<td>0.5 M NaSO₃CF₃/DEGDME</td>
<td>18</td>
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<tr>
<td>vertically aligned carbon nanotubes (VACNTs)</td>
<td>80 m² g⁻¹</td>
<td>4500 mAh g⁻¹ (~6.3 mAh cm⁻²)</td>
<td>67 mA g⁻¹ (0.09 mA cm⁻²)</td>
<td>1.5 mg cm⁻²</td>
<td>0.5 M NaSO₃CF₃/TEGDME</td>
<td>22</td>
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<tr>
<td>CNT</td>
<td>215 m² g⁻¹</td>
<td>1530 mAh g⁻¹ (4.22 mAh cm⁻²)</td>
<td>65 mA g⁻¹ (0.2 mA cm⁻²)</td>
<td>0.6 g cm⁻³</td>
<td>0.5 M NaSO₃CF₃/DEGDME</td>
<td>111</td>
</tr>
<tr>
<td></td>
<td>CNT-CF</td>
<td>CNT-CB</td>
<td>Nitrogen doped carbon nanotube-carbon paper (NCNT-CP)</td>
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<tr>
<td>----------------</td>
<td>-----------</td>
<td>-----------</td>
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<td></td>
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<tr>
<td>Area m² g⁻¹</td>
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<td>128</td>
<td>27</td>
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<td>530</td>
<td>1349</td>
<td></td>
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<tr>
<td>Rate mA g⁻¹</td>
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<td>46</td>
<td>12</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Mass g</td>
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<td>0.82</td>
<td>0.26</td>
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<table>
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<tr>
<th></th>
<th>800 mAh g⁻¹ (4.37 mAh cm⁻²)</th>
<th>530 mAh g⁻¹ (2.30 mAh cm⁻²)</th>
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<tr>
<td>Rate mA g⁻¹</td>
<td>0.2 mA cm⁻²</td>
<td>0.2 mA cm⁻²</td>
</tr>
<tr>
<td>Mass g</td>
<td>126</td>
<td>126</td>
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Figure 1.14: Typical catalysts adopted for Na-O₂ batteries. SEM and XRD patterns of (a) NiCo₂O₄, (b) CaMnO₃, and (c) Pt@graphene nanosheets air electrodes. (d) Charge and discharge curves and schematic graph of a typical Na-O₂ cell with soluble NaI catalyst in electrolyte. Adapted from ref. 23, 24, 83 and 126.
Besides the above-mentioned “solid-state” catalyst fixed at the substrates of air electrodes, a family of “soluble” catalysts is attracting more research interests. The concept of these catalysts are based on certain dissolved chemicals with suitable redox potentials into the electrolytes of Li/Na-O\textsubscript{2} batteries. These mobile catalytic centers can easily transport inside the cell and perform as redox mediators. The involved reactions can be demonstrated as follow:

**ORR:**

\[ A_{\text{ox}} + e^- \rightarrow A_{\text{red}} \]  \hspace{1cm} (1.38)

\[ A_{\text{red}} + O_2 \rightarrow A_{\text{ox}} + O_2^- \]  \hspace{1cm} (1.39)

\[ O_2^- + \text{Li/Na} \rightarrow \text{LiO}_2/\text{NaO}_2 \]  \hspace{1cm} (1.40)

**OER:**

\[ B_{\text{red}} \rightarrow B_{\text{ox}} + e^- \]  \hspace{1cm} (1.41)

\[ 2B_{\text{ox}} + \text{Li}_2\text{O}_2/\text{Na}_2\text{O}_2 \rightarrow 2B_{\text{red}} + 2\text{Li}^+/\text{Na}^+ + O_2 \]  \hspace{1cm} (1.42)

Clearly, the required redox potential for ORR (discharge) and OER (charge) catalysts is different. Therefore, alternate mediators have been reported for enhancing ORR and OER reactions in Li/Na-O\textsubscript{2} batteries, respectively. Owen and co-workers demonstrated an ethyl viologen redox couple \text{EtV}^{2+}/\text{EtV}^{+} as ORR catalyst with ionic liquid electrolyte in Li-O\textsubscript{2} cell.\textsuperscript{118} Afterward, four families of halide anions (e.g. Cl\textsuperscript{−}, Br\textsuperscript{−}, I\textsuperscript{−}), aromatic compounds, quinones/quinoids, and transition metal complexes were also reported to be active for oxygen evolution in metal-oxygen batteries.\textsuperscript{119} The effect of the soluble catalyst on OER reactions in Li-O\textsubscript{2} batteries has also been shown to be remarkable. Bruce and co-workers found that tetrathiafulvalene (TTF) redox catalyst significantly reduced the charging potential of the Li-O\textsubscript{2} cell by around 0.6 V and enabled 100 consecutive discharge and charge cycles.\textsuperscript{120} Thereafter, various soluble catalysts were reported for Li-O\textsubscript{2} batteries.\textsuperscript{121-125}
Fu and co-workers reported the applicability of soluble NaI catalyst for Na-O\(_2\) cell for the first time. The cell employing NaI soluble catalyst maintained 150 cycles with a cut-off discharge capacity of 1000 mAh g\(^{-1}\) (Figure 1.14d).\(^{126}\) Later, the same group also reported that the cycling life of Na-O\(_2\) cell with soluble ferrocene catalyst can be further extended to 230 cycles using the same 1000 mAh g\(^{-1}\) cut-off capacity.\(^{127}\) These results highlight the efficiency of the redox mediator catalysts in Na-O\(_2\) batteries. In addition, Nazar and co-workers proved that trace amount of H\(^+\) (either from H\(_2\)O or other acid mediums) acts as a proton phase transfer catalyst (PPTC) and plays a critical role in determining: discharge capacity, NaO\(_2\) morphology, and recharging behavior of Na-O\(_2\) batteries.\(^{105}\) The authors synthesized pure home-made NaOTf salts via a chemical method to prepare a truly “water-free” electrolyte (0 ppm according to the authors). The Na-O\(_2\) cell with “water-free” electrolyte exhibited diminished discharge capacity and elevated charge overpotential compared to the electrolyte containing commercial NaOTf. Interestingly, when a small amount of water (8 ± 1 ppm) or around 10 ppm of organic acid (benzoic and/or acetic acids) was intentionally added to this “water-free” electrolyte, the corresponding Na-O\(_2\) cells exhibited similar electrochemical behavior to the cell with the electrolyte containing commercial NaOTf. To examine the charging (OER) process, the authors extracted NaO\(_2\) air electrodes from a discharged cell with electrolyte containing 10 ppm water and tried to recharge them in either the same water-containing or water-free electrolyte. The authors observed a low charging voltage plateau for the cell with water-containing electrolyte and a much higher voltage range, up to 4.5 V in the “water-free” electrolyte. Accordingly, the authors proposed that PPTC is critical for both ORR and OER processes of the Na-O\(_2\) cell. Meanwhile, considering the reactivity between water/acid and metallic sodium anode, employing a protective membrane for a practical cell is also suggested by the authors. These results indicate that even in a “catalyst-free” design of Na-O\(_2\) battery, trace amount of resident water in electrolyte contributes to reduce the charging overpotential of the cell, implying the indispensable role of catalysts in Na-O\(_2\) batteries.

Overall, comparing to the tremendous reports on the catalysts for Li-air batteries, the corresponding study on Na-air studies has been barely started. Nevertheless, it can be undoubtedly anticipated a rapid growth in this field in the near future. Various 3D
structured solid-state catalysts or soluble catalysts can be expected for future Na-O₂ batteries.

1.6 Summary and conclusion remarks

Alkali metal-O₂ batteries are considered as the next generation electrochemical storage devices with high energy density. These batteries can compete with gasoline in terms of theoretical energy density and therefore are promising candidates for future’s electric vehicles. However, there are still lots of challenges that must be addressed in order to employ alkali metal-O₂ batteries in practical applications. These challenges involve all three major components of the cell including metallic Na and Li electrodes, organic electrolyte, and air electrode of the cells. Both of metallic Na and Li electrodes form dendrite structures during consecutive discharge and charge cycles of the cells. Continuous formation and corrosion of these high surface area dendrite structures consume the metallic electrode and organic electrolyte of the cell and results in capacity failure as well as safety issues in these cells. In addition, conventional organic electrolytes of these cells are unstable against highly oxidative environment of alkali metal-O₂ cells and undergo chemical and electrochemical decomposition reactions which in turn results in poor cyclic performance of the cells. Search for a stable organic electrolyte or other alternative types such as solid state electrolyte for alkali metal-O₂ cells is an ongoing research area. Such a stable electrolyte system may address the described challenges involving negative electrode and electrolyte of alkali metal-O₂ cells.

There are also several challenges associated with the positive air electrode of alkali metal-O₂ cells. In the case of Na-O₂ cells, various metal oxides species might be formed during the discharge cycle of the cell based on the physiochemical condition of the cell. In addition, these various metal oxide products decompose at different charging potentials. Therefore, it is essential to define the most affecting experimental factors which determine the chemical composition of the discharge products to control the charging overpotential of the cell. This become even more critical when considering the fact that most important advantage of Na-O₂ cell over Li-O₂ is lower charging overpotential. As it was
comprehensively discussed earlier in the current chapter, there is no agreement among researchers on chemical composition of the discharge products in Na-O₂ cells and more fundamental studies are needed to clarify the matter. In the case of Li-O₂ cell, on the other side, there is a large charging overpotential associated with stable discharge products of the cell, Li₂O₂, which decreases the energy efficiency of the cell. Application of various homogeneous and/or heterogeneous catalyst systems has been proposed to decrease the charging overpotential of the cell. However, the mechanism and functionality of these catalytic materials is a point of controversy among the researchers in this field. More studies on both fundamental understanding of electro/chemical reaction mechanism of these alkali metal-O₂ cells as well as synthesis and application of stable electrolyte and catalytic systems are needed to address the current challenges facing development of the cells.

1.7 Thesis objectives

The conducted studies in the current thesis is aimed to increase the cyclic performance of alkali metal-O₂ cells. The studies presented here are focused on the positive air electrode of the cell. These studies can be divided into two major categories:

i) Design and synthesis of air electrodes

Various air electrodes are designed, synthesized and employed in Na-O₂ and Li-O₂ battery systems to increase the cyclic performance of the cells. Two major criteria have been considered for designing the air electrodes: a) decreasing the charging overpotential of the cell by controlling the morphology and chemical composition of the discharge products. b) suppressing the formation of side products during discharge and charge cycles of the cells. The synthesized air electrodes were characterized using various analytical techniques and the obtained data were correlated to the observed electrochemical performances. The acquired results then were employed as a feedback for further modification of initial electrode design.

ii) Study the electrochemical mechanism of the cells
The chemical and electrochemical reaction mechanism of the cells were also investigated in details, especially in the case of Na-O₂ cells. These studies were aimed to determine the most influential physicochemical factors controlling the chemical composition and morphology of discharge products in Na-O₂ cells. In addition, the mechanism behind the role of solid state catalysts in Na-O₂ and Li-O₂ cells was also studied.

1.8 Thesis organization

This thesis includes seven chapters (including two introductory chapters, four experimental chapters and one conclusive chapter), satisfying the requirements of “Integrated-Article” format as outlined in the Thesis Regulation Guide by the School of Graduate and Postdoctoral Studies (SGPS) of the Western University. Specifically, the present thesis includes the following parts:

**Chapter 1** presents an introduction to Na-O₂ cells including general working principles, chemical and electrochemical reactions, origin of charging overpotential, morphology and chemical composition of discharge products and side products, and various designs for air electrode and catalysts.

**Chapter 2** outlines the experimental methods and analytical techniques used to synthesized and characterize the electrode materials.

**Chapter 3** describes the synthesis and characterization of powder based carbonaceous electrode materials with controlled surface area and porosity using a heat-treatment procedure. The synthesized air electrodes were then employed in Na-O₂ cells and the correlation between air electrode surface area and electrochemical behavior of the cells were studied.

**Chapter 4** presents the synthesis and characterization of a binder-free three-dimensional air electrode composed of vertically aligned NCNT on carbon paper. The electrochemical studies demonstrate the significant advantage of the three-dimensional design of air electrode to increase the discharge capacity of the cell by enhancing the utilization of the
electrode materials. The chemical study on the failure mechanism of the cell also shows that formation of carbonate-based side products restricts the cycling performance of Na-O2 cells.

Chapter 5 reports the synthesis and characterization of an ultimate air electrode design for Na-O2 and Li-O2 cells. The synthesized air electrode is composed of graphene foam loaded with high surface area NCNT, mesoporous Mn3O4 and Pd nanoclusters. The synthesized mesoporous Mn3O4 increases the surface area of the air electrode and also protect the carbonaceous framework from oxidation by superoxide intermediate. In addition, Pd nanoclusters act as solid-state OER catalyst. The prepared air electrode showed a stable cycling performance in Na-O2 and Li-O2 cells. In addition, the mechanism behind the role of solid-state catalyst in alkali metal-O2 cells was studied in detail.

Chapter 6 represents the effect of oxygen-containing functional groups on the morphology and chemical composition of discharge products in Na-O2 and Li-O2 cells. Different hydrophobic and hydrophilic air electrode surfaces were synthesized and employed in the cells and the electrochemical behavior of the cells were studied. The results imply that discharge products of the cells react with oxygen-containing functional groups at the air electrode surface and affect the morphology and electrochemical response of the cells.

Chapter 7 summarizes the results and contributions of the present thesis. Furthermore, the author gives some personal opinions and suggestions regarding future research direction.
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Chapter 2

2 Experimental methods

2.1 Synthesis of electrode materials

2.1.1 Mesoporous carbon black with controlled porosity

The positive electrode materials were prepared using commercial carbon black (N330). The carbon black was heat-treated under NH$_3$ or CO$_2$ (with or without H$_2$) atmospheres at elevated temperatures. Precise amount of carbon black were heat-treated in a fused silica reactor under NH$_3$ or CO$_2$ atmosphere at 1050°C under varying durations. A small portion of the CO$_2$-treated samples was further pyrolysed under H$_2$ at 950°C to remove oxygen containing functional groups introduced by CO$_2$-treatment. Heat-treatment of carbon black removes disordered graphitic structures from the carbon, producing a porous carbon structure. The amount of the carbon mass lost during the heat-treatment was measured using initial and final masses and are presented in supplementary Table S1.

Table 2.1: BET specific surface area of heat treated carbon materials under different atmospheres.

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<th></th>
<th>CO$_2$</th>
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<th>CO$_2$/H$_2$</th>
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<td>Specific Surface area (m$^2$/g)</td>
<td>Mass Loss (%)</td>
<td>Specific Surface area (m$^2$/g)</td>
<td>Mass Loss (%)</td>
<td>Specific Surface area (m$^2$/g)</td>
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<td>1390.14</td>
<td>90</td>
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</tr>
</tbody>
</table>
2.1.2 Three-dimensional nitrogen doped carbon nanotubes on carbon paper

The nitrogen doped carbon nanotubes on carbon paper (NCNT-CP) electrode was prepared using a spray pyrolysis chemical vapor deposition (SPCVD) method according to the synthesis method which has been developed previously in our group.\textsuperscript{1} In a typical synthesis, a piece of carbon paper (CP) was sputtered with a 30 nm of aluminum as the buffer layer which can arise a rough surface absorbing iron atoms into the traps of the alumina layer forming uniform and well dispersed catalytic particles to obtain uniform and high density NCNTs on the CP. The sputtering was carried out under a pressure of 4.0 mTorr and at a power of 300 W. The CP was then fixed inside of a quartz tube (Ø 2.2cm × 70cm) with two gas inlets at the top and one gas outlet at the bottom. The quartz tube was then placed in center of a vertical furnace and argon gas (99.999\%) was purged into the tube at a flow rate of 500 sccm for 20 minutes. The furnace was then heated up to 850°C (see Figure 2.1).
The precursor solution was prepared by mixing 2 g of imidazole and 0.2 g of ferrocene in 10 ml of acetonitrile. The mixture was kept into an ultrasonic bath for 10 min to obtain a homogeneous solution. The solution was then transferred into a syringe and injected into an ultrasonic probe at a 250 µl/min feeding rate with the aid of a syringe pump. In the ultrasonic probe, the solution fed by the injection pump is atomized in an ultrasonic processor (VCX 130 PB, Sonics & Materials Inc.), and sprayed out at 45% amplitude as tiny droplets into the quartz tube. The produced droplets were carried into the center of the quartz tube by Ar carrier gas, where the growth of NCNT occurred onto the CP surface. After injection of the precursor solution for various synthesis times ranging from 3 to 10 minutes, the furnace was turned off and the system cooled down to room temperature in the flowing Ar gas.
2.1.3 Three-dimensional nitrogen doped carbon nanotubes on graphene foam

**Synthesis of graphene foam.** Graphene (Gr) foam was synthesized using a chemical vapor deposition (CVD) technique according to a previously reported procedure. The synthesis procedure is briefly described as follow: A piece of Ni foam (1.2 mm in thickness) was used as a self-sacrificing template and catalyst surface to grow graphene. Ni foam was cut into the desired dimensions and placed in a quartz tube. The quartz tube were transferred into a horizontal furnace and purged with Ar (500 sccm) and H\(_2\) (50 sccm) for 15 min. The furnace was then heated up to 1000 °C and kept at this temperature for 15 min to remove the surface contaminants and oxide layer from Ni foam. CH\(_4\) was then introduced into the tube as the carbon source at a flow rate of 0.5 sccm for 1 h. Then the sample was cooled down to room temperature under flowing Ar and H\(_2\). Afterward, the sample was placed in a 3 M HCl solution at 50°C overnight to completely dissolve Ni template.

**Synthesis of Gr/NCNT.** Gr/NCNT foam was synthesized using a modified spray pyrolysis chemical vapor deposition (SPCVD) method described in section 2.1.2. In a typical synthesis, Gr foam (with Ni template) was physically sputtered with a 30 nm of aluminum as the buffer layer and a 10 nm of iron as CVD catalyst. The Fe catalyst applied for NCNT growth was physically sputtered on the Gr surface in the modified SPCVD method, in contrast to the conventional process in which the catalyst was being sprayed on the desired surface. The modified SPCVD method provides better control over the density of NCNT. The sputtered Gr foam then fixed inside a quartz tube and transferred into a vertical furnace. The quartz tube was purged with Ar (500 sccm) for 15 min to remove the air. The furnace was then heated up to 850 °C and a solution containing 2 g of imidazole in 10 mL of acetonitrile was introduced into the tube with the aid of an ultrasonic probe sonicator at a flow rate of 250 μL/min for 10 min. The Ni template was consequently removed using the aforementioned etching procedure.

**Synthesis of Gr/NCNT/MnO.** Mesoporous Mn\(_3\)O\(_4\) was synthesized on NCNT surface using a chemical precipitation method. In a typical synthesis procedure, as-prepared Gr/NCNT sample were transferred into a solution containing KMnO\(_4\) (10 mg/ml) and
H$_2$SO$_4$ (5\%) at 45 °C for 3 min. The Gr/NCNT/MnO was then transferred into cold distilled water to stop the reaction and washed several times using water and ethanol.

**Synthesis of Gr/NCNT/MnO/Pd.** The Pd catalyst was deposited using an Arradiance GEMstar-8 ALD system using alternating exposure of Pd(II) hexafluoroacetylacetonate, Pd(hfac)$_2$, and formalin at a processing pressure of 0.8 Torr. Both precursors were obtained from Sigma Aldrich and used as received. Formalin solution was composed of 37\% formaldehyde in water containing 10-15\% methanol to prevent polymerization. Pd(hfac)$_2$ was held in a stainless steel bubbler at 50°C to maintain a vapor pressure slightly less than 0.1 Torr. Manifold temperature was maintained at 100°C while deposition temperature was kept constant at 200°C. Ultrahigh purity nitrogen (99.999\%) was used as a carrier gas and purge gas throughout the experiment with a mass flow of 20 sccm. ALD deposition can be expressed as $t_1$-$t_2$-$t_3$-$t_4$ where $t_1$ is the exposure time for the first precursor (Pd(hfac)$_2$) and $t_2$ is the purge time following the first precursor and $t_3$ and $t_4$ are second precursor pulse (formalin) and purge respectively. A timing sequence of 2-30-1-30 s was used for the deposition of Pd to produce the Gr/NCNT/MnO/Pd electrode.

### 2.2 Characterization techniques

#### 2.2.1 Morphological observation

Morphological studies were performed by Hitachi S-4800 field-emission scanning electron microscope (SEM, Figure 2.2), Hitachi H-7000 transmission electron microscopy (TEM, Figure 2.3) and high-resolution TEM (HRTEM, JEOL 2010FEG) scanning transmission electron microscopy (STEM). Electron microscopy techniques provide information of the surface topography and structure of materials. SEM and TEM use a focused high energy beam of electrons which interact with the sample surface and produce secondary electrons, back scattered electrons and characteristic X-ray. The produced electrons and characteristic x-ray can be detected using various detectors providing information about the morphology and composition of the samples.
Figure 2.2: Digital photo of SEM (Hitachi, S-4800) machine.

Figure 2.3: Digital photo of TEM (Hitachi, H-7000) machine.
2.2.2 X-ray diffractometry

X-ray diffractograms (XRD) were obtained using a Bruker D8 Advance (Cu-Kα source, 40 kV, 40 mA). XRD technique provides information about the crystal structure and physical properties of material. For the X-ray diffraction (XRD) measurements, the Na-O\textsubscript{2} cells were dissembled in the Ar-filled glovebox (MBRUAN, with water and oxygen contents below 0.1 ppm) after testing, and the positive electrode materials were placed into an air-sensitive XRD sample holder. The air-sensitive XRD sample holder then was transferred into the XRD machine (Figure 2.4) and analyzed immediately.

![Digital photo of Bruker D8 Advance XRD machine.](image)

Figure 2.4: Digital photo of Bruker D8 Advance XRD machine.
2.2.3 X-ray absorption spectroscopy

X-ray absorption spectroscopy (XAS) measurements were obtained at the Canadian Light Source (CLS) on the spherical grating monochromator (SGM) or hard X-ray microanalysis (HXMA) beamlines. In order to examine the discharge product of the cells, the discharged cells were dissembled inside the glovebox, the air electrodes were sealed and then moved to the analysis place, where the samples were opened in the second glovebox and placed into the XAS vacuum chamber. The samples were kept under pure argon atmosphere before the analytical measurements, without any exposure to the atmospheric air. The vacuum during the XAS experiments was around $10^{-8}$ Torr.

2.2.4 Other techniques

$N_2$ adsorption/desorption isotherms were obtained using a Folio Micromeritics TriStar II 3020 Surface Area and Pore Size Analyzer. The surface area of the electrodes was calculated by the Brunauer, Emmett, and Teller (BET) model by taking at least six data points where $0.07 < P/P_0 < 0.2$. Pore size distribution was obtained by the Barrett, Joyner, and Halenda (BJH) model using the desorption branch of the isotherm. Thermogravimetric analysis (TGA) was performed using a SDT Q600 TGA unite from room temperature (RT) to 900 °C in air at a heating rate of 10 °C min$^{-1}$. Fourier transform infra-red (FTIR) spectra and Raman scattering spectra were recorded using a Nicolet 380 and a HORIBA Scientific LabRAM HR Raman spectrometer system (Figure 2.5) equipped with a 532.4 nm laser, respectively. For the FTIR measurements, the sealed testing box containing Na–air cells was moved to an argon-filled glove box and the KBr disks containing 1% w/w of electrode materials were prepared in a glove box. Then, the prepared KBr disks were sealed and moved to the FTIR measurement chamber, while nitrogen gas was flushed into the chamber. For Raman analysis, the tested Na–air cells were moved to the glove box and the positive electrode materials were squeezed and sealed between two pieces of the glass slide.
2.3 Electrochemical measurements

Swagelok-type cells composed of sodium foil anode, Celgard 3500 separator (5/8 in. in diameter), different air electrode, and a stainless steel mesh as current collector were used to carry out electrochemical measurements. The employed Swagelok cell configuration is illustrated in Figure 2.6. The air electrodes were cut into circular pieces (3/8 in. in diameter) with the geometric surface area of 0.71 cm$^2$. A fresh sodium or lithium foil (3/8 in. in diameter) was used as negative electrode material. The electrolyte used in these study was 0.5 M sodium or lithium triflate (Na/LiSO$_3$CF$_3$, Aldrich) dissolved in diethylene glycol diethyl ether (DEGDME, Anhydrous ≥ 99.5%, Aldrich). Sodium and lithium triflate electrolyte salt was dried at 80 °C under vacuum for 48 h, and the water content of DEGDME solvent was removed using molecular sieves (3Å) for at least 10 days. The amount of electrolyte in the cell was ∼200 µL. The assembled Na or Li-O$_2$ cells were placed into a homemade testing box inside the glovebox and then transferred to the testing room. The argon content of testing box was moderately vacuumed out and then pure oxygen (purity 5.0) was purged into the box. The pressure of testing box was kept at 1.0 atm during the electrochemical tests. Discharge/charge characteristics were performed using an Arbin BT-2000 battery station at RT (25 °C).
Figure 2.6: The Swagelok cell configuration.

References


Chapter 3

3 On Rechargeability and Reaction Kinetics of Sodium-Air Batteries*

Rechargeable metal-air batteries are widely considered as the next generation high energy density electrochemical storage devices. The performance and rechargeability of these metal-air cells is highly dependent on the positive electrode material, where oxygen reduction and evolution reactions take place. Here, for the first time, we provide a detailed account of the kinetics and rechargeability of sodium-air batteries through a series of carefully designed tests on treated commercial carbon material. Surface area and porous structure of the positive electrode material was modified in order to gain detailed information surrounding the reaction kinetics of sodium-air batteries. The results indicate that discharge capacity is linearly correlated with surface area while morphology of the solid discharge product is strongly dependent on specific surface area and pore size. Furthermore, it was found that the chemical composition of discharge products as well as charging overpotential is affected by discharge reaction rate.

* This study has been published in *Energy Environ. Sci.*, 2014, 7, 3747-3757.
3.1 Introduction

Wide spread use of fossil fuels in the past few decades, has resulted in a substantial increase to greenhouse gas concentrations and has been a prime contributor to the serious issue of global warming. Since fossil fuels are predominantly consumed for transportation purposes, a switch from the conventional internal combustion engines (ICEs) to electric vehicles (EVs) has received enormous consideration. Furthermore, electric engines have higher conversion efficiency than ICEs making them even more attractive. Lithium-ion batteries (LIBs) have been the technology of choice for application in EVs due to their relatively high volumetric and gravimetric energy density as well as longer battery cycle life in comparison with other available battery systems. However, current LIB-EVs are restricted to low-mileage applications as a result of limited specific energy density, long charge time as well as high cost.

Metal-air cells, which use a different chemistry from intercalating LIBs, have theoretical specific energy densities high enough to compete with gasoline. The high specific energy densities seen for metal-air batteries is related to the use of high energy alkaline metals as anodes and oxygen, from ambient air, as cathode materials. Using light metal elements, such as lithium, as the anode material to form a lithium-air (Li-air) battery system has attracted a great deal of attention. However, large charge overpotentials in these batteries limit their cycle life to less than 100 cycles. A recently considered alternative metal-air battery is the sodium-air (Na-air) battery, in which lithium is replaced by sodium metal. Na-air battery systems have a lower theoretical specific energy density (1605 or 1108 Wh/kg considering Na$_2$O$_2$ or NaO$_2$ as discharge products, respectively) compared to Li-air battery systems. However, Na-air batteries also demonstrate lower charge overpotential which may result in better cyclic performance.

Only a few studies address the Na-air battery system with only a limited understanding behind the chemistry of the cell. For instance, various sodium oxides have been reported as discharge products of the Na-air battery system. Fu’s et al. has investigated Na-air cells with carbonate and ether based electrolytes while different carbon materials were used as the air electrode. Based on selected area electron diffraction (SAED), their results report the production of sodium peroxide (Na$_2$O$_2$) as a discharge product with the use of either
carbonate or ether electrolytes. At the same time, different charge/discharge mechanisms with various discharge products are proposed by Kim et al.\textsuperscript{11} using carbonate and ether based electrolytes. In this study sodium carbonate and hydrated sodium peroxide were produced as discharge products in carbonate and ether based electrolytes, respectively. More recently, sodium superoxide (NaO\textsubscript{2}) has also been shown to be the discharge product of the Na-air battery systems with the use of an ether based electrolyte.\textsuperscript{12,13} In addition, same research group investigated the electrochemistry and thermodynamic of the Na-air cell in a series of systematic studies in which sodium superoxide was the major discharge product.\textsuperscript{14,15} McCloskey et al. also studied the chemical and electrochemical differences of the Na- and Li-air cells and found “cleaner” chemistry in the case of Na-air cell with lower amount of parasitic products during the charge cycle of the cell.\textsuperscript{17} The lower amount of decomposition products and hence lower charging overpotential in Na-air cell are related to the more stability of NaO\textsubscript{2} compared to Li\textsubscript{2}O\textsubscript{2} as the major discharge products of Na- and Li-air cells, respectively.\textsuperscript{17} Meanwhile, Ceder’s research group showed using theoretical calculations that Na\textsubscript{2}O\textsubscript{2} is the stable phase in bulk form and NaO\textsubscript{2} is only more stable at nanoscale below 10 nm in particle size.\textsuperscript{18} Based on the aforementioned studies, it can be concluded that kinetic factors play a significant role in Na-air cells, resulting in formation of different phases of sodium oxides at various studies.

Even though sodium and lithium share many physiochemical properties, the chemistry of the Li-air and Na-air cells is not the same. While sodium forms stable sodium superoxide, lithium superoxide is thermodynamically unstable.\textsuperscript{9} Therefore, it is expected that both of sodium peroxide and superoxide would be formed under different physiochemical environments, however kinetic factors may stabilize a certain phase over the other oxide. In the present study, we show that the morphology and chemical composition of the discharge products in Na-air battery system depends on various factors including current density and air electrode materials. In addition, charge performance of the Na-air system can be controlled by manipulating the discharge products.
3.2 Experimental

3.2.1 Positive electrode material preparation

The positive electrode materials were prepared using commercial carbon black (N330). The carbon black was heat-treated under NH$_3$ or CO$_2$ (with or without H$_2$) atmospheres at elevated temperatures. The preparation procedure is fully described elsewhere.$^{19}$ Briefly, precise amount of carbon black were heat-treated in a fused silica reactor under NH$_3$ or CO$_2$ atmosphere at 1050°C under varying durations. A small portion of the CO$_2$-treated samples was further pyrolysed under H$_2$ at 950°C to remove oxygen containing functional groups introduced by CO$_2$-treatment. Heat-treatment of carbon black removes disordered graphitic structures from the carbon, producing a porous carbon structure. The amount of the carbon mass lost during the heat-treatment was measured using initial and final masses and are presented in Table 2.1.

3.2.2 Physical characterizations

Morphological studies were performed by Hitachi S-4800 field-emission scanning electron microscope (SEM) operated at 10.0 kV. N$_2$ adsorption/desorption isotherms were obtained using a Folio Micromeritics TriStar II Surface Area and Pore Size Analyzer. Fourier transform infra-red (FTIR) spectra and Raman scattering spectra were recorded using a Nicolet 380 and a HORIBA Scientific LabRAM HR Raman spectrometer system equipped with a 532.4 nm laser, respectively. For the FTIR measurements, the sealed testing box containing Na-air cells were moved to an argon-filled glove box (MBRUAN, with water and oxygen contents below 0.1 ppm) and the KBr disks containing 1%w/w of electrode materials were prepared in glove box. Then, the prepared KBr disks were sealed and moved to the FTIR measurement chamber, while nitrogen gas was flushing into the chamber. For Raman analysis, the tested Na-air cells were moved to the glove box and the positive electrode materials were squeezed and sealed between two pieces of glass slide. The Raman analysis was performed on 5 spots of the sealed samples. X-Ray diffractograms were obtained using a Bruker D8 Advance (Cu-K$_{\alpha}$ source, 40 kV, 40 mA). For the XRD measurements, The Na-air cells were moved to the glove box after testing, and the positive electrode materials of at least 4 cells were collected and placed into an air-sensitive XRD
sample holder. XPS measurements were made using a glove box-equipped Omicron XM1000 X-ray tube with Al Kα source (1486.7 eV) under operating pressure of 10^{-10} Torr. In the case of XPS measurements, positive electrodes of Na-air cells were washed with the same solvent that used for preparing the electrolyte. Afterward, the electrodes were dried and sealed inside the glove boxed and then moved to the XPS place, where the samples were opened in the second glove box and directly introduced to the XPS chamber. A nickel mesh was used to correct the charging effect. The samples were only kept under pure argon atmosphere for all analytical measurements, without any exposure to the atmospheric air.

3.2.3 Electrochemical Measurements

Gas diffusion electrodes were prepared by casting a mixture of carbon materials and Polyvinylidene fluoride (PVDF, Alfa Aesar) with a weight ratio of 9:1 on a separator (Celgard 3500). The electrodes were 3/8 inch in diameter with a loading of ~0.25 mg. Swagelok type cells comprised of sodium foil anode, Celgard 3500 separator, different cathodes and a stainless steel mesh as current collector were used to carry out electrochemical measurements. A fresh sodium foil was prepared with the aid of a homemade press machine using the sodium metal stick (from Aldrich) as starting sodium metal inside the argon-filled glove box. The electrolyte used in this study was a 0.5 M sodium triflate (NaSO_3CF_3 98%, Aldrich) dissolved in diethylene glycol diethyl ether (reagent grade ≥98%, Aldrich). Sodium triflate electrolyte salt was dried at 80°C under vacuum for 48 hours and the water content of diethylene glycol diethyl ether solvent was removed using molecular sieves for at least 10 days. The assembled Na-air cells were placed into a homemade testing box inside the glove box and then transferred to the testing room. The argon content of testing box was moderately vacuumed out and then pure oxygen (purity 4.3) purged into the box. The pressure of testing box was kept at 1.0 atm during the electrochemical tests. Discharge/charge characteristics were performed using an Arbin BT-2000 battery station at room temperature (25 °C).
3.3 Results and discussion

The gas diffusion electrode serves as a diffusing medium for positive active material (oxygen) in metal-air batteries, as well as a substrate for the accumulation of discharge products making the final electrochemical performance of the metal-air system strongly dependent on efficiency of the air electrode. The gas diffusion electrode material used in this work was prepared via heat-treatment of carbon black under various corrosive atmospheres, as outlined in Figure 3.1. Using the heat-treated carbon materials enables the precise control over the porosity and surface area of the air electrode materials. This heated-treated carbon material based on commercially-used carbon black with the post-treatments has been intensively used in various systems such as fuel cells and high energy batteries.19-21

![Figure 3.1: Schematic diagram of carbon black electrode material during the heat-treatment process](image)

The heat-treated carbon materials allow us to understand correlations between discharge capacity, surface area and porosity of the cathode materials. Carbon black is primarily
composed of graphitic crystallites bound together by disordered carbon.\textsuperscript{22} Heat-treatment of carbon black removes disorder carbon, resulting in a highly porous structure. Micropore boundaries grow with increasing treatment time and eventually result in the formation of mesopores.\textsuperscript{22} Initially, as treatment time increases, the number of mesopores with a size of less than 10 nm increases while further treatment results in an increase of pore volume. As a result, heat-treated carbons with higher mass losses demonstrate elevated specific surface area values, higher edge to surface ratios, and larger pore size.\textsuperscript{19} The SEM micrographs of N330 and NH\textsubscript{3}-treated carbons are also shown in Figure 3.2.

Figure 3.2: SEM micrographs of (a) N330 and NH\textsubscript{3}-treated carbon black with (b) 13\%, (c) 35\%, (d) 50\%, (e) 75\% and (f) 85\% mass losses.
Nitrogen adsorption/desorption measurements were carried out to illustrate the surface porosity characteristics. The nitrogen adsorption isotherms of the pristine carbon (N330) and heat-treated carbon material under different atmospheres and with various mass losses are shown in Figure 3.3. The pristine N330 carbon presents isotherm of type II, while for heat-treated carbons the type of isotherm is gradually changing from type II to type IV with increase of mass loss. In addition, the nitrogen adsorption ability of heat-treated carbon is also considerably increasing with the increase of mass loss, indicating the increase of the active surface area. The pore size distributions and pore volumes of the carbon materials were obtained from the Barret, Joyner, and Halenda (BJH) analysis using the adsorption branch of each isotherm. Pore size distribution of NH$_3$-treated carbon material is plotted against mass loss, and presented in Figure 3.4a (similar data for CO$_2$ and CO$_2$/H$_2$-treated carbons is shown in Figure 3.4b and c). Heat-treatment of carbon materials under NH$_3$, CO$_2$, and CO$_2$/H$_2$ atmospheres results in a considerable increase to specific surface area in the range of mesopores less than 10 nm (see also Table 2.1). The advantage of using heat-treated carbon materials is that various morphologies, surface areas and functional groups can be produced by simply altering pretreatment parameters.
Figure 3.3: Nitrogen adsorption/desorption isotherms of different heat-treated carbon materials under (a) NH$_3$; (b) CO$_2$ and (C) CO$_2$/H$_2$ atmospheres with various mass losses.
Figure 3.4: Pore size distribution plots for (a) NH$_3$; (b) CO$_2$- and (c) CO$_2$/H$_2$-treated carbon materials with different mass losses from 0 to 90%.
As-prepared carbon materials were tested as gas diffusion electrodes for Na-air cells. Figure 3.5a shows the discharge curves of different NH₃-treated carbon samples. All treated carbon materials indicate a flat discharge plateau at 2.2 V, delivering increasing specific discharge capacity with an increase in mass loss (see also Figure 3.5b). The plot of specific surface area of treated carbon material as a function of mass loss percentage indicates that specific discharge capacity increases with specific surface area, as shown in Figure 3.5b. Specific discharge capacity values increase quantitatively from 505 to 2783 mAh g⁻¹ with a mass loss increase of 10 to 85%. In fact, higher surface area presents a greater density of accumulation sites for deposition of solid discharge products, resulting in an increase to the specific discharge capacity of the cell. In addition, a highly porous air electrode structure results in a greater diffusion path for both of oxygen and sodium species, causing decreased mass transfer resistance, and increased cell capacity by postponing the potential drop. Similar trends were also observed for CO₂ and CO₂/H₂ treated carbon materials (Figure 3.6). The specific discharge capacity per actual surface area (calculated based on the specific discharge capacity (mAh g⁻¹) and the specific surface area of the corresponding electrode (m² g⁻¹)) of the electrode materials was plotted as a function of mass loss percentage, as shown in Figure 3.5c. Apart from the original N330 sample, all other treated carbon materials demonstrated a constant specific capacity per surface area. These constant values for different treated carbon materials illustrate the substantial effect of surface area on specific capacity for the Na-air battery system. In other words, actual surface area resulting from mesopores of the electrode materials dominantly determines the specific capacity of the air electrode. It should also be noted that the nature of porosity for pristine carbon black is different than other treated carbon materials;¹⁹,²⁰ the porosity of pristine carbon black originates from pores that exist between carbon particles, and have an average size of 30 nm. The porosity of treated carbon materials, however, stems from mesopores produced during the heat-treatment process and is chemically different in nature. Furthermore, heat-treating of carbon also results in creating small pores in the micropores region. Although these micropores increase the BET surface area, they are not accessible by the electrolyte and hence oxygen diffusion into these micropores is restricted. Therefore, pristine carbon demonstrates higher area-normalized specific capacity compared with heat-treated carbon materials.
Figure 3.5: (a) Discharge curves of Na-air cells using NH$_3$-treated carbon materials with different mass losses from 0 to 85% as cathode electrode recorded at a current
density of 75 mA g\(^{-1}\); (b) Plot of specific capacitance and specific surface area of the cathode electrode materials of the cells depicted at Fig. 3.5a as a function of mass loss; (c) Area-normalized specific capacity of the cells depicted at Fig. 3.5a as a function of mass loss.

Figure 3.6: Plots of specific capacitance and specific surface area of the cathode electrode materials of the cells using (a) CO\(_2\)- and (b) CO\(_2\)/H\(_2\)-treated carbon materials as a function of mass loss.
The total pore volume of heat-treated carbons are also plotted as a function of mass loss and shown in Figure 3.7. Although the total pore volume of heat-treated carbons also shows a growing trend, but it does not show a direct correlation with specific capacity in Na-air cell.

![Figure 3.7: Total pore volume of different heat-treated carbon materials under NH₃; CO₂ and CO₂/H₂ atmospheres plotted versus mass losses.](image)

Morphology of discharge products is another crucial factor that influences the discharge properties of metal-air systems, as well as the charge characteristic and performance of the cell.²³²⁶ Figures 3.8a-f display SEM micrographs of discharge products for carbon material under various durations of NH₃ treatment. The discharge products observed for pristine carbon black displays rod-shaped particles which are stacked upon each other (Figure 3.8a). The rod-shaped particles can also be observed in the case of NH₃-treated carbons with mass loss of 10-54%. However, as mass loss increases, dimension of discharge products shrink and gradually transform from rod-shaped particles to a thin film structure with a thickness of a few nanometers. The discharge products of treated carbon samples with an elevated mass loss (Figure 3.8e and f), predominantly exists as ultrathin nanosheets, uniformly covering the carbon surface.
Figure 3.8: Morphology of discharge products of the Na-air cells using different NH$_3$-treated carbon materials with 0 (a), 13 (b), 35 (c), 50 (d), 75 (e) and 85% (f) mass losses as cathode electrode (Discharge current density: 75 mA g$^{-1}$).

The same morphological changes were also observed for samples treated with CO$_2$ and CO$_2$/H$_2$ (Figure 3.9 and 3.10). SEM images of initial and charged NH$_3$-treated carbon electrode are also shown in supplementary Figure 3.11 for comparison purposes.
Figure 3.9: Morphology of discharge products of the Na-O$_2$ cells using different CO$_2$-treated carbon materials with 10 (a), 30 (b), 50 (c), 75 (d) and 90% (e) mass losses as cathode electrode.
Figure 3.10: Morphology of discharge products of the Na-O\textsubscript{2} cells using different CO\textsubscript{2}/H\textsubscript{2}-treated carbon materials with 10 (a), 30 (b), 50 (c), 75 (d) and 90\% (e) mass losses as cathode electrode.
Figure 3.11: SEM micrographs of carbon (NH$_3$-heat treated with 85% mass loss) electrode before discharge (a-c) and after charge (d-f) with different magnifications.

To identify the growth mechanism for the produced nanosheets, morphological changes were observed at different depths of discharge for treated carbon samples with 85% mass loss. The morphologies of discharge products after 8, 16, 24 and 36 hours of discharge are depicted in Figure 3.12. Tiny separated fibrils of solid discharge product can be observed.
after 8 hours of discharge (Figure 3.12a), while a major part of the carbon surface is left uncovered. After 16 hours of discharge the initial fibrils increase in size and begin to partially connect with one another in the form of island-shaped structures (Figure 3.12b). The same morphology can be observed after 24 hours of discharge, but to a greater extent with a greater degree of connection between the formed islands. Following 36 hours of discharge, the carbon surface is totally covered with a uniform wrinkled film of discharge product (Figure 3.12d). The thin layer is composed of interconnected primary discharge particles. More SEM micrographs with various magnifications of positive electrode after multiple steps of discharge process are also shown in supplementary Figure 3.13.

**Figure 3.12:** Morphology of discharge products of the Na-air cell using NH$_3$-treated carbon material with 85% mass loss as cathode electrode after (a) 8, (b) 16, (c) 24 and (d) 36 hours of discharge (Discharge current density: 75 mA g$^{-1}$).
Figure 3.13: SEM micrographs with different magnifications of discharge products of the Na-O$_2$ cell using NH$_3$-treated carbon material with 85% mass loss as cathode electrode after (a, b) 8, (c, d) 16, (e, f) 24 and (g, h) 36 hours of discharge.
The morphology of discharge products can be specified by the equilibrium between nucleation and growth rate. Greater density of nucleation sites, as seen with higher surface area materials, will result in smaller-sized particles being produced. However, lower surface area materials have limited nucleation sites, resulting in the formation of larger-sized particles. Recently, an in-situ AFM study by Wen et al.\textsuperscript{26} on Li-O\textsubscript{2} electrochemical reaction mechanism revealed that the nucleation process of discharge product (Li\textsubscript{2}O\textsubscript{2}) mainly occurs at step edges of the carbon substrate due to the higher surface energy at these locations. The same mechanism is likely to be responsible for different morphologies of discharge products in the Na-air cells. Heat-treatment of carbon materials under corrosive conditions results in the production of new pores, inevitably leading to an increase in edge/plate ratio. The edge plane carbon sites serve as nucleation points for discharge products due to elevated electron transfer reactions occurring at these locations compared to the basal carbon plane.\textsuperscript{27} As a result, the nucleation rate outpaces the growth rate on the carbon materials with longer treatment time as a consequence of greater edge sites, leading to the dominant production of a film-like structure. The proposed mechanism for discharge product formation is schematically illustrated in Figure 3.14. The control of discharge product morphology is critical in rechargeable metal-oxygen battery systems. It is paramount for the produced discharge product to revert back into the starting materials in order for the cell to be considered rechargeable. Solid discharge products larger in size have greater charging overpotential due to their limited interaction with the substrate. In addition, charging overpotential has a smaller value at substrate/discharge product interface (which is accessible by the electrolyte) compared to the bulk of products. Therefore, decomposition process begins at these interfaces. Progression of the decomposition process at interface sites hereupon cuts off the electrical contact to the remaining discharge particles and prevent them to entirely revert back, leading to a limited cycling performance, as reported by Hartmann et al.\textsuperscript{13} However, a uniform thin layer of discharge product may result in enhanced charging process by increasing the interaction between substrate and discharge product.
To investigate the charging performance of the electrode materials, NH$_3$-treated carbon materials with 85% mass loss was subjected to discharge down to a specific capacity of 1.0 Ah g$^{-1}$ and then subsequently charged back at a current density of 75 and 40 mA g$^{-1}$, respectively as outlined in Figure 3.15. Three distinct charge regions with a potential range of 2.3-2.75 (region I), 2.75-3.4 (region II) and 3.4-3.9 V (region III) can be distinguished during the charge process. These three charge potential regions will be referred as lower, middle and higher potentials, respectively. Similar charge profiles were observed for CO$_2$ and CO$_2$/H$_2$ treated carbon materials as well (Figure 3.16). Based on the thermodynamic standard potentials of different sodium oxides ($E^{0}_{\text{Na$_2$O}} = 1.95$, $E^{0}_{\text{Na$_2$O$_2$}} = 2.33$ and $E^{0}_{\text{NaO$_2$}} = 2.27$ V)$^{12}$ and considering the discharge voltage of the cell (Figure 3.5a), the most probable discharge product for Na-air system is either sodium peroxide (Na$_2$O$_2$) and/or sodium superoxide (NaO$_2$). Both of these oxides have been previously reported as major products for Na-air battery systems.$^{9-17}$ However during charging three notable steps are observed, as shown in Figure 3.15, indicating that the charge reaction is not a simple one-species decomposition reaction but rather the formation of multiple initially products produced during discharge.
Figure 3.15: Limited discharge/charge curves of Na-air cell using NH$_3$-treated carbon with 85% mass loss at current densities of 75 and 40 mA g$^{-1}$, respectively.

Figure 3.16: Limited discharge/charge curves of Na-O$_2$ cells using CO$_2$- and CO$_2$/H$_2$-treated carbon materials with 90% mass loss as cathode electrode.
To better understand the chemistry of Na-air batteries, discharge product of the Na-air cell was examined by X-ray diffraction (XRD) technique. The recorded patterns were obtained from air electrode materials before and after discharge to 1.8 V and are depicted in Figure 3.17. The XRD confirms the existence of multiple discharge products. However, the major discharge product correlates well with hydrated sodium peroxide (Na$_2$O$_2$.2H$_2$O, JCPDS reference card No. 015-0064), as opposed to the expected sodium peroxide. The minor peaks found in the spectrum can be associated with sodium superoxide (NaO$_2$, JCPDS reference card No. 006-0500).

The presence of hydrated sodium peroxide as a discharge product of the Na-air cells using ether (TEGDME) based electrolyte has been previously reported by Kim et al.\textsuperscript{11} and more recently by Jian et al.\textsuperscript{16} Kim et al. have also proposed a reaction mechanism in which TEGDME was subjected to reaction with superoxide ions to produce carbon dioxide and water. However, Nazar et al.\textsuperscript{25} previously reported in a systematic study on Li-air cell chemistry, that TEGDME does not significantly undergo decomposition in presence of superoxide ions. However, PVDF readily reacts with this ion and produces hydrogen...
peroxyde.\textsuperscript{25} In the case of Na-air battery system sodium superoxide can react with hydrogen peroxyde to produce hydrated sodium peroxyde. Thus, the following mechanism can be adopted for the positive electrode in Na-air cells discharge reactions of Na-air cell at positive electrode can be proposed as follow:

\[
\text{Na}^+ + \text{O}_2 + \text{e}^- \rightarrow \text{NaO}_2 \quad (3.1)
\]

\[
2\text{Na}^+ + \text{O}_2 + 2\text{e}^- \rightarrow \text{Na}_2\text{O}_2 \quad (3.2)
\]

Furthermore, the following side reactions may also occur:

\[
\text{O}_2^- + -(\text{CH}_2-\text{CF}_2)^- \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 + -(\text{CH}=\text{CF})^- + \text{F}^- \quad (3.3)
\]

\[
\text{NaO}_2 + \text{Na}^+ + 2\text{H}_2\text{O}_2 \rightarrow \text{Na}_2\text{O}_2.2\text{H}_2\text{O} + \text{O}_2 \quad (3.4)
\]

\[
\text{Na}_2\text{O}_2 + 2\text{H}_2\text{O}_2 \rightarrow \text{Na}_2\text{O}_2.2\text{H}_2\text{O} + \text{O}_2 \quad (3.5)
\]

In addition, XRD patterns of positive electrode after charging the cell to 2.75, 3.60 and 4.0 V (corresponding to the various charging steps indicated in Figure 3.15) are shown in Figure 3.18. The peaks related to NaO\textsubscript{2} phase are disappeared after charging the cell to 2.75 V, indicating that the decomposition of NaO\textsubscript{2} takes place at the region I of charge cycle. Charging the cell to 3.6 and 4.0 V results in degradation of peaks related to the Na\textsubscript{2}O\textsubscript{2} phase.

Further, discharge products of the Na-air cell after discharge and charge to different potentials (shown in Figure 3.15) were also examined by Raman spectroscopy. The resultant spectra combined with reference NaSO\textsubscript{3}CF\textsubscript{3}, Na\textsubscript{2}O\textsubscript{2} and Na\textsubscript{2}CO\textsubscript{3} for comparison purposes are depicted in Figure 3.19. The obtained spectra from positive carbon electrode shows two characteristic D and G bands related to the disordered and graphitic carbons, respectively. Additional peak at 1141 cm\textsuperscript{-1} appeared after discharge of the cell to 1.8 V is related to NaO\textsubscript{2} phase\textsuperscript{28} which is disappeared after charging the cell to 2.75 V. No Raman peak associating with Na\textsubscript{2}O\textsubscript{2} phase was detected, probably due to its weaker Raman signal.
Figure 3.18: XRD patterns of positive electrode after discharge of the Na-air cell to 1.8 V and also after charge to 2.75, 3.60 and 4.0 V.

Figure 3.19: Raman spectra of positive electrode after discharge and first charge step shown in Fig. 3.15, the peak marked with asterisk refers to NaO$_2$ phase.
Raman and IR spectroscopies are complementary analytical techniques, since transitions allowed in Raman may be forbidden in IR or vice-versa. As a result, the compound with weak Raman signal may show strong absorbance in IR. Accordingly, FTIR spectra of positive electrode at different electrochemical states were also recorded, as shown in Figure 3.20. Comparison of FTIR spectra of electrode materials before and after discharge to 1.8 V reveals a characteristic peak at 879 and 1442 cm\(^{-1}\), attributed to \(\text{Na}_2\text{O}_2\), providing further evidence as to the production of sodium peroxide during discharge.\(^{29}\) It should also be noted that \(\text{NaO}_2\) does not show any characteristic peak in IR due to the homopolar nature of superoxide ion.\(^{29}\) In addition, the \(\text{Na}_2\text{O}_2\) characteristic peaks remained in the spectra until charging the cell to 4.0 V (corresponding to the region III of Figure 3.15).

![Figure 3.20: FTIR spectra of positive electrode after discharge and charge to the various regions shown in Fig. 3.15.](image)

Based on XRD, Raman and FTIR results, it can be concluded that the charge plateau at lower (region I) and higher (region III) potentials are related to the decomposition reactions
of NaO₂ and Na₂O₂, respectively (see also Figure 3.15). However, deeper understanding about discharge product of the Na-air cell is required to figure out the nature of other charge plateau at middle (region II) potentials.

The formation of superoxide ions is a result of a single electron transfer process resulting in the formation of NaO₂ being kinetically more favorable, while Na₂O₂ is thermodynamically more stable than NaO₂ (ΔG⁰_Na₂O₂ = -449.7 KJ mol⁻¹; ΔG⁰_NaO₂ = -218.8 KJ mol⁻¹). Accordingly, the chemical composition of the discharge product would change under various discharge conditions. To examine this hypothesis, Na-air cells were discharged at different current densities and then charged back under a constant current density. Discharge curves of Na-air cells obtained at different current densities from 75 to 300 mA/g are depicted in Figure 3.21a.

![Discharge curves of Na-air cells using NH₃-treated carbon material with 85% mass loss as cathode electrode recorded at different current densities of 75, 150 and 300 mA g⁻¹.](image)

**Figure 3.21: Discharge curves of Na-air cells using NH₃-treated carbon material with 85% mass loss as cathode electrode recorded at different current densities of 75, 150 and 300 mA g⁻¹.**

As discharge current density increases, the discharge voltage and specific discharge capacity decrease slightly. Furthermore, the discharge curve obtained at a current density of 75 mA/g indicates a flat plateau situated at 2.2 V. However, the discharge curve recorded at current density of 150 mA/g shows an initial plateau at around 2.2 V with an additional sloping region at 2.0 V. Similar behavior can also be observed for discharge curve obtained
at a current density of 300 mA/g, except for lower discharge voltages mainly because of charge and mass transfer resistances. Based on the standard equilibrium potentials of sodium oxides species, the first (higher potential) and second (lower potential) discharge plateaus can be respectively attributed to the formation of Na$_2$O$_2$ and NaO$_2$. In addition, a relatively large change can be observed between the discharge capacity for cells discharged at current densities of 75 and 150 mA g$^{-1}$ (compared with the cell discharged at 300 mA g$^{-1}$), which can be attributed to the difference between the number of electrons exchanged in equations (3.1) and (3.2).

X-ray photoelectron spectroscopy (XPS) analysis was employed to further identify the chemical composition of discharge products at different current densities. Because of the high sensitivity of XPS in analytical speciation measurements, it is chosen to study the chemical composition of discharge products at different current densities. The XPS results for O 1s of reference sodium peroxide and discharge products of the cells discharged at current densities of 75 and 300 mA g$^{-1}$ are depicted in Figure 3.22. The spectrum of reference sodium peroxide demonstrates one peak at 530.9 eV related to the peroxide ion and also a small Auger peak around 536 eV (Na KLL). The discharged product obtained from lower current densities of 75 mA g$^{-1}$, shows a similar chemical composition consisting primarily of sodium peroxide. Additional minor fitted peak at 532.3 eV can be correlated to deficient sodium peroxide phase (Na$_{2-x}$O$_2$, vide infra). The discharge product obtained at an elevated current density of 300 mA g$^{-1}$ shows broader XPS peak, indicating wider variety of sodium oxide species. The fitted peaks at 530.9 and 532.3 eV are related to peroxide and deficient sodium peroxide species, respectively. In addition, sodium ion Auger peak is also broader and appeared at higher binding energy which is probably a result of overlapping with superoxide ion peak. However, discharge product obtained at elevated current density of 300 mA g$^{-1}$ exhibit more content of oxygen rich phases which is in accordance with charge and discharge results. The broadening clearly indicates the presence of superoxide (O$_2^-$), a paramagnetic species which exhibits multiplet splitting (broadening) with one unpaired electron. Similar conclusion may be obtained from Na 1s spectra shown in Figure 3.23.
Figure 3.22: (a) Oxygen 1s spectra of reference sodium peroxide; and discharged products resulted at current densities of (b) 75 and (c) 300 mA g⁻¹.
Figure 3.23: Sodium 1s spectra of reference sodium peroxide as well as discharged products resulted at current densities of 75 and 300 mA g\(^{-1}\).

In addition, XRD patterns of positive electrode materials after discharge of the cell to 1.8 V at different current densities of 75 and 300 mA g\(^{-1}\) are recorded and presented in Figure 3.24. With increase of discharge current density, the intensity of all peaks in the XRD pattern is decreased which is probably related to the formation of “quasi-crystalline” phase of sodium oxide at higher current density. Similar behavior is also reported in the case of Li-air cells.\(^{33}\)

Based on discharge curves recorded at different current densities as well as XPS results, it can be concluded that there is a competing reaction between the formation of NaO\(_2\) and Na\(_2\)O\(_2\), proceeding via equations (3.1) and (3.2). The formation of more thermodynamically stable peroxide ion (O\(_2^{2-}\)) at lower current densities is favorable, while the formation rate of superoxide ion (O\(_2^{-}\)) is favored at higher current densities. In other words, equation (3.1) is the dominant discharge reaction at higher current densities while equation (3.2) is responsible for discharge reaction at lower current densities.
Figure 3.24: XRD patterns of positive electrode materials after discharge of the cell to 1.8 at different current densities of 75 and 300 mA g\(^{-1}\).

To determine the effect of discharge current density on charge behavior of Na-air batteries, cells previously discharged to specific capacity of 1.0 Ah g\(^{-1}\) at different current densities of 75 to 300 mA g\(^{-1}\), were charged back at constant current density of 40 mA g\(^{-1}\). The resultant curves are shown in Figure 3.25. As the discharge current density increases from 75 to 300 mA g\(^{-1}\), the charge capacity related to the first charge step (the decomposition of NaO\(_2\)) increases. The increase in the first charge step coupled with the observed increase in current density indicates that the formation of NaO\(_2\) is favored at higher current densities. Recently, a computational study on the charging mechanism of Li-air cells demonstrated that the formation of off-stoichiometric phase of Li\(_{2-x}\)O\(_2\) is kinetically favorable in order to reduce the charging overpotential of the cell,\(^{30}\) which has also been confirmed experimentally.\(^{31-33}\) Similarly, the formation of deficient phase sodium peroxide with the general formula of Na\(_{2-x}\)O\(_2\) (0 < x < 1) at higher discharge current densities is highly
probable, especially since the oxygen-rich phase of sodium oxide (NaO$_2$) is more stable than lithium’s counterpart.

Figure 3.25: Limited discharge and charge curves of Na-air cells using NH$_3$-treated carbon material with 85% mass loss as cathode electrode recorded at different discharge current densities of 75, 150 and 300 mA g$^{-1}$ and a constant charge current density of 40 mA g$^{-1}$.

To better understand the charge behavior, Na-air cells were subjected to discharge under different limited capacities, from 250 to 1000 mAh g$^{-1}$, at an elevated current density of 300 mA g$^{-1}$ and then charged back at a constant current density of 75 mA g$^{-1}$. The resultant charge-discharge curves are depicted in Figure 3.26. A plateau can be observed under lower potentials while two ill-defined plateaus are observed at middle and higher potentials during the charge process of the cell discharged to 250 mAh g$^{-1}$. However, an increase in the discharge capacity limit from 500 to 1000 mAh g$^{-1}$, results in a more pronounced plateau at middle and higher potentials. With an increase in discharge capacity limit the charge capacity corresponding to the lower potential plateau subsequently increases. However, an increase of discharge capacity limit also results in an increase to charge capacity corresponding to the middle and higher potential plateaus as well. The appearance of the middle and higher discharge plateaus with increasing discharge capacity limit.
indicates that chemical composition of the discharge products is changing. Since the formation of NaO₂ is favorable at higher current densities, and that the thermodynamic stability of Na₂O₂ is higher (vide supra), it can be concluded that disproportionation reaction of NaO₂ is responsible for the change in chemical composition seen for the discharge products as well as the appearance of different plateaus during the charge process. Such disproportionation reactions can be performed either chemically or electrochemically at the positive electrode via the following reaction mechanism:

\[ 2\text{NaO}_2 \rightarrow \text{Na}_2\text{O}_2 + \text{O}_2 \quad (3.6) \]

\[ \text{NaO}_2 + (1-x)e^- + (1-x)\text{Na}^+ \rightarrow \text{Na}_{(2-x)}\text{O}_2 \quad (0 \leq x \leq 1) \quad (3.7) \]

Figure 3.26: Limited discharge (from 250 to 1000 mAh g⁻¹) and charge curves of Na-air cells using NH₃-treated carbon material with 85% mass loss as cathode electrode recorded at constant discharge and charge current densities of 300 and 75 mA g⁻¹, respectively.

The discharge/charge curves restricted to the low discharge capacity (250 mAh g⁻¹) can also be compared with cyclic voltammetry (CV) curve (Figure 3.27). The CV curve show
a slopping region in cathodic and two distinct peaks around 2.8 and 3.6 V in anodic cycle related to the oxygen reduction and evolution reactions which are in accordance with discharge/charge curves, respectively. Based on the results obtained from charge-discharge curves at various current densities and different discharge capacity limits, multiple charge steps can be attributed to the decomposition reaction of different phases of sodium oxides. The lower potential charge plateau is related to a decomposition reaction of oxygen-rich phased sodium superoxide ($x \approx 1$); the middle potential charge plateau is related to decomposition of deficient phase sodium peroxide ($0 < x < 1$); while the higher potential charge plateau is related to decomposition of sodium-rich phased sodium peroxide ($x \approx 0$).

Figure 3.27: Cyclic voltammogram of Na-air cell recorded at a potential sweep rate of 10 mV s$^{-1}$ in a potential range of 1.8 to 4.0 V. The CV recording was started by the cathodic sweep from 2.5 to 1.8 V followed by the anodic sweep from 1.8 to 4.0 V and terminated to the start point.

In addition, the first three limited discharge and charge curves of Na-air cell recorded at a current density of 150 mA g$^{-1}$ is depicted in Figure 3.28. All consecutive cycles show complete charging with similar profiles. However, the discharge capacity starts to drop down at higher cycle numbers, mainly due to the mechanically failure of the positive electrode material as a result of binder decomposition.
Figure 3.28: First three limited discharge and charge curves of Na-air cell recorded at current density of 150 mA g\(^{-1}\).

The present study demonstrates the effects of discharge reaction kinetics on the chemical composition as well as charge characteristics of Na-air battery system. The results suggest that the charge overpotential and efficiency of the cell can be controlled by modifying kinetic parameters related to the discharge reaction. The discharge process of Na-air cells at elevated current densities results in an increase to the amount of NaO\(_2\) produced during discharge as well as decreases the charge reaction overpotential. However it also increases the chemical disproportionation reaction of NaO\(_2\). On the other side, an increase to depth of discharge increases the amount of deficient phase sodium peroxide, a critical component in lowering charge overpotential. These results are supported by recent reports from Zhai et al.\(^{34}\) and Yang et al.\(^{35}\) for Li-air battery system, indicating the existence of similar chemistry occurring between the two systems. The common point for both studies is application of high surface area carbon materials as a positive electrode which reveals the dominant effect of active surface area in metal-air battery performance.

It should be also emphasized that the experimental conditions have a great influence on the chemistry of Na-air cells via altering the kinetic factors involving in the discharge and
charge reactions of the cells. More kinetic studies are required to further understand the chemistry behind the Na-air cells and the major affecting parameters to control the chemical composition and charge overpotential of the cell.

3.4 Conclusion

In summary, discharge capacity, morphological changes and chemical composition of discharge products produced by a Na-air battery system has been investigated in detail and the study was based around the use of a specifically-design and heat-treated carbon material as oxygen diffusion electrode. The specific discharge capacity of the electrode materials with varying specific surface areas demonstrated that discharge capacity is strongly dependent on electrode surface area. In addition, the result revealed that the morphology of the discharge product is also strongly dependent on surface area as well as pore size. The edge planes of carbon substrate were proposed to serve as nucleation sites for the formation of a solid-state discharge product in the Na-air battery system. XRD, Raman, FTIR and XPS analysis of Na-air batteries indicated that both sodium peroxide and superoxide are produced during discharge cycles of the cell and decomposed at different charge steps. In addition, the formation of a deficient phased sodium peroxide (Na$_{2-x}$O$_2$, 0 < x < 1) is showed to be likely. Cells discharged at different current densities also exhibited different charge profiles accompanied by a different chemical composition for the discharge product.
References
Chapter 4

4 Three-Dimensional Nanostructured Air Electrode for Sodium-Oxygen Batteries: A Mechanism Study toward the Cyclability of the Cell

A binder-free 3D nanostructured air electrode composed of vertically grown nitrogen doped carbon nanotubes on carbon paper (NCNT-CP) is developed and applied to Na-O_2 cells. The 3D architecture of the air electrode results in increased discharge capacity by optimizing the utilized area of the electrode material. The chemical and electrochemical reaction mechanisms of the cell are also explored with the use of synchrotron-based X-ray absorption spectroscopy (XAS). Investigation of the discharge product of Na-O_2 cells during discharge and charge cycles using X-ray absorption near edge structure (XANES) indicates that both sodium superoxide and peroxide are produced under various physicochemical conditions and can be subsequently decomposed with different overpotentials. Furthermore, formation of carbonate-based parasitic products is also shown to restrict the cyclability of the cell.

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4.1 Introduction

Rechargeable non-aqueous alkali metal-O$_2$ batteries, such as Li- and Na-O$_2$, have recently attracted a great amount of attention due to their high theoretical energy density.$^{1-4}$ This high theoretical energy density is related to the use of high energy alkali metals as a negative and oxygen, from ambient air, as the positive electrode materials. The primary discharge products of these cells are typically metal oxides which are insoluble in non-aqueous electrolytes, resulting in accumulated on the porous air electrode surface. Based on this, an ideal air electrode should have a porous structure with appropriate pore volume and pore size distribution, in addition to necessary characteristics such as conductivity, chemical stability, high surface area and low cost.$^5$ The porous structure of the air electrode serves to increase oxygen diffusion into the positive electrode materials, as well as appropriately accommodate formation and storage of the discharge product.$^5, 6$ Reversing the solid-state discharge products of these cells requires overcoming a relatively large charging overpotential, which is one of the major challenges facing the development of alkali metal-O$_2$ batteries.$^4$ Formation of parasitic side products are also believed to contribute to the large overpotential required during the charge cycle.$^7, 8$

Chemical composition of the discharge products may also greatly affect the charging overpotential of alkali metal-O$_2$ cells. It has been almost well established that the major discharge product of the Li-O$_2$ cell in a relatively stable electrolyte is lithium peroxide (Li$_2$O$_2$)$^2, 9-11$ However, some reports indicate the presence of a lithium superoxide-like phase alongside Li$_2$O$_2$, resulting in a lower charging overpotential.$^{12-15}$ Nevertheless, the chemical composition of discharge product in Na-O$_2$ cells remains still a point of controversy. Both sodium peroxide (Na$_2$O$_2$) and superoxide (NaO$_2$) are almost evenly identified as the major discharge product for Na-O$_2$ cells. Liu et al. and Li et al. identified formation of Na$_2$O$_2$ in Na-O$_2$ cell using an ether-based electrolyte and a charging overpotential of $\sim$1.5 V.$^{16, 17}$ A hydrated form of sodium peroxide (Na$_2$O$_2$:2H$_2$O) has also been found in other studies.$^{18, 19}$ Interestingly, Hartmann et al. investigated the Na-O$_2$ cell in which a unique structure of cubic NaO$_2$ in micrometer size range was observed as the discharge product and decomposed below 2.5 V vs. Na/Na$^+$ (charging overpotential of $\sim$0.2 V).$^3, 20, 21$ Furthermore, using differential electrochemical mass spectrometry (DEMS)
analysis, McCloskey et al. showed that the discharge product of Na-O₂ cells is predominantly NaO₂. More recently, Zhao et al. showed that NaO₂ is the main product under static oxygen atmosphere, while Na₂O₂.2H₂O was obtained under flowing oxygen gas. Theoretical calculations have also been applied to predict the discharge product of these Na-O₂ cells. NaO₂ phase was suggested by first-principle DFT calculations to be stable discharge product of Na-O₂ cell under standard conditions (300 K and 1 atm). On the other side, by combining the surface energies of various sodium oxide crystals with the energy of bulk compounds, Cedar et al. demonstrated that bulk Na₂O₂ is the more stable phase under the standard conditions and NaO₂ is more stable at the nanoscale and/or under higher oxygen partial pressures.

Since various metal oxides exhibit different overpotentials during the charge cycle, manipulating the formation of the discharge products is an attractive way to control the charge overpotential of the cell. Our group has recently demonstrated that the discharge product of Na-O₂ cells is composed of both peroxide and superoxide phases. In addition, the chemical composition and consequently the charge overpotential of the Na-O₂ cell was shown to be controlled by changing the kinetic parameters of the cell. In the present study, a high surface area binder-free air electrode with a 3D-structure is developed and employed in a Na-O₂ cell. We show that the capacity of the air electrode can be significantly increased by using a 3D structured air electrode through the increasing of the electrode material utilization. Additionally, the chemical composition of Na-O₂ cell products is traced during the discharge and charge cycles of the cell with the aid of a synchrotron-based XAS technique. Meanwhile, the binder-free nature of the 3D-structured air electrode in the present study eliminates any uncertainty regarding the probable contribution from the binder decomposition in the chemical and electrochemical responses of the cell.

### 4.2 Experimental

#### 4.2.1 Preparation of the air electrode

The NCNT-CP electrode was prepared using a spray pyrolysis chemical vapor deposition (SPCVD) method, as described elsewhere. In a typical synthesis, a piece of carbon paper
(CP) was sputtered with a 30 nm of aluminum as the buffer layer. The CP was then fixed inside of a quartz tube and transferred into a vertical furnace. The quartz tube was purged with argon gas (99.999%) at a flow rate of 500 sccm for 20 minutes. The furnace was then heated up to 850°C. After the temperature was fixed at 850°C, a solution containing 2 g of imidazole and 0.2 g of ferrocene in 10 ml of acetonitrile was introduced into the tube with the aid of an ultrasonic probe sonicator at a flow rate of 250 µl/min for various times from 3 to 10 minutes (See section 2.1.2 for detailed synthesis process).

4.2.2 Physical characterizations

Morphological studies were performed by Hitachi S-4800 field-emission scanning electron microscope (SEM) and Hitachi H-7000 transmission electron microscope (TEM) operated at 10 and 100 kV, respectively. N\text sub{2} adsorption/desorption isotherms were obtained using a Folio Micromeritics TriStar II Surface Area and Pore Size Analyzer. The surface area of the electrodes was calculated by the Brunauer, Emmett and Teller (BET) model by taking at least 6 data points where 0.07 < P/P\text sub{0} < 0.2. Pore size distribution was obtained by the Barrett, Joyner and Halenda (BJH) model using the desorption branch of the isotherm. Thermogravimetric analysis (TGA) was performed using a SDT Q600 TGA unite from RT to 900°C in air at a heating rate of 10°C min\textsuperscript{-1}. X-Ray photoelectron spectroscopy (XPS) were carried out by a Kratos Axis Ultra Al-α spectrometer operated at 14kV. Raman data were collected using a HORIBA Scientific LabRAM HR Raman spectrometer operated with an incident laser beam at 532.03 nm. X-Ray diffractograms were obtained using a Bruker D8 Advance (Cu-K\textalpha{} source, 40 kV, 40 mA). For the XRD measurements, the Na-O\textsubscript{2} cells were dissembled in the Ar-filled glove box after testing and the positive electrode materials were placed into an air-sensitive XRD sample holder. XAS measurements were obtained at the Canadian Light Source (CLS) on the spherical grating monochromator (SGM) beamline. The air electrodes of Na-O\textsubscript{2} cells were washed with the same solvent that was used for preparing the electrolyte. Afterward, the electrodes were dried and sealed inside the glove box and then moved to the analysis place, where the samples were opened in the second glove box and directly introduced to the XAS vacuum chamber. The samples were kept under pure argon atmosphere before the analytical measurements, without any exposure to the atmospheric air. The vacuum during the XAS experiments was around 10\textsuperscript{-4}. 

124
4.2.3 Electrochemical Measurements

Swagelok type cells comprised of sodium foil anode, Celgard 3500 separator (5/8 inches in diameter), different air electrode and a stainless steel mesh as current collector were used to carry out electrochemical measurements. The air electrodes were cut into circular pieces (3/8 inches in diameter) with the geometric surface area of 0.71 cm$^2$. The average weight of 20 pieces of CP electrodes was measured and applied as the weight of CP substrate. The average geometric surface area and weight of the CP substrate was 0.71 cm$^2$ and 5.8 mg. The loading of NCNTs was calculated based on the TGA data to be 0.24 mg cm$^{-2}$. The whole weight of NCNT + CP or geometric surface area of the air electrode has been used for calculating the specific capacity of the NCNT-CP air electrode. A fresh sodium foil was prepared with the aid of a homemade press machine using the sodium metal stick (from Aldrich) as starting sodium metal and cut into circular pieces (3/8 inches in diameter) inside the argon-filled glove box. The electrolyte used in this study was a 0.5 M sodium triflate (NaSO$_3$CF$_3$ 98%, Aldrich) dissolved in diethylene glycol diethyl ether (DEGDME, reagent grade ≥ 98%, Aldrich). Sodium triflate electrolyte salt was dried at 80°C under vacuum for 48 hours and the water content of DEGDME solvent was removed using molecular sieves for at least 10 days. The amount of electrolyte in the cell was ~200 µl. The assembled Na-O$_2$ cells were placed into a homemade testing box inside the glove box and then transferred to the testing room. The argon content of testing box was moderately vacuumed out and then pure oxygen (purity 4.3) purged into the box. The pressure of testing box was kept at 1.0 atm during the electrochemical tests. Discharge/charge characteristics were performed using an Arbin BT-2000 battery station at room temperature (25 °C).

4.3 Results and discussion

The porous structure of the air electrode plays a major role in the overall performance of alkali metal-O$_2$ cells. This electrode must be able to allow sufficient oxygen and metal ion
diffusion while simultaneously providing adequate storage for discharge products. In order to address these requirements, a new air electrode is developed based on the 3D structure of carbon paper (CP), which is covered by vertically grown nitrogen-doped carbon nanotubes (NCNTs) through a one-step spary pyrolysis chemical vapor deposition (SPCVD) method. NCNT grown on carbon paper was chosen as the air electrode in this study, since conjugation between the nitrogen lone-pair electrons and graphite \( \pi \)-system enhances the electrical conductivity and electrocatalytic activity of CNT. The structure of the CP substrate and NCNT-CP air electrode was observed using SEM and TEM, as shown in Figure 4.1. The CP substrate (Figure 4.1a) is composed of randomly oriented fibers with a diameter of around 10 \( \mu \)m, exhibiting a 3D structure with diverse micrometer sized pores. After growing NCNTs on CP (Figure 4.1b-d) through a SPCVD process, a uniform layer of NCNTs with around 10 \( \mu \)m in length covers the carbon fibers. The high resolution SEM and TEM micrographs of NCNTs shown in Figure 4.1e and f exhibit bamboo-like structure with stacked-cone structure which is characteristic of NCNTs (see Figure 4.2 for more TEM images).

Figure 4.1: SEM (a-e) and TEM (f) micrographs of pristine CP (a) and NCNT-CP (b-f) air electrode synthesized via SPCVD method for 3 minutes.
The structure of NCNT-CP air electrodes prepared via longer SPCVD reaction times are shown in Figure 4.3. The length of NCNTs is increased with increasing synthesis time. Prolonged duration of synthesis results in higher surface area air electrodes, but decreased number of macropores. The NCNT-CP air electrodes with NCNT lengths of 10 µm was selected for the remaining tests because of its appropriate compromise between the surface area and macropores.

The nitrogen adsorption/desorption isotherm of the NCNT-CP electrode material (Figure 4.4a) shows a mixed shape of type II (at medium pressures) and type IV (at higher pressures) according to the IUPAC classification. This result indicates the presence of both macropores (pore diameter > 50 nm) as well as the mesopores (2 nm < pore diameter < 50 nm). The BET surface area and total pore volume of NCNT-CP electrode was determined to be 27.3 m² g⁻¹ and 0.106 cm³ g⁻¹, respectively. Pore size distribution plot (Figure 4.4b) of the NCNT-CP air electrode also confirms the presence of the macro and mesopores. This is a dual-porous structure, in which large micrometer sized pores existing between the
individual fibers increase volume of oxygen and sodium ions transportation while the solid state discharge product can be captured within the mesopores space provided by the NCNTs. In addition, XPS analysis of the NCNTs (Figure 4.5) indicated the nitrogen content of NCNTs to be 5% (calculated based on the peak area ratio between nitrogen and carbon divided by their atomic sensitivity factors). Various types of nitrogen including pyridine-like N, graphite-like N, molecular N and chemisorbed N-oxide (from low to high binding energies, respectively) are recognizable in the high resolution XPS N1s spectrum.

Figure 4.3: SEM micrographs of NCNT-CP air electrode synthesized via SPCVD method for prolonged synthesis times of 5 (a-c) and 10 (d-f) minutes.
Figure 4.4: (a) Nitrogen adsorption/desorption isotherm of the synthesized NCNT-CP air electrode; (b) Pore size distribution plot of the NCNT-CP air electrode.

Figure 4.5: XPS survey scan of NCNTs prepared using the spray pyrolysis CVD method; inset: high resolution N1s spectrum.
Further, Raman spectra of the NCNT-CP air electrode (Figure 4.6) exhibit two main peaks around 1350 and 1590 cm$^{-1}$, corresponding to the D-band and the G-band respectively. The D-band is originated from atomic displacement and disorder induced features caused by lattice defect or distortion, while the G-band indicates the presence of crystalline graphitic carbon. The intensity ratio of D and G bands ($I_D/I_G$) is used to evaluate the disorder in the materials. The $I_D/I_G$ ratio of synthesized NCNTs was calculated to be 1, indicating high amount of defects and disorder in NCNTs as a result of N-doping into the CNT structure.

![Raman spectra of NCNT-CP air electrode.](image)

The specific capacities based on both of the geometric surface area (mAh cm$^{-2}$) and the total weights (mAh g$^{-1}$) of CP and NCNT-CP electrodes obtained at a current density of 0.1 mA cm$^{-2}$ are compared in Figure 4.7a. The NCNT-CP electrode exhibits a specific capacity 17 times higher than bare CP electrode. The increase in specific capacity is related to the increased surface area provided by NCNTs allowing for discharge product to form, while the micrometer sized pores of CP structure guarantee the continuous supply of oxygen and sodium ions onto the electrode surface. This 3D structure fosters a uniform coverage of discharge products on the electrode surface while maintaining sufficient respiration. The capability of the NCNT-CP air electrode to supply sufficient amounts of oxygen and sodium ions was also examined by discharging the cell under elevated current densities (Figure 4.7b). The specific capacity of the Na-O$_2$ cell is reduced by 1.7 times.
when increasing the discharge current density from 0.1 to 0.5 mA cm$^{-2}$, indicating the proper structure of the breathing air electrode.

![Discharge curves](image)

**Figure 4.7:** Discharge curves of pristine CP and NCNT-CP air electrodes (NCNT length of 10 µm) at a current density of 0.1 mA cm$^{-2}$ (a); Discharge curves of NCNT-CP air electrodes obtained at different current densities of 0.1, 0.2, 0.5 mA cm$^{-2}$ (b), the specific capacities are calculated based on the geometric surface area (mAh cm$^{-2}$) and also based on the total weights of CP and NCNT-CP electrodes (mAh g$^{-1}$)

The discharge/charge curves of the NCNT-CP air electrode under various current densities and full discharge depth are also shown in Figure 4.8. Full discharge of the cell also results in formation of a thick discharge product film on the air electrode surface. The
decomposition process during the charge cycle of the cell, however, may isolate a portion of the discharge products and prevent the complete charging process. The noisy voltage response of the cell during the charge cycle under the full discharge depth is probably due to the electrically disconnection of the discharge products from the air electrode surface.

![Graph showing discharge/charge curves](image)

**Figure 4.8:** The discharge/charge curves of the NCNT-CP air electrode under various current densities and full discharge depth.

It should also be noted that the major of weight for the NCNT-CP air electrode stems from the underlying CP substrate. The weight percentage of NCNTs was calculated based on Thermogravimetric analysis (TGA) and determined to comprise of only 3% of the overall weight (Figure 4.9). Replacing the CP substrate with a more lightweight material may further increase both specific gravimetric capacity and rate capability of the cell. Recalculation of the specific capacity of NCNT-CP air electrode (after subtraction of 80 mAh g\(^{-1}\) for CP) based on only the weight of NCNTs results in an incredible value of 42.29 Ah g\(^{-1}\)\(^{NCNTs}\), illustrating the increased utilization of NCNTs in the 3D air electrode architecture.
In Figure 4.10 the specific capacity of NCNT-CP air electrode is compared with corresponding values from literature for other CNTs containing air electrodes with alternate architectures including powder-based electrode, CNT paper and vertically aligned CNTs.\textsuperscript{19, 23, 32} In all cases the air electrodes are discharged under a current density of 0.1 mA cm$^{-2}$ while the specific capacity is calculated based on either the electrodes geometric surface area or the weight of CNTs and NCNTs. The obtained specific capacity of the NCNT-CP air electrode is significantly higher than that of other reported air electrodes. Discharge curves for NCNT-CP air electrodes prepared with longer NCNTs displays similar discharge curves, as shown in Figure 4.11. However, electrodes with longer NCNTs of 15 and 25 µm show lower discharge capacities compared to electrodes with 10 µm long NCNTs. Furthermore, increasing the discharge current density for electrodes prepared with longer NCNTs resulted in larger capacity drops as a result of decreased macropore volume (see also Figure 4.3).
Figure 4.10: the specific capacity for NCNT-CP and other CNTs containing air electrodes with different architectures including powder-based, CNTs paper and vertically aligned CNTs from the literature.

Figure 4.11: Discharge curves of Na-O₂ cell using NCNT-CP air electrodes prepared through the prolonged synthesis times.
Recently, we showed that the chemical composition, and consequently the charge overpotential of the Na-O\(_2\) cell, may be altered via modifying kinetic parameters such as discharge current density.\(^{26}\) Figure 4.12a shows the electrochemical response of Na-O\(_2\) cells discharged to a restricted capacity of 0.5 mAh cm\(^{-2}\) at various current densities from 0.1 to 1.0 mA cm\(^{-2}\) and subsequently charged back using a constant current density of 0.1 mA cm\(^{-2}\). Two charge plateaus beginning at 2.9 and 4.0 V can be seen for cells discharged at a low current density of 0.1 mA cm\(^{-2}\). For cells discharged at an increased current density of 0.5 mA cm\(^{-2}\), the charge cycle exhibits a small plateau at 2.3 V and then the charge potential increases to 2.9 and 4.0 V, forming the second and third plateaus. In the case of Na-O\(_2\) cell discharged at a high current density of 1.0 mA cm\(^{-2}\), three clearly distinct charge plateaus are observed starting at 2.3, 2.9 and 4.0 V. This correlation between charge overpotential and discharge current density has also been observed for Li-O\(_2\) cell.\(^{13-15}\)

To identify the nature of various charge plateaus, the NCNT-CP air electrodes were discharged to cut-off potential of 1.8 V at various current densities and then examined by synchrotron-based X-ray absorption (XAS) technique. XAS technique is chosen to analyze the chemical composition of the discharge product of the Na-O\(_2\) cell, since it exhibits both selectivity and sensitivity toward the various sodium oxide phases presented in the cell product. The normalized O K and Na K-edge XANES spectra of the NCNT-CP air electrodes discharged under different current densities along with a standard Na\(_2\)O\(_2\) sample was recorded under the both surface sensitive total electron yield (TEY) and the bulk sensitive fluorescence yield (FLY) modes, as shown in Figure 4.12b-e. All discharged electrodes, as well as the standard Na\(_2\)O\(_2\) sample, exhibit a feature around 534.3 eV in the O K-edge XANES spectra (Figure 4.12b and d), relating to the excitation of the 1s electrons to empty \(3\sigma_u (\sigma^\#)\) molecular orbital of Na\(_2\)O\(_2\).\(^{33-35}\) Interestingly, a new feature at 532.9 eV appears when the discharge current density is increased from 0.1 to 0.5 and 1.0 mA cm\(^{-2}\). This new feature, which increases in prominence with increased discharge current density, is related to the excitation of the 1s electrons to a semi-filled \(1\pi_g (\pi^\#)\) molecular orbitals of superoxide molecules.\(^{33-35}\) This same transition can also be seen in the case of standard Na\(_2\)O\(_2\) sample, indicating the superoxide impurity phase of commercial Na\(_2\)O\(_2\) sample (the pale yellow color of the commercial Na\(_2\)O\(_2\) samples is a result of \(\pi_0-\pi_g\) transition in the O\(_2^-\)
Figure 4.12: Restricted discharge and charge curves of Na-O\textsubscript{2} cell using NCNT-CP air electrode recorded at different discharge current densities of 0.1, 0.5 and 1.0 mA cm\textsuperscript{-2} and a constant charge current density of 0.1 mA cm\textsuperscript{-2} (a); Normalized O (b and d) and Na (c and e) K-edge XANES spectra recorded under the TEY (b and c) and FLY (d and e) modes for the NCNT-CP air electrodes discharged under different current densities of 0.1, 0.5 and 1.0 mA cm\textsuperscript{-2} as well as standard Na\textsubscript{2}O\textsubscript{2} sample.
These π* features are associated with unsaturated bonding occurring between oxygen in O₂ and O₂⁻.

In order to confirm the existence of the superoxide phase (NaO₂) in the Na₂O₂ standard sample, the O K-edge XANES spectra of standard Li₂O₂, Na₂O₂, and KO₂ samples was also obtained (Figure 4.13). The standard Li₂O₂ sample displays a broad feature at around 532 eV which is related to electron excitation into the σ* molecular orbitals. Furthermore, the KO₂ standard sample displays two features at around 533 and 534.5 related to 1s electron excitations to the π* and σ* molecular orbitals, respectively. The same superoxide characteristic feature (532.9 eV) also appears in the case of Na₂O₂ standard sample, which confirms the existence of superoxide impurity phase. It should also be noted that the small energy difference between σ* molecular orbitals of superoxide and peroxide phases cannot be distinguished here. However, a higher ratio of σ* to π* in the case of Na₂O₂ over KO₂ is probably a result of an overlap between the 1s electron excitations to the σ* molecular orbitals of superoxide and peroxide phases.

![Normalized O K-edge spectra](image)

**Figure 4.13:** The normalized O K-edge spectra recorded in the TEY mode for potassium superoxide (KO₂), sodium peroxide (Na₂O₂) and lithium peroxide (Li₂O₂) standard samples.
Similar features can also be found in the O K-edge XANES spectra of the discharged electrodes recorded under the FLY mode (Figure 4.12d). The difference between chemical composition of surface and bulk components of the discharge products can be obtained by comparing of XANES spectra collected under TEY and FLY modes, respectively. Preforming this comparison for discharged electrodes reveals that the bulk of the discharge product is predominantly composed of a superoxide-like phase. Reduced amount of superoxide-like phase at the external superficial layer of the discharge product is probably related to the side reaction between the highly oxidative superoxide phase of the discharge product and the electrolyte. Appearance of such a side product has not been observed in the previous studies involving the superoxide phase as the discharge product. However, occurrence of the side reaction can be rationalized considering the high surface area air electrode employed in this study compared to the previous reports. Such a high surface area air electrode provides a vast interface between the discharge product and the electrolyte, resulting in formation of higher amount of side products. The nature of the side product in Na-O₂ cell will be more discussed in the following parts. It should also be mentioned that the difference between the spectra of the standard Na₂O₂ sample at around 534.3 eV recorded under the TEY and FLY modes is due to the different distribution of the two phases.

The XANES spectra for Na₂O₂ recorded in both TEY and FLY are also compared in a single plot in Figure 4.14. The feature at 534.3 eV in the spectrum recorded under the TEY mode cannot be seen under the FLY mode which is related to the self-absorption effect of the surface layer. The corresponding Na K-edge XANES spectra recorded under the TEY and FLY modes are presented in Figure 4.12c and e. The Na K spectra of discharged electrodes display the same oxidation state for atomic sodium as standard Na₂O₂. However, the intensity of the feature at around 1083 eV flattens out with increasing discharge current density, indicating increasing disorder in discharge products obtained at higher current densities which is in accordance with XRD results (Figure 4.15).
Figure 4.14: The normalized O K-edge spectra recorded in both TEY and FLY modes for Na$_2$O$_2$ standard sample.

Figure 4.15: XRD patterns of the pristine NCNT-CP air electrode as well as the air electrodes discharged at lower and higher current densities of 0.1 and 0.5 mA cm$^{-1}$ in Na-O$_2$ cell.
Figure 4.16: (a) Restricted discharge and charge curves of Na-O$_2$ cell using NCNT-CP air electrode recorded at discharge and charge current density of 1.0 and 0.1 mA cm$^{-2}$, respectively; Normalized O (b and d) and Na (c and e) K-edge XANES spectra recorded under the TEY (b and c) and FLY (d and e) modes for the NCNT-CP air electrodes charged to the various cut-off potentials of 2.75, 3.5 and 4.3 V as well as the discharged air electrode and the standard Na$_2$O$_2$ sample.

NCNT-CP air electrodes were also subjected to restricted discharge capacity of 0.5 mAh cm$^{-2}$ and subsequently charged back to the charge plateaus of 2.75, 3.5, and 4.3 V, as
displayed in Figure 4.16a. The NCNT-CP air electrodes were then examined by XAS technique to identify the chemical composition of discharge product at each plateau. Normalized O and Na K-edge XANES spectra of NCNT-CP air electrodes charged to the various plateaus along with a standard Na$_2$O$_2$ a sample recorded under the both TEY and FLY modes are depicted in Figure 4.16b-e. The spectra of the discharged electrode are also added into the plot for the comparison purposes. After charging the air electrode to 2.75 V, the feature associated with superoxide phase at 532.9 eV is disappeared (Figure 4.16b and d), indicating decomposition of the superoxide phase. The disappearance of the peak can be observed more obviously on the spectra recorded under the bulk-sensitive FLY mode (Figure 4.16d). Charging the NCNT-CP air electrode to 3.5 and 4.3V reduces the feature at 534.3 eV, indicating decomposition of the peroxide phase. Additionally, charging the electrode to 3.5 and 4.3 V also results in the appearance of another feature located at 533 eV, which can be correlated to the presence of a carbonate-like phase (see also Figure 4.17).

![Figure 4.17: The normalized O K-edge spectra recorded in the TEY mode for NCNT-CP air electrode charged to 4.3 V as well as standard samples of Na$_2$O$_2$, Na$_2$CO$_3$ and NaSO$_3$CF$_3$ as the references.](image-url)
It should also be noted that the features related to NaO$_2$ and Na$_2$CO$_3$ are very close. However, the feature at 532.9 eV disappears after charging the cell to the cut-off voltage of 2.75 V, whereas Na$_2$CO$_3$ does not decompose under 4.0 V vs. Na/Na$^+$. So, the feature at 532.9 eV which disappears with charging the cell to 2.75 could not be related to the carbonate phase. The nature of the feature at 533 eV will be discussed more in the following part. Similar to the O K-edge, the Na K-edge also indicates the decomposition of products, as shown in Figure 4.16c and e. However, no obvious changes can be detected between the Na K spectra of the discharged air electrode and the electrode charged back to the 2.75 V. This may be due to the superoxide phase not showing any prominent peaks in the Na K spectra. However, the feature around 1078 eV significantly decreases when the electrode is charged to 3.5 and 4.3 V, indicating decomposition of the peroxide phase during the second and third charge plateaus. The Na K-edge spectra of the NCNT-CP air electrode charged to 4.3 V is compared with standard Na$_2$O$_2$, Na$_2$CO$_3$, and NaSO$_3$CF$_3$ samples in Figure 4.18.

![Figure 4.18: The normalized Na K-edge spectra recorded in the TEY mode for NCNT-CP air electrode charged to 4.3 V as well as standard samples of Na$_2$O$_2$, Na$_2$CO$_3$ and NaSO$_3$CF$_3$ as the references.](image_url)
XAS results suggest that a carbonate-like phase is formed during the discharge cycle of the cell and decomposed during the third charging plateau. The formation of carbonate-based parasitic products on the carbonaceous air electrodes has also been observed for Li-air system.\textsuperscript{7, 8, 37} The formation of carbonate-based phase is discussed in the following section.

The NCNT-CP air electrode was also subjected to consecutive discharge and charge cycles restricted to capacities ranging from 0.14 to 1.0 mAh cm\textsuperscript{-2} (Figure 4.19a). The discharge and charge curves restricted to a capacity of 0.5 mAh cm\textsuperscript{-2} cycled between 1.8 and 4.3 V under a current density of 0.1 mAh cm\textsuperscript{-2} is depicted in Figure 4.19b.

![Figure 4.19: (a) Cycling profiles of Na-O\textsubscript{2} cells using NCNT-CP air electrode restricted to the different discharge capacities of 0.14, 0.28, 0.5 and 1.0 mAh cm\textsuperscript{-2}; (b) Consecutive restricted discharge and charge curves of Na-O\textsubscript{2} cell using NCNT-CP air electrode cycled between 1.8 and 4.3 V at a current density of 0.1 mA cm\textsuperscript{-2}.](image)
Increasing cycle numbers leads to increased charge overpotential. While 70% of the formed product was charged back below 3.5 V during the first charge cycle, this value was decreased to 14% in the 15th cycle. To determine the nature of the remaining products after cycling, the NCNT-CP air electrodes were cycled in a Na-O₂ cell with a restricted capacity of 1.0 mAh cm⁻² under a current density of 0.1 mA cm⁻² and examined using XAS. The O and Na K-edge XANES spectra of the cycled air electrode as well as standard Na₂O₂ and Na₂CO₃ samples are presented in Figure 4.20a and b.

Figure 4.20: Normalized O (a), and Na (b) K-edge XANES spectra recorded under the TEY mode for the cycled air electrode as well as the standard Na₂O₂ and Na₂CO₃ samples.
The comparison of the cycled air electrode with the reference samples reveals that a carbonate-like phase as well as Na$_2$O$_2$ remains on the electrode after cycling. This insulating carbonate layer imposes an additional overpotential to the cell during the charge cycle and prevents complete decomposition of the discharge products.$^7$ Such a gradual increase in the charging overpotential of the cell can also be seen in the consecutive discharge and charge curves shown in Figure 4.19b. In addition, the cycled air electrodes restricted to different discharge capacities of 0.5 and 1.0 mAh cm$^{-2}$ were also examined by FTIR along with standard sodium peroxide and sodium carbonate samples (Figure 4.21). The FTIR results also confirm the existence of a carbonate phase on the cycled air electrodes as well.

![FTIR spectra](image)

**Figure 4.21:** FTIR spectra of Na$_2$CO$_3$ (a); Na$_2$O$_2$ (b); as-prepared NCNT-CP air electrode (c); and NCNT-CP air electrode cycled in Na-O$_2$ cell restricted to different discharge capacities of 0.5 (d) and 1.0 mAh cm$^{-1}$ (e).

Recently, McCloskey et al. compared the Li- and Na-O$_2$ cells using DEMS technique under similar experimental conditions and showed that unlike Li-O$_2$ cell, Na-O$_2$ undergoes less chemical and electrochemical decomposition during the first discharge/charge cycle.$^{22}$
However, based on the XANES data presented here it can be concluded that parasitic side products may also be produced and accumulated on the air electrode of Na-O₂ cell, especially when using a high surface area carbon material as the air electrode. High surface area air electrode provides a vast interface between the discharge products and the electrolyte, resulting in the accelerated formation of the side products. Accumulation of the parasitic side products on the air electrode in turn results in increased cell overpotential and capacity fading. The Na-O₂ operational mechanism is schematically illustrated in Figure 4.22.

Figure 4.22: Schematic illustration of the Na-O₂ cell operational mechanism.
The source for the decomposition products is believed to mainly originate from the side reaction between the oxygen-rich phase of the discharge product (NaO$_2$) and the electrolyte.$^{38}$ Similar reaction mechanisms are expected to occur in Li-O$_2$ and Na-O$_2$ cells and the formation of a superoxide intermediate is likely to occur for both cases.$^{39,40}$ In Li-O$_2$ cells, the superoxide intermediate reacts with either the electrolyte or the carbonaceous air electrode to form Li$_2$CO$_3$ during the first discharge/charge cycle of the cell.$^{7,8,38}$ In the case of Na-O$_2$ cells, however, higher thermodynamic stability of NaO$_2$ may contribute to decreased parasitic side reactions occurring due to the stabilization of the superoxide intermediate. As a result, a lower amount of parasitic side products is expected to be formed in a Na-O$_2$ cell compared to Li-O$_2$ cells.

4.4 Conclusion

In conclusion, XANES study of the discharge products produced in Na-O$_2$ cell using a binder-free high surface area air electrode revealed that both sodium superoxide and peroxide are formed. Various sodium oxide phases formed during the discharge cycle of the cell exhibit dissimilar charging overpotentials. In addition, a parasitic side product with a carbonate-like structure was detected on the air electrode surface during the electrochemical cycling. It is believed that the quantity of the parasitic products in Na-O$_2$ cell is lower than that of Li-O$_2$ cell due to the higher thermodynamic stability of NaO$_2$ phase compared to LiO$_2$. However, the presence of carbonate parasitic side product cannot be ignored on a high surface area carbonaceous air electrode. Control of chemical composition of the discharge products in Na-O$_2$ cell either by manipulating the kinetic parameters affecting the discharge reaction as well as investigation for a more stable electrolyte might be considered as a potential solution in increasing the cyclability of Na-O$_2$ cells.
References

Solid state catalysts play a critical role in peroxide alkali metal-O\textsubscript{2} cells. However, the underlying mechanism behind the catalytic activity remains controversial due to the different nature of ORR and OER in these cells compared to those in classic solution based reactions. In the present study, we reveal a detailed spectroscopic and electrochemical picture of the mechanism of catalytic activity in Na- and Li-O\textsubscript{2} cells. The employed air electrode in this study is composed of atomically deposited Pd nanoclusters on mesoporous Mn\textsubscript{3}O\textsubscript{4} decorated on a 3D high surface area carbonaceous framework. XAS characterization combined with EXAFS modeling of the air electrode indicated that Pd nanoclusters are composed of atomic layers of Pd located within the vicinity of oxygen. Electrochemical examination of the air electrode showed a synergetic effect occurring between Pd nanoclusters and the underlying Mn\textsubscript{3}O\textsubscript{4} substrate toward reducing the charge overpotential in Na- and Li-O\textsubscript{2} cells. Spectroscopic studies revealed that the synergetic effect between Pd and Mn\textsubscript{3}O\textsubscript{4} is a result of the bridging effect of O 2p between Pd 4d and Mn 3d orbitals. We demonstrate that ORR and OER catalytic activity in alkali metal-O\textsubscript{2} cells primarily originates from the stabilization of O\textsuperscript{2-} intermediate on the catalyst surface during electrochemical reaction. The findings of the present study help to better understand the function of solid state catalysts in peroxide alkali metal-O\textsubscript{2} cells.

* This study has been submitted to Energy & Environmental Science.
5.1 Introduction

Alkali metal (Li and Na)-O\(_2\) cells are considered as the next generation of electrochemical energy storage technology with potential applications for electrical transportation.\(^1\) The high energy density produced by alkali metal-O\(_2\) cells is based on coupling a high energy alkali metal (negative electrode) with a breathing oxygen electrode (positive electrode). The resulting reaction, known as an oxygen reduction reaction (ORR), produces superoxide (O\(_2^\cdot\)) ions which combine with alkali metal ions, from the negative electrode, to form a solid metal oxide complex as the discharge product.\(^4,6\) The superoxide then further reduced (chemically or electrochemically) to peroxide (O\(_2^{2-}\)) in Li-O\(_2\) cell and produces lithium peroxide (Li\(_2\)O\(_2\)) as the major discharge product of the cell.\(^7\) In the case of Na-O\(_2\) cell, however, the larger radii of the sodium ion stabilizes the superoxide intermediate and results in formation of either sodium superoxide (NaO\(_2\)) or peroxide (Na\(_2\)O\(_2\)) as the product of the cell.\(^8\) The formed solid discharge product of the cells are then forced to decompose back to molecular oxygen and alkali metal during the charge cycle. However, the oxygen evolution reaction (OER) in the air electrode of alkali metal-O\(_2\) peroxide cells requires a large overpotential, thereby significantly reducing the energy efficiency of the cell.\(^1\)\(^3\)\(^5\)

The large charging overpotential in Li- and Na-O\(_2\) peroxide cells originates from various factors including the irreversible electrochemistry of O\(_2\)/O\(_2^{2-}\) redox pair,\(^6\) poor electric conductivity of the discharge product,\(^14\)-\(^20\) instability of the electrolyte and air electrode,\(^21,22\) and formation of insulating parasitic products during the discharge and charge cycles of the cells.\(^10,23,24\) On the other side, Li- and Na-O\(_2\) cells with superoxide discharge products exhibit a lower charging overpotential compared to their peroxide counterparts.\(^4,12,13,25\) The low charging overpotential observed in superoxide cells stems from the reversible electrochemical reaction of O\(_2\)/O\(_2^\cdot\) redox pair. In contrast, peroxide cells undergo an ECC mechanism during the discharge cycle, followed by a one-step decomposition reaction during the charge cycle.\(^5\) This large overpotential required to reverse the products produced in peroxide cells typically results in significantly diminished cycle life.\(^2,9,26\) Critical components of the cell, such as the electrolyte and air electrode, are unstable at high positive potentials and produce insulating parasitic side products in an oxidative decomposition process. Accumulation of parasitic side products at the electrode/electrolyte
interface further increases the charging overpotential of the cell, resulting in capacity failure. Meanwhile, cycle life in superoxide cells is also limited to a few tens of cycles. Chemical instability of the oxygen-rich discharge product against the cell electrolyte and/or mechanical detachment of the micrometer-sized crystalline superoxide product at the early stage of the charge process, often results in limited cycle life of the superoxide cells.

Solid state catalysts have been widely employed in peroxide cells to reduce the charging overpotential and improve the cycle life of cells. However, the mechanism behind the catalytic activity in these alkali metal-O₂ cells is a point of controversy. On one side, formation of the very first layers of the solid products during the discharge cycle is argued to hinder the catalytic activity very quickly. On the other side, solid state catalysts have been proven to enhance the electro/chemical performance of the peroxide cells. Multiple interpretations have been proposed as the potential mechanism behind the function of solid state catalysts in Li-O₂ cells. Bruce et al. showed that the catalytic activity in nanoporous gold and TiC based air electrodes is based on the suppression of side reactions occurring due to the air electrode and electrolyte degradation. Nazar et al. attributed the advanced performance of mesoporous pyrochlore catalyst to the presence of defect sites with oxygen vacancy on a conductive nanoporous network. Shao-Horn et al. also proposed that the Pt-Au nanoparticles boost the sluggish kinetics of ORR and OER in non-aqueous electrolytes. In addition, catalysts may alter the chemical composition, size, structure, density and electronic conductivity of the metal oxide discharge products in alkali metal O₂ cells by stabilizing various oxygen-metal intermediates during the ORR. Recently, growth of stable LiO₂ phase on iridium nanoparticles further highlighted the role of catalyst in controlling the chemical composition of the discharge product in Li-O₂ cell. Similarly, catalytic activity is also expected to enhance the electro/chemistry of Na-O₂ superoxide and peroxide cells.

In the present paper, we reveal detailed spectroscopic evidence toward the mechanism governing catalytic function in Na- and Li-O₂ peroxide cells. Herein, a 3D structured air electrode with bifunctional catalytic activity was synthesized and employed in Na- and Li-O₂ peroxide cells. The air electrode was composed of a light weight graphene foam as a
macroporous framework, facilitating rapid oxygen and metal ions transportation into and from the air electrode. Nitrogen doped carbon nanotubes (NCNT) were also synthesized on the graphene foam substrate to increase the active surface area of the air electrode. Additionally, a mesoporous Mn$_3$O$_4$ network combined with atomically deposited Pd nanoclusters as ORR and OER catalysts were mounted on the carbonaceous framework. We show that the catalytic activity in alkali metal-O$_2$ cells is a result of dynamic interaction occurring between the catalyst and the discharge product. Besides, the observed synergetic effect between Mn$_3$O$_4$ and Pd is shown to originate based on an electron exchange between the noble metal and the metal oxide.

5.2 Experimental

5.2.1 Synthesis of electrode materials

**Synthesis of Gr foam.** Gr foam was synthesized using a chemical vapor deposition (CVD) technique previously reported. The synthesis procedure is briefly described as follow: A piece of Ni foam (1.2 mm in thickness) was used as a self-sacrificing template and catalyst surface to grow graphene. Ni foam was cut into the desired dimensions and placed in a quartz tube. The quartz tube were transferred into a horizontal furnace and purged with Ar (500 sccm) and H$_2$ (50 sccm) for 15 min. The furnace was then heated up to 1000 °C and kept at this temperature for 15 min to remove the surface contaminants and oxide layer from Ni foam. CH$_4$ was then introduced into the tube as the carbon source at a flow rate of 0.5 sccm for 1 h. The sample was then cooled down to room temperature under flowing Ar and H$_2$. Afterward, the sample was placed in a 3 M HCl solution at 50°C overnight to completely dissolve Ni template.

**Synthesis of Gr/NCNT.** Gr/NCNT foam was synthesized using a modified spray pyrolysis chemical vapor deposition (SPCVD) method. In a typical synthesis, Gr foam (with Ni template) was physically sputtered with a 30 nm of aluminum as the buffer layer and a 10 nm of iron as a CVD catalyst. The Fe catalyst applied for NCNT growth was physically sputtered on the Gr surface in a modified SPCVD method, in contrast to the conventional process where the catalyst was being sprayed on the desired surface. The modified
SPCVD method provides better control over NCNT density. The sputtered Gr foam was then fixed inside a quartz tube and transferred into a vertical furnace. The quartz tube was purged with Ar (500 sccm) for 15 min to produce an inert atmosphere. The furnace was then heated up to 850 °C and a solution containing 2 g of imidazole in 10 mL of acetonitrile was introduced into the tube with the aid of an ultrasonic probe sonicator at a flow rate of 250 µL/min for 10 min. The Ni template was consequently removed using the aforementioned etching procedure.

Synthesis of Gr/NCNT/MnO. Mesoporous Mn₃O₄ was synthesized on NCNT surface using a chemical precipitation method. In a typical synthesis procedure, as-prepared Gr/NCNT sample were transferred into a solution containing KMnO₄ (10 mg/ml) and H₂SO₄ (5%) at 45 °C for 3 min. The Gr/NCNT/MnO was then transferred into cold distilled water to stop the reaction and washed several times using water and ethanol.

Synthesis of Gr/NCNT/MnO/Pd. The Pd catalyst was deposited using an Arradiance GEMstar-8 ALD system using alternating exposure of Pd(II) hexafluoroacetylacetonate, Pd(hfac)₂, and formalin at a processing pressure of 0.8 Torr. Both precursors were obtained from Sigma Aldrich and used as received. Formalin solution was composed of 37% formaldehyde in water containing 10-15% methanol to prevent polymerization. Pd(hfac)₂ was held in a stainless steel bubbler at 50°C to maintain a vapor pressure slightly less than 0.1 Torr. Manifold temperature was maintained at 100°C while deposition temperature was kept constant at 200°C. Ultrahigh purity nitrogen (99.999%) was used as a carrier gas and purge gas throughout the experiment with a mass flow of 20 sccm. ALD deposition can be expressed as \( t_1-t_2-t_3-t_4 \) where \( t_1 \) is the exposure time for the first precursor (Pd(hfac)₂) and \( t_2 \) is the purge time following the first precursor and \( t_3 \) and \( t_4 \) are second precursor pulse (formalin) and purge respectively. A timing sequence of 2-30-1-30 s was used for the deposition of Pd to produce the Gr/NCNT/MnO/Pd electrode.

5.2.2 Physical Characterizations

Morphological studies were performed by Hitachi S-4800 field-emission scanning electron microscope (SEM) and high-resolution TEM (HRTEM, JEOL 2010FEG) scanning transmission electron microscopy (STEM). N₂ adsorption/desorption isotherms were
obtained using a Folio Micromeritics TriStar II 3020 Surface Area and Pore Size Analyzer. The surface area of the electrodes was calculated using a Brunauer, Emmett, and Teller (BET) model by taking at least six data points where $0.07 < P/P_0 < 0.2$. Pore size distribution was obtained by the Barrett, Joyner, and Halenda (BJH) model using the desorption branch of the isotherm. Thermogravimetric analysis (TGA) was performed using a SDT Q600 TGA unite from room temperature (RT) to 900 °C in air at a heating rate of 10 °C min$^{-1}$. Raman data was collected using a HORIBA Scientific LabRAM HR Raman spectrometer operated with an incident laser beam at 532.03 nm. X-ray diffractograms were obtained using a Bruker D8 Advance (Cu-Kα source, 40 kV, 40 mA).

For the X-ray diffraction (XRD) measurements, the Na-O$_2$ cells were dissembled in an Ar-filled glovebox following electrochemical cycling, and the positive electrode materials were placed into an air-sensitive XRD sample holder. XAS measurements were obtained at the Canadian Light Source (CLS) on the spherical grating monochromator (SGM) and hard X-ray micro-analysis (HXMA) beamlines. In order to examine the discharge product of the cells, the discharged cells were dissembled inside a glovebox, the air electrodes were then sealed transferred to the beamline end-station, where the samples were opened in a second glovebox and placed into the XAS vacuum chamber. The samples were kept under pure argon atmosphere before the analytical measurements, without any exposure to the atmospheric air. The vacuum during the XAS experiments was around 10$^{-8}$ Torr.

5.2.3 Electrochemical Measurements

Swagelok-type cells composed of sodium foil anode, Celgard 3500 separator (5/8 in. in diameter), different air electrode, and a stainless steel mesh as current collector were used to carry out electrochemical measurements. The employed Swagelok cell configuration is described elsewhere.$^2$ The air electrodes were cut into circular pieces (3/8 in. in diameter) with the geometric surface area of 0.71 cm$^2$. A fresh sodium or lithium foil (3/8 in. in diameter) was used as negative electrode material. The electrolyte used in this study was 0.5 M sodium or lithium triflate (Na/LiSO$_3$CF$_3$, Aldrich) dissolved in diethylene glycol diethyl ether (DEGDME, Anhydrous ≥ 99.5%, Aldrich). Sodium and lithium triflate electrolyte salt was dried at 80 °C under vacuum for 48 h, and the water content of DEGDME solvent was removed using molecular sieves (3 Å) for at least 10 days. The
amount of electrolyte in the cell was \( \sim 200 \mu L \). The assembled Na or Li-O\(_2\) cells were placed into a homemade testing box inside the glovebox and then transferred to the testing room. The argon content of testing box was moderately vacuumed out and then pure oxygen (purity 5.0) was purged into the box. The pressure of testing box was kept at 1.0 atm during the electrochemical tests. Discharge/charge characteristics were performed using an Arbin BT-2000 battery station at RT (25 °C).

## 5.3 Results and Discussion

The air electrode designed in this study is based on the 3D structure of Ni foam as the underlying skeleton. This 3D skeleton exhibits a macroporous structure which serves for fast oxygen and ion transportation into the air electrode. However, large void mass of the Ni foam dramatically decreases the specific capacity of the air electrode. Therefore, Ni foam was employed as both a template and CVD catalyst at a same time to synthesize graphene. The Ni foam was then removed through an etching process, leaving a hollow and light-weight graphene foam (Gr). The resultant Gr foam maintained the underlying 3D structure of the Ni foam following Ni removal, while simultaneously decreasing the electrode mass (Figure 5.1). Nonetheless, Gr foam presents a limited surface area due to its macroporous structure. To increase the surface area of the electrode, the synthesized Gr foam was then covered by nitrogen doped carbon nanotubes (NCNT). A modified spray pyrolysis chemical vapor deposition (SPCVD) method was employed to synthesize NCNT. As depicted in Figure 5.2a-c, the Gr foam is uniformly covered by randomly oriented NCNTs. The random orientation of the NCNT provides increased void volume, exposing ample surface area for catalyst deposition as well as electrolyte accessibility and accommodation of discharge products. In the next synthesis step, Mn\(_3\)O\(_4\) with mesoporous structure was synthesized on Gr/NCNT electrode using a chemical precipitation method. The obtained electrode is denoted as Gr/NCNT/MnO throughout the text. Mesoporous Mn\(_3\)O\(_4\) not only serves as an ORR catalyst, but also increases the active surface area of the air electrode and provides appropriate pore sizes for accommodation of discharge
products.9 The microstructure of Gr/NCNT/MnO electrode (Figure 5.2d-f) shows uniform deposition of mesoporous Mn$_3$O$_4$ all over NCNT surface.

Figure 5.1: SEM micrographs of Gr foam before and after Ni removal.
An ultrathin Pd film was then deposited on the Gr/NCNT/MnO surface using atomic layer deposition (ALD). The thickness of Pd film can be precisely controlled by controlling the number of ALD cycles employed. Cycle numbers of 50, 100 and 150 were applied to the final air electrode which is denoted as Gr/NCNT/MnO/Pd-(50C, 100C or 150C) throughout the text. To further clarify the synergetic effect between Mn$_3$O$_4$ and Pd, control air electrodes without Mn$_3$O$_4$ were also synthesized and are denoted as Gr/NCNT/Pd-(50C, 100C or 150C). Raman spectra of Gr, Gr/NCNT and Gr/NCNT/MnO electrodes are shown in Figure 5.3. Gr foam exhibits two peaks around 1570 and 2730 cm$^{-1}$ corresponding to G and 2D bands, respectively. The 2D peak in Gr foam spectrum is relatively wide and short compared to single-layer graphene which is a result of peak splitting due to the added forces from interactions between layers of AB-stacked graphene. In addition, the sharp and intense G-band indicates the presence of high crystalline graphitic carbon. The Raman spectra of Gr/NCNT, however, displays two peaks around 1370 and 1580 cm$^{-1}$, related to D and G bands, respectively. The high intensity D-band ($I_D/I_G \sim 1$) which is originated from atomic displacement and disorder induced features caused by lattice defect or distortion indicates a high amount of defects and disorders in NCNT. The Raman spectrum of Gr/NCNT/MnO shows a single peak at 657 cm$^{-1}$ which can be correlated to the $A_{1g}$
mode of Mn₃O₄ and is corresponding to the Mn-O stretching vibration of divalent manganese ions in the tetrahedral coordination.

![Raman spectra of electrodes](image)

**Figure 5.3: Raman spectra of Gr, Gr/NCNT and Gr/NCNT/MnO electrodes.**

The relative mass fraction of the electrode materials was examined by thermogravimetric analysis (TGA) which is presented in Figure 5.4. Gr shows a significant mass reduction from 600 to 800 °C with the remaining mass of less than 3% which indicates the total removal of Ni through etching process. Gr/NCNT exhibits two consecutive reduction steps starting at 500 °C related to the NCNT decomposition followed by Gr removal. The mass fraction of NCNT can be estimated to be ~26% based on the first mass reduction step. Similar two-steps mass reduction curve was obtained for Gr/NCNT/MnO with ~17% remaining mass which is corresponding to the Mn₃O₄ mass fraction.

SEM micrographs of Gr/NCNT/MnO/Pd and Gr/NCNT/Pd with various ALD cycles are depicted in Figure 5.5. Pd is deposited as nanoparticles with dimensions less than 5 nm following 50 ALD cycles on NCNT surface. Both the size and density of the Pd nanoparticles increases with increasing the ALD cycle number to 100 and 150. Most of the NCNT surface is covered by Pd particles with a diameter of around 10 nm after 150 ALD
cycles. However, Pd nanoparticles cannot be observed in the SEM micrographs of Mn$_3$O$_4$ surface even after increasing the ALD cycle number to 150.

The microstructure of the Gr/NCNT/MnO/Pd electrode was further examined using scanning transmission electron microscopy (STEM). High resolution TEM images of Gr/NCNT/MnO and Gr/NCNT/MnO/Pd-100C are presented in Figure 5.6. Comparing the TEM images of the two electrodes reveals the presence of Pd nanoclusters on the Mn$_3$O$_4$ surface. High angle annular dark field (HAADF) image of the samples are also shown in Figure 5.6. HAADF STEM images are formed by very high angle scattered electrons which are sensitive to variations in the atomic number. HAADF STEM images of Pd-deposited electrodes exhibits a large number of high-contrast points which represent Pd nanoparticles. Moreover, HRTEM image of the Pd-deposited electrode displays a higher degree of crystallinity compared to the bare Mn$_3$O$_4$, resulting from a combination of Mn$_3$O$_4$ with highly ordered Pd. Furthermore, thermogravimetric analysis (TGA) of
NCNT/MnO/Pd electrode materials with various ALD cycles (Figure 5.7) demonstrates increasing residual mass with increased number of ALD cycles, illustrating Pd deposition on the Mn$_3$O$_4$ surface. The rate of increased residual mass is lower for the first 50 ALD cycles, due to an initial nucleation process of the Pd ALD.

Figure 5.5: SEM micrographs of Gr/NCNT/MnO/Pd and Gr/NCNT/Pd with various ALD cycles.
Figure 5.6: TEM, HAADF and HRTEM micrographs of Gr/NCNT/MnO electrode before and after 100 cycles of Pd deposition by ALD.
Since the Gr foam is the dominant component in the total electrode weight, the TGA experiment for the Pd containing samples was conducted using powder-based samples (without Gr foam). The samples were prepared using NCNT as the starting materials using the same Pd ALD procedure. TGA of NCNT/MnO/Pd electrode materials with various number of Pd ALD cycles demonstrates increasing residual mass with increased number of ALD cycles, illustrating Pd deposition on the Mn$_3$O$_4$ surface. The rate of increased residual mass is lower for the first 50 ALD cycles, due to an initial nucleation process of the Pd ALD.

![Figure 5.7: TGA results of NCNT/MnO/Pd electrode materials before and after various number of Pd ALD cycles.](image)

The porous structure of the synthesized electrode materials was examined by BET analysis (Figure 5.8). The nitrogen adsorption/desorption isotherm of Gr/NCNT exhibits a type II diagram, indicating unrestricted monolayer-multilayer adsorption on a non-porous or macroporous adsorbent. Both Gr/NCNT/MnO and Gr/NCNT/MnO/Pd-100C electrodes show a type IV isotherm with a H3-type hysteresis loop at high p/p$_0$ which is indicative of capillary condensation within the mesopores. It is also noteworthy that
Gr/NCNT/MnO/Pd-100C shows a low pressure hysteresis which is due to the chemisorption of N$_2$ on the Pd surface.

![Nitrogen adsorption/desorption isotherms of Gr/NCNT, Gr/NCNT/MnO and Gr/NCNT/MnO/Pd-100C electrodes.](image)

**Figure 5.8: Nitrogen adsorption/desorption isotherms of Gr/NCNT, Gr/NCNT/MnO and Gr/NCNT/MnO/Pd-100C electrodes.**

Similar adsorption/desorption isotherms were observed for the electrodes with 50 and 150 ALD cycles (Figure 5.9). The BET surface area of the electrodes was calculated to be 16.8, 95.0 and 64.1 m$^2$ g$^{-1}$ for Gr/NCNT, Gr/NCNT/MnO and Gr/NCNT/MnO/Pd-100C, respectively (see also Table 5.1). The surface area of the electrode material increases significantly by precipitating mesoporous Mn$_3$O$_4$ on NCNT and then slightly decreases upon Pd deposition. The decrease in BET surface area of Gr/NCNT/MnO/Pd is due to the increased weight of the electrode as well as pore clogging by Pd deposition (see also Figure 5.10). The pore volume of the electrodes throughout the entire pore diameter range slightly decreases with increase of the ALD cycles, indicating the uniform Pd deposition onto the electrode porous structure. Moreover, the pore volume reduction is more significant after the first 50 ALD cycles especially in the pore diameter range of 10-50 nm which shows the partial clogging of the pores during the initial steps of the deposition process.
Figure 5.9: Nitrogen adsorption/desorption isotherms of Gr/NCNT/MnO/Pd-100C electrodes with various number of Pd ALD cycles.

Figure 5.10: Pore volume distribution of Gr/NCNT/MnO in comparison with that of Gr/NCNT/MnO/Pd electrodes with various cycles of Pd deposition by ALD.
Table 5.1: Comparison of BET surface area of the synthesized electrodes.

<table>
<thead>
<tr>
<th>Electrode material</th>
<th>BET Surface Area (m² g⁻¹)</th>
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<tbody>
<tr>
<td>Gr/NCNT</td>
<td>16.8</td>
</tr>
<tr>
<td>Gr/NCNT/MnO₂</td>
<td>95.5</td>
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<tr>
<td>Gr/NCNT/MnO₂/Pd-50C</td>
<td>65.5</td>
</tr>
<tr>
<td>Gr/NCNT/MnO₂/Pd-100C</td>
<td>64.1</td>
</tr>
<tr>
<td>Gr/NCNT/MnO₂/Pd-150C</td>
<td>43.8</td>
</tr>
</tbody>
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The electrode materials were further analyzed by XRD (Figure 5.11). While Gr/NCNT exhibits a typical graphite peak at 2θ = 26°, the additional peaks in the Gr/NCNT/MnO diffractogram matches well with tetragonal Mn₃O₄ (JCPDF ref. card No. 007-1841). No Pd peak was detected in the diffractogram of Gr/NCNT/MnO/Pd electrode, probably due to the low thickness of the deposited Pd layer. However, Pd peaks were detected on the Gr/NCNT/Pd electrode (Figure 5.12), confirming the formation of metallic Pd nanoparticles on NCNT.

Figure 5.11: XRD pattern of Gr/NCNT, Gr/NCNT/MnO and Gr/NCNT/MnO/Pd-100C electrodes.

167
Figure 5.12: XRD pattern of Gr/NCNT and Gr/NCNT/Pd-100C electrodes.

X-ray absorption spectroscopy (XAS) was employed to confirm the chemical composition of Mn$_3$O$_4$ as well as formation of Pd on Mn$_3$O$_4$. The normalized Mn K-edge X-ray absorption near-edge structure (XANES) spectra of Gr/NCNT/MnO and Gr/NCNT/MnO/Pd is compared to standard sample of Mn$_3$O$_4$ in Figure 5.13a. All XANES spectra display a weak pre-edge absorption peak which can be attributed to a forbidden 1s dipole transition to unoccupied 3d orbitals. The main absorption edge of synthesized Mn$_3$O$_4$, correlated to the Mn 1s → 4p transition, appears at a slightly higher energy compared to the standard sample, indicating a higher oxidation state for the synthesized Mn$_3$O$_4$. In addition, no changes can be seen in the XANES spectra of Gr/NCNT/MnO before and after Pd deposition, suggesting that the Mn$_3$O$_4$ substrate is stable during the ALD process. However, a distinct change can be seen between the O k-edge spectra of Gr/NCNT/MnO and Gr/NCNT/MnO/Pd electrodes (Figure 5.13b). The standard Mn$_3$O$_4$ sample as well as Gr/NCNT/MnO exhibit a feature around 531 eV. This excitation is split into two peaks due to the ligand field and has been attributed to the electron transition from core O 1s orbitals to 2p-3d hybridized Mn orbitals ($t_{2g}$ and $e_g$ symmetry bands). Meanwhile, the broad feature around 534 eV is related to unoccupied oxygen p states mixed with the manganese 4sp band. The O k-edge spectra of MnO$_2$, Mn$_2$O$_3$ and Mn$_3$O$_4$ standard samples are also depicted in Figure 5.14 for comparison. In the case of
Gr/NCNT/MnO/Pd electrode, however, the pre-edge feature ($T_{2g}$) is followed by an intense and broad feature which overlaps the $e_g$ peak. Appearance of this broad feature after Pd deposition is a result of overlapping between O 2p with Mn 3d and Pd 4d orbitals. In fact, the O K-edge XANES results illustrate that O 2p orbitals bridge between Mn 3d and Pd 4d orbitals. Further, similar features are appeared in the O k-edge spectra recorded under FLY mode (Figure 5.15), confirming that both mesoporous Mn$_3$O$_4$ and Pd nanoclusters are composed of thin layers with uniform surface and bulk properties.

Figure 5.13: Normalized Mn (a) and TEY O (b) K-edge XANES spectra of standard Mn$_3$O$_4$, Gr/NCNT/MnO and Gr/NCNT/MnO/Pd electrodes
Figure 5.14: Normalized O k-edge XANES spectra of MnO₂ and Mn₂O₃ and Mn₃O₄ standard samples recorded under TEY mode.

Figure 5.15: Normalized O k-edge XANES spectra of standard Mn₃O₄, Gr/NCNT/MnO and Gr/NCNT/MnO/Pd electrodes recorded under FLY mode.
The normalized Pd K-edge XANES spectra for Gr/NCNT/Pd and Gr/NCNT/MnO/Pd electrodes, along with Pd foil are presented in Figure 5.16a. The Gr/NCNT/Pd shows the same characteristic features as the Pd foil, indicating that the ALD Pd nanoparticles on the NCNT surface exhibit an oxidation state, as well as local structure, similar to bulk Pd. Gr/NCNT/MnO/Pd electrode also demonstrates the same adsorption edge as Pd foil, confirming the presence of metallic Pd at zero-valence state on the Mn$_3$O$_4$ surface. However, in contrast to the Pd nanoparticles on NCNTs, the local structure of the deposited Pd on Mn$_3$O$_4$ is obviously different from the bulk Pd. Figure 5.16b shows the Fourier transform $K^3$-weighted extended X-ray absorption fine structure (EXAFS) spectra of the electrode materials. The simulated results for Pd and PdO crystals are also shown for comparison. The feature around 2.6 Å represents the Pd-Pd bond and can be seen in EXAFS spectra for all electrodes. In addition, comparing the EXAFS data of Gr/NCNT/Pd with Pd foil confirms the metallic nature of Pd nanoparticles on NCNT. The $R$-space analysis of Gr/NCNT/MnO/Pd, however, shows a significant decrease in the relative intensity of Pd-Pd along with an additional feature at 1.5 Å which can be correlated to a Pd-O bond. Meanwhile, the Pd-Pd feature appearing at 2.6 Å (compared with the Pd-Pd in PdO crystal at 3 Å) contradicts the formation of PdO. The low intensity of the Pd-Pd peak implies that the Pd layer on Mn$_3$O$_4$ is composed of nanoclusters. In addition, the presence of the first shell Pd-O peak in the EXAFS spectra for the Gr/NCNT/MnO/Pd electrode illustrates the presence of an oxygen layer within the vicinity of the Pd layer, bridging between the Pd and Mn atoms. To determine the structural parameters of Pd on various substrates, the experimental data was fitted using a non-linear least-squares curve fitting procedure (Figure 5.17). The obtained structural parameters from curve fitting are presented in Table 5.2. The comparison of Pd-Pd coordination number (CN) for Gr/NCNT/Pd with Pd foil indicates that the Pd nanoparticles on the NCNT surface are slightly oxidized. In the case of Gr/NCNT/MnO/Pd, however, the Pd-Pd CN is significantly decreased while the Pd-O CN is increased, confirming the formation of planar nanoclusters of Pd on Mn$_3$O$_4$ surface.
Figure 5.16: (a) normalized Pd K-edge XANES spectra of standard Pd foil, Gr/NCNT/Pd and Gr/NCNT/MnO/Pd electrodes; (b) Fourier transform $K^3$-weighted EXAFS spectra of standard Pd foil, Gr/NCNT/Pd and Gr/NCNT/MnO/Pd electrodes alongside with simulated results for Pd and PdO crystals.

Table 5.2: The structural parameters obtained from curve fitting depicted in Figure 5.17.

<table>
<thead>
<tr>
<th></th>
<th>Pd-Pd Coordination</th>
<th>Pd-O Coordination</th>
<th>Pd-Pd Debye-Waller factor (Å$^2$)</th>
<th>Pd-O Debye-Waller factor (Å$^2$)</th>
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<tbody>
<tr>
<td>Gr/NCNT/MnO/Pd</td>
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<td>4.91×10$^{-3}$</td>
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<td>Pd foil</td>
<td>12</td>
<td>-</td>
<td>5.41×10$^{-3}$</td>
<td>-</td>
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</table>
Figure 5.17: Fourier transform signal $\chi(R)$ of the experimental (circles) and calculated (solid line) Pd K-edge EXAFS $\chi(k)$ for standard Pd foil, Gr/NCNT/Pd and Gr/NCNT/MnO/Pd electrodes. The crystal structures of Pd/O used as fitting model are also given.

XAS results alongside SEM, TEM and XRD illustrate that the structure of deposited Pd on Mn$_3$O$_4$ is different from the Pd nanoparticles on NCNT surface. This structural difference originates from the distinct ALD growth mechanisms on these surfaces. The half-reaction
of Pd on the surface of a substrate has preferential deposition toward high-energy defect sites on a non-uniform substrate like NCNT, resulting in nucleation of Pd. With increasing number of ALD cycles, the initially formed nucleation sites grow in size to form islands of Pd on the NCNT surface. This island growth regime is also known as Volmer-Weber mechanism. In contrast to NCNT, Mn₃O₄ provides a more uniform surface which leads to formation of Pd nanoclusters on the oxide surface. Increasing the ALD cycles on Mn₃O₄ surface results in planar expansion of Pd nanoclusters. These nanoclusters may grow and coalesce together after multiple ALD cycles to form a continuous film. Based on the XAS analysis, formation of Pd nanoclusters on Mn₃O₄ is highly likely. The Pd deposited on Mn₃O₄ demonstrates a significantly lower Pd-Pd CN than Pd nanoparticles on NCNT (see table 5.2). This low Pd-Pd CN suggests that Pd nanoclusters on Mn₃O₄ have a thickness of a few atomic layers. The ALD growth mechanisms on NCNT and Mn₃O₄ surfaces are also schematically outlined in Figure 5.18.

Figure 5.18: The schematic diagram for Pd ALD growth mechanisms on NCNT and Mn₃O₄ surfaces.
The electrochemical response of the prepared electrodes were examined in both Na- and Li-O_2 cells. The discharge/charge curves of the prepared electrodes in Na- and Li-O_2 cells are presented in Figure 5-19a and b, respectively. Gr/NCNT electrodes exhibit the typical discharge/charge behavior seen for carbonaceous materials with large charging overpotentials occurring for both cells.\textsuperscript{2,10} A noticeable increase in the discharge potential of both Na- and Li-O_2 cells can be seen for Gr/NCNT/MnO electrodes. This increase in discharge potential is greater in Li-O_2 cell. Similar electrocatalytic effects for Mn_3O_4 on the ORR in alkaline solutions\textsuperscript{43-45} as well as Li-O_2 cells\textsuperscript{46} has been reported previously. Presence of surface defects and hydroxyl (-OH) functional groups on the surface of manganese oxide facilitates the adsorption of oxygen onto the reaction sites and decreases the ORR activation energy. Moreover, the redox reaction involving Mn species is also believed to contribute to the high electrocatalytic activity of manganese oxide.\textsuperscript{47} The charging overpotential in both Na- and Li-O_2 cells is also diminished by either the addition of mesoporous Mn_3O_4 or Pd nanoparticles onto the NCNT surface.

Figure 5.19: Discharge/charge curves for Gr/NCNT, Gr/NCNT/MnO, Gr/NCNT/Pd-150C and Gr/NCNT/MnO/Pd-150C electrodes in Na- (a) and Li-O_2 (b) cells; the cycling performance of Gr/NCNT/MnO/Pd-150C electrode in Na- (c) and Li-O_2 (d) cells.
The discharge/charge curves of Gr/NCNT/Pd electrodes with various ALD cycles in both Na- and Li-O₂ cells are also depicted in Figure 5.20. The charging overpotential in both cells negligibly decreases with increasing number of Pd ALD cycles, from 50 to 150. Since the Pd coverage on NCNT surface increases with ALD cycle number (see Figure 5.5), one would expect the overpotential of the cells to decrease accordingly. However, the growth mechanism of Pd on NCNT surface by ALD follows the Volmer-Weber mechanism. By increasing the ALD cycles to 100 and 150, the initially formed nanoparticles grow in size to make larger Pd particles, resulting in similar electrocatalytic performance to 50 ALD cycles of Pd. In other words, the increase of ALD cycles to 100 and 150 increases the bulk Pd which does not contribute to reducing the overpotential during OER. The slight improvement in charging overpotential from 50 to 150 ALD cycles, however, can be attributed to the formation of new nucleation sites formed during increased number of ALD cycles.

![Figure 5.20: The discharge and charge curves of Gr/NCNT/Pd electrodes with various number of Pd ALD cycles for both Na- (a) and Li-O₂ (b) cells.](image)
The mechanism behind the catalytic activity of noble metals, transition metals and metal oxides toward the OER of alkali metal-O\(_2\) cells is not fully understood.\(^5,37\) However, the catalytic behavior observed here could be attributed to the multiple factors. The poor electric conductivity of alkali metal oxides as a discharge products for Na- and Li-O\(_2\) has been considered as one of the reasons for the large charging overpotential observed in these cells.\(^{14,15,18,19}\) The increased active surface area in the case of Gr/NCNT/MnO electrode decreases the thickness of the insulating discharge products on the electrode surface by providing ample room for deposition of discharge product. Therefore, mesoporous Mn\(_3\)O\(_4\) decreases the charging overpotential of the cells by enhancing both charge and mass transfer through the discharge product layer.\(^{48}\) Besides, the formation of an insulating carbonate-based parasitic product, as a result of oxidative reaction between discharge products of Na- and Li-O\(_2\) with carbonaceous air electrodes, has been shown to significantly increase the charging overpotential of the cell.\(^{10,22,23}\) The shielding effect of the catalyst layer over the NCNT surface may also contribute toward reducing the overpotential by preventing the formation of insulating carbonate species at the air electrode/discharge product interface.

Meanwhile, a different electrocatalytic mechanism is responsible for decreasing the charge overpotential for Gr/NCNT/Pd electrodes. Presence of Pd nanoparticles on the carbon surface is believed to enhance the electronic transport across the electrode/electrolyte interface and hence decrease the charging overpotential of the cell.\(^{40}\) Interestingly, Gr/NCNT/MnO/Pd electrode displays a significant decrease in charging overpotential for both Na- and Li-O\(_2\) cells, while maintaining the high discharge potential observed for Gr/NCNT/MnO. Evidently, Gr/NCNT/MnO/Pd demonstrates a bifunctional catalytic performance in alakali metal-O\(_2\) cells by improving both the discharge and charge potentials.\(^{35}\) Quantitatively, Gr/NCNT/MnO/Pd reduces the charging overpotential of Na- and Li-O\(_2\) cells by 1.0 and 0.8 V, respectively, compared to Gr/NCNT electrodes. The decrease in overpotential observed for Gr/NCNT/MnO/Pd is greater than the summation of the reduction in overpotential seen for Gr/NCNT/MnO and Gr/NCNT/Pd electrodes, indicating a synergetic effect occurring between Mn\(_3\)O\(_4\) and Pd.
Discharge/charge curves of Gr/NCNT/MnO/Pd electrodes with various ALD cycles are also shown in Figure 5.21. Unlike Gr/NCNT/Pd, Gr/NCNT/MnO/Pd electrodes demonstrate a stronger correlation between reduction in charging overpotential and ALD cycle number. The different correlation between Pd ALD cycles on NCNT and Mn$_3$O$_4$ surfaces with electrochemical response of the electrodes is related to the distinct growth mechanisms occurring on these surfaces. As mentioned earlier, nucleation originates at defect sites on the NCNT surface and produces island-like nanoparticles. However, the Mn$_3$O$_4$ surface provides a rich number of defect sites for Pd nucleation resulting in the formation of nanoclusters and/or atomic films. Increasing the ALD cycles on NCNT formed bulky Pd particles, while multiple ALD cycles on Mn$_3$O$_4$ results in planar expansion of Pd nanoclusters to make a thin film while also increasing the density of active Pd. Therefore, an increase in the number of ALD cycles on Mn$_3$O$_4$ results in enhanced OER performance due to higher coverage of Pd nanoclusters.

Figure 5.21: Discharge and charge curves of Gr/NCNT/MnO/Pd electrodes with various number of Pd ALD cycles in both Na- (a) and Li-O$_2$ (b) cells.
The cycling performance of Gr/NCNT/MnO/Pd-150C electrode in Na- and Li-O₂ cells is depicted in Figure 5.19c and d, respectively while the corresponding chronopotentiograms are shown in Figure 5.22. The prepared electrode maintains a low overpotential for 100 consecutive discharge and charge cycles. The difference between discharge and charge potentials of the cells starts to increase during the last 20 cycles. This is most likely related to degradation of the negative electrode. In addition, decomposition of the cell electrolyte by oxidative discharge products formed in the cells may also produce carbonate-based parasitic side-products and result in increased overpotential.

![Graph](image)

**Figure 5.22:** The chronopotentiogram curves of the consecutive discharge and charge test of Gr/NCNT/MnO/Pd-150C electrode in bor Na- and Li-O₂ cells for the data shown in Figure 5.19c and d.

The cycling performance of Gr/NCNT/Pd and Gr/NCNT/MnO/Pd electrodes with various Pd ALD cycles in both Na- and Li-O₂ cells is also presented in Figures 5.23 and 5.24 for comparison. The advanced catalytic performance of Gr/NCNT/MnO/Pd originates from two basic characteristics of the electrode: (1) high surface area of mesoporous structured Mn₃O₄ and (2) bifunctional and synergistic catalytic activity of Mn₃O₄/Pd toward ORR and OER. The high surface area of the Mn₃O₄ provides an increased number of reaction sites for oxygen molecules during the ORR. Surface defects and hydroxyl functional groups on the surface of the metal oxide aid in facilitating oxygen adsorption onto the air electrode. Therefore, Mn₃O₄ serves as an ORR catalyst by reducing the activation energy.
of the reaction as well as improving mass transfer kinetics at the electrode surface. In addition, the mesoporous structure of Mn₃O₄ is ideal for accommodating the discharge products of Na- and Li-O₂ cell. Furthermore, Pd nanoclusters on the surface of Mn₃O₄ improves the charge transfer at the electrode/product interface.

Figure 5.23: The cycling performance of Gr/NCNT/Pd and Gr/NCNT/MnO/Pd electrodes with various cycles of Pd deposition by ALD in Na-O₂ cell.
The cycling performance of the cells is obviously improved with increased number of Pd ALD cycles for Gr/NCNT electrode. The improved cycle life of the cells can be attributed to the enhanced charge transfer at Pd/NCNT interface as well as shielding effect of Pd nanoparticles over the carbon surface to prevent carbonate formation. In addition, both Na- and Li-O₂ cells exhibit 100 consecutive discharge and charge cycles using Gr/NCNT/MnO electrode, probably due to the high surface area mesoporous structure of the electrode. The high surface area electrode decreases the thickness of the discharge products on the air...
electrode surface and decreases the charging overpotential of the cell by improving the charge and mass transfer through the discharge product layer. In addition, the charging overpotential of the cells decreases with increased number of Pd ALD cycles for both Gr/NCNT and Gr/NCNT/MnO electrodes which is likely due to the enhanced charge transfer at Pd/air electrode interface.

In order to explore the mechanism behind the electrocatalytic activity in alkali metal-O₂ peroxide cells, the discharge product of Na-O₂ cells on various electrodes was examined using XAS technique. XAS provides both selectivity and sensitivity toward multiple metal oxide phases that may be present in the discharge product of Na-O₂ cells.¹⁰ The normalized O K-edge XANES spectra for the various discharged electrodes were recorded using surface sensitive total electron yield (TEY) as well as bulk sensitive fluorescence yield (FLY) modes for both Na- and Li-O₂ cells, as shown in Figure 5.25. A single feature centered at 534 eV for the TEY O K-edge spectra of the discharged electrodes in Na-O₂ cells (Figure 5.25a) is related to the excitation of the 1s electrons to empty 3σ_u (σ*) molecular orbitals of Na₂O₂, indicating the presence of a peroxide discharge product in these cells. In the case of Gr/NCNT/MnO/Pd electrode, however, a feature at 530 eV is present which can be related to the excitation of 1s electrons to a semi-filled 1π_g (π*) molecular orbitals of superoxide molecules.¹⁰ The second feature at 534 eV is related to the 1s-σ* transition in superoxide compounds which may overlap with σ* orbitals present in peroxide. Nevertheless, the small energy difference between σ* molecular orbitals of superoxide and peroxide phases cannot be distinguished here. A similar conclusion can also be obtained from the FLY spectra obtained for discharged electrodes (Figure 5.25b). However, a small feature at 530 eV is present in the Gr/NCNT/MnO spectra, indicating the presence of a superoxide phase at the bulk of product on the Mn₃O₄ surface. For Li-O₂ cells, both peroxide and superoxide peaks can be observed at relatively lower energies. However, an increased amount of superoxide phase was detected on the surface of Gr/NCNT/MnO electrode (Figure 5.25c and d).

Formation of superoxide products on Gr/NCNT/MnO/Pd electrode is in agreement with the low overpotential observed during the charge cycle of Na- and Li-O₂ cells (Figure 5.19a and b). Accordingly, the electrocatalytic activity of Pd nanoclusters on Mn₃O₄ can be
correlated to the strong oxygen bonding present at the catalyst surface.\textsuperscript{50} Pd nanoclusters not only facilitate the reduction of \( O_2 \) to \( O_2^- \), but also aid in stabilizing superoxide radicals. The \( O_2^- \) ion then combines with \( Na^+ \) or \( Li^+ \) to form adsorbed \( NaO_2 \) or \( LiO_2 \) films as a discharge product of the cells. Conversion of discharge product of peroxide \( Li-O_2 \) cells into an oxygen-rich superoxide phase on catalyst surface has also been reported recently.\textsuperscript{4}

![Normalized O K-edge XANES spectra of the discharged electrodes on Gr/NCNT, Gr/NCNT/MnO, Gr/NCNT/Pd-150C and Gr/NCNT/MnO/Pd-150C electrodes recorded under the both surface sensitive TEY (a and c) and bulk sensitive FLY (b and d) modes for both Na- (a and b) and Li-O_2 (c and d) cells.](image)

**Figure 5.25:** Normalized O K-edge XANES spectra of the discharged electrodes on Gr/NCNT, Gr/NCNT/MnO, Gr/NCNT/Pd-150C and Gr/NCNT/MnO/Pd-150C electrodes recorded under both surface sensitive TEY (a and c) and bulk sensitive FLY (b and d) modes for both Na- (a and b) and Li-O_2 (c and d) cells. To confirm the proposed role of catalysts in alkali metal-O_2 cells, the Gr/NCNT/MnO/Pd electrode was also examined by XAS during the first electrochemical discharge/charge cycle in Na-O_2 cell. Normalized Mn and Pd K-edge XANES spectra of Gr/NCNT/MnO/Pd electrode at the end of the 1\(^{st}\) discharge and 1\(^{st}\) discharge and charge cycle in a Na-O_2 cell is compared with those of pristine electrodes in Figure 5.26a and b. The Mn K-edge XANES spectra of the electrodes demonstrate a positive shift following cell discharge,
Illustrating partial oxidation of Mn$_3$O$_4$ during the discharge process. At the same time, Pd K-edge XANES spectra exhibit a slight negative shift with cell discharge. This likely stems from electron reception from adsorbed O$_2^-$ ions on the Pd surface.

Figure 5.26: Normalized Mn (a) and Pd (b) K-edge XANES spectra of Gr/NCNT/MnO/Pd-150C electrode at the end of 1st discharge and 1st discharge and charge cycle in a Na-O$_2$ cell

Following the initial discharge/charge cycle, a reverse trend can be seen to some extent in which Pd exhibits a slight positive shift compared to the discharged electrode, while Mn$_3$O$_4$ is slightly reduced. The reverse trend of oxidation/reduction is observed for Mn$_3$O$_4$ and Pd during discharge/charge cycling, confirming mutual electron exchange occurring between two species. During the discharge cycle, electrons are shuttled between the Mn 3d orbitals and the Pd 4d orbitals to reduce oxygen at the electrode surface. As a result, Mn is partially oxidized at the end of discharge cycle while Pd is slightly reduced. Reverse migration of
electron density takes place during the charging process, resulting in partial oxidation of Pd and reduction of Mn at the end of charge. Such an electron transfer between Mn$_3$O$_4$ and Pd nanoclusters explains the synergetic effect observed in the catalytic activity of the electrodes.

To further confirm the electron exchange between Mn$_3$O$_4$ and Pd nanoclusters, the Pd K-edge XANES spectra of Gr/NCNT/Pd control electrode was also recorded at the end of the 1st discharge and 1st discharge/charge cycle in a Na-O$_2$ cell (Figure 5.27). Gr/NCNT/Pd electrode demonstrates a similar absorption edge at different discharge and charge cycles, suggesting that electron exchange is not occurring between the Pd nanoparticles and the carbon surface. However, Pd nanoparticles on NCNT exhibit a structural change in EXAFS spectra, probably due to the adsorption of oxygen onto the Pd surface.

![Figure 5.27: The Pd K-edge XANES spectra of Gr/NCNT/Pd electrode before 1st discharge, after 1st discharge and after 1st discharge/charge cycle.](image)

Pd K-edge XANES spectra of Gr/NCNT/MnO/Pd electrodes before and after 100 discharge/charge cycles in Na-O$_2$ cell (terminated after charge cycle) are depicted in Figure 5.28a. The cycled electrode displays a very close Pd absorption edge before and after cycling in the cell. However, the R-space analysis of EXAFS spectra (Figure 5.28b)
illustrates that the relative intensity of the Pd-O over Pd-Pd peak is increases with cycling (see also Figure 5.16b). The structural parameters of Pd following multiple charge/discharge cycles in Na-O_2 cell were also obtained by fitting the experimental data (Figure 5.29) and are compared with data obtained for pristine Gr/NCNT/MnO/Pd electrode in Table 5.3. The fitting results indicate that the Pd-O coordination number increases following cell cycling. The increase in the Pd-O coordination number with cycling indicates that Pd nanoclusters are interacting with the discharge products of the cell during discharge and charge cycles. The results also confirm the dynamic role of solid state catalyst in the electrochemical reaction of Na-O_2 cell.

Figure 5.28: (a) normalized Pd K-edge XANES spectra of Gr/NCNT/MnO/Pd-150C electrode before and after 100 discharge/charge cycles in Na-O_2 cell (terminated after charge cycle); (b) Fourier transform K^3-weighted EXAFS spectra of Gr/NCNT/MnO/Pd-150C electrode before and after 100 discharge/charge cycles in Na-O_2 cell.
Figure 5.29: Fourier transform signal $\chi(R)$ of the experimental (circles) and calculated (solid line) Pd K-edge EXAFS $\chi(k)$ for Gr/NCNT/MnO/Pd electrode before and after 100 cycles in a Na-O$_2$ cell.

Table 5.3: The structural parameters obtained from curve fitting depicted in Figure 5.29.

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<th>Pd-O Coordination</th>
<th>Pd-Pd Debye-Waller factor ($\text{Å}^2$)</th>
<th>Pd-O Debye-Waller factor ($\text{Å}^2$)</th>
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<tr>
<td>Gr/NCNT/MnO/Pd</td>
<td>3.581</td>
<td>2.188</td>
<td>7.52$\times10^{-3}$</td>
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<tr>
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<td>2.385</td>
<td>6.51$\times10^{-3}$</td>
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Morphology of the discharge products in alkali metal-O$_2$ cells has also been used to derive information pertaining to the mechanism of electro/chemical reactions occurring within cells.$^{51-53}$ Discharge product morphology in Li- and Na-O$_2$ cells using various air electrodes following discharge to 1.0 mAh cm$^{-2}$ are shown in Figure 5.30 and 5.31, respectively. The products formed in Li-O$_2$ cells using Gr/NCNT electrode are observed to be composed of toroidal particles with a diameter of 1 $\mu$m. A similar morphology can be seen for Gr/NCNT/Pd electrode. However, the diameter of the toroid particles found on this electrode are on the order of 100 nm. Gr/NCNT/MnO and Gr/NCNT/MnO/Pd electrodes, however, display a formation of a very uniform, amorphous product, being formed within the mesopores of the electrode.

Figure 5.30: Morphology of the discharge products in Li-O$_2$ cell using various air electrodes after discharge to 1.0 mAh cm$^{-2}$ under a current density of 0.2 mA cm$^{-2}$. 

188
Similar amorphous phase products were also observed for Na-O$_2$ cells using air electrodes composed of Gr/NCNT/MnO and Gr/NCNT/MnO/Pd (Figure 5.31).

![Figure 5.31: Morphology of the discharge products in Na-O$_2$ cell using various air electrodes after discharge to 1.0 mAh cm$^2$ under a current density of 0.2 mA cm$^2$.](image)

Two distinct growth mechanisms have been proposed for the formation of Li$_2$O$_2$ in Li-O$_2$ cells. On one side, the surface-mediated electrochemical mechanism forms a conformal surface coating with a thicknesses dictated by charge transport through the product film.$^{53}$ On the other side, the solution-mediated growth mechanism involves partial solvation of O$_2^-$ in non-aqueous electrolytes and produces micron-sized Li$_2$O$_2$ toroids.$^{4,52,53}$ The latter growth mechanism is also suggested to be responsible for formation of cubic NaO$_2$ discharge product in Na-O$_2$ cells.$^{13,54}$ Direct observation of product growth on various
electrode surfaces here indicates that the growth mechanism is switched from a solution-mediated one for NCNTs to a surface-mediated mechanism for Mn$_3$O$_4$ and/or Pd surfaces. The increased active surface area given by Mn$_3$O$_4$ greatly increases the nucleation sites available for ORR. In addition, elevated oxygen bonding toward the surface of Mn$_3$O$_4$ and Pd contributes to stabilize the $\text{O}_2^-$ intermediate and decreases its solubility into the electrolyte. As a result, the morphology of the discharge products changes from micron-sized toroids on NCNT to a conformal film on Mn$_3$O$_4$ and Pd surfaces. The observed changes in the morphology of the discharge products are in precise accordance with the transformation in the chemical composition of the products in Li- and Na-O$_2$ cells.

The presented spectroscopic data provides insightful evidence toward the mechanism governing the electrocatalytic activity of solid-state catalysts in alkali metal-O$_2$ cells. The catalytic activity during ORR mainly involves the ability of the catalyst surface to absorb molecular oxygen and reduce the activation energy required for ORR. In the case of Gr/NCNT/MnO/Pd electrode employed in this study, Pd nanoclusters deposited on high surface area mesoporous Mn$_3$O$_4$ provides a strong interaction between the active surface and molecular oxygen and therefore facilitates the reduction reaction by forming a chemisorbed oxygen layer. However, atomically deposited Pd nanoparticles on the NCNT substrate does not show a significant ORR activity. The increased ORR catalytic activity observed for Pd on Mn$_3$O$_4$ originates from both structural and electronic configurations. The relatively uniform surface of Mn$_3$O$_4$ results in the formation of planar Pd nanoclusters with high surface area, providing an increased number of active reaction sites. XAS results demonstrated that the Pd nanoclusters formed on the Mn$_3$O$_4$ surface contains a few atomic layers of Pd located in the vicinity of oxygen rich environments. In addition, O K-edge XANES results confirmed the interaction of O 2p with both Mn 3d and Pd 4d orbitals. Thus, the formation of planar Pd nanoclusters on mesoporous Mn$_3$O$_4$ enables the electron exchange between d orbitals of Pd and Mn$_3$O$_4$. As a result, the electron density in Pd 4d orbitals decreases due to the O 2p bridging effect between Mn 3d and Pd 4d orbitals. The reduced electron density in Pd 4d orbitals facilitates the chemisorption of molecular oxygen onto Pd surface. Accordingly, the synergetic effect seen between Pd and Mn$_3$O$_4$ can also be correlated to the electron exchange between these metallic d orbitals. The catalytic
mediated discharge/charge reaction mechanism in Na- and Li-O₂ cells is schematically outlined in Figure 5.32.

![Figure 5.32: Schematic diagram of catalytic mediated discharge and charge reaction mechanisms on Mn₃O₄/Pd surface.](image)

The OER catalytic activity, however, relies on the ability of the catalyst to stabilize the superoxide intermediate. XAS examination of the discharge product in Na-O₂ cell using Gr/NCNT/MnO/Pd air electrode revealed that the product of the cell is mainly composed of superoxide compounds. However, the product formed in the cells using Gr/NCNT and Gr/NCNT/Pd air electrodes was mainly peroxide phase. In addition, a significant transformation in the morphology of discharge products was also observed alongside the corresponding changes in the chemical composition of the products on various electrode surfaces. The observed changes in the growth mechanism of the products are also in agreement with the increase of oxygen bonding availability of the electrode surfaces from NCNT to Mn₃O₄ and Pd. Therefore, changes in chemical composition as well as morphology of the discharge products are both contributing factors in reducing the charge overpotential of alkali-metal cells. Recent studies have demonstrated that trace amounts of electrolyte additives such as water, may act as an electrochemical mediator and enhance the discharge capacity of alkali metal-O₂ cells. However, these soluble additives may also impose destructive influences to the cyclability of cells by reacting with the discharge...
products and increasing the occurrence of non-Faradaic side-reactions. Employing solid state catalysts with the capability of stabilizing superoxide discharge products eliminates the side effects of soluble additives, while maintaining the advantages of superoxide cells.
References


Effect of solvent donor number (DN) on the chemical composition of discharge products of Na-O₂ cell is investigated in this study. Electrochemical discharge/charge curves of Na-O₂ cell using electrolytes with different DN showed lower charging overpotential for electrolytes with higher DN. Synchrotron based X-ray absorption spectroscopy (XAS) was employed to analyze the discharge product of the cells using different electrolytes. Higher content of NaO₂ was found in the discharge product of cells using solvents with higher DN. In addition, effect of air electrode surface on the morphology of discharge products was also studied using carbonaceous air electrodes with different hydrophobic and hydrophilic surfaces. We show that the air electrode surface has a significant influence on the morphology of discharge products in Na-O₂ cells. Two distinct growth mechanisms, i.e. solution-mediated and surface-mediated, are responsible to form crystalline and film-like products on hydrophobic and hydrophilic electrode surfaces, respectively.
6.1 Introduction

The stability of the electrolyte is one of the most severe challenges facing the development of Na-O$_2$ batteries even on the research scale. Such a desired electrolyte should tolerate the highly oxidative environment of Na-O$_2$ cell for a long cycling life and enable the cell to form and decompose the discharge products of the cell reversibly. It is well recognized that the electrolyte not only affects the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) mechanisms, but also the chemical composition of discharge products and reversibility of the cell.  

As it was mentioned in introduction section, the influence of the electrolyte solvent on the ORR mechanism in non-aqueous Li-O$_2$ cells was first studied by Abraham et al. The solvents employed in this study were chosen to cover a range of donor numbers (DN), which is a quantitative measure of the Lewis basicity of cations. Interestingly, it was found that electrolyte solvents with larger DN may influence the ORR kinetics in the presence of Li$^+$ by stabilizing the O$_2^-$ intermediate and hindering it from further reduction. Based on the HSAB theory, the Li$^+$-solvent bond strength increases with the solvent’s DN. As a result, the formed Li$^+$-(solvent)$_n$ complex in high-DN solvents acts as a moderately soft acid, resulting in a more effective interaction with the moderately soft O$_2^-$ ion. On the other side, the Li$^+$-(solvent)$_n$ complex in low-DN solvents behaves as a hard acid due to the weak Li$^+$-solvent bond, making a more effective interaction with O$_2^{2-}$ ion which is a hard base. Consequently, high-DN solvents may stabilize the superoxide ion via making stronger Lewis acid-base complexes, while low-DN solvents facilitate the chemical or electrochemical reduction of O$_2^-$ to O$_2^{2-}$ ion.

Similar results were also reported by Bruce et al. The electrochemical response of oxygen showed a strong dependency on the solvent’s DN in the presence of Li$^+$ ions. Two reaction mechanisms have been proposed based on the different electrochemical responses for the ORR in low- and high-DN solvents. In low-DN solvents, according to the authors, the produced LiO$_2$ adsorbs on the electrode surface where it quickly disproportionates to Li$_2$O$_2$. In high-DN solvents, however, LiO$_2$ initially dissolves into the electrolyte and then disproportionates to Li$_2$O$_2$ via a currently undefined process. Furthermore, high-DN solvents demonstrate a considerable increased discharge capacity compared to low-DN
solvents. Higher discharge capacity in high-DN solvents has been correlated to the Li$_2$O$_2$ growth from the solution in contrast to its formation on the electrode surface in low-DN solvents.

In this study, we investigate the role of solvent DN on the chemical composition and charging overpotential of Na-O$_2$ cells. It is expected that solvent DN shows a bigger influence on composition of discharge products and hence charging overpotential of Na-O$_2$ compared to Li-O$_2$ cell due to the higher stability of sodium superoxide phase. The electrochemical behavior of the Na-O$_2$ cell was recorded using three different electrolytes with various DN. In addition, the chemical composition and morphology of the discharge products were also monitored. The obtained results indicated that more sodium superoxide are produced during the discharge cycle of the cell using electrolytes with higher DN. Furthermore, the effect of hydrophilicity of the carbonaceous electrode surface on the product morphology and electrochemical response of the Na-O$_2$ cell was studied too.

6.2 Experimental

6.2.1 Preparation of the air electrode

Commercial plain carbon cloth (CC) gas diffusion layer was employed as the air electrode in this study. Plain CC which provides a hydrophobic surface was also oxidized in a 0.2 mg/ml of KMnO$_4$ solution to increase the hydrophilicity of the surface. The treated CC was then washed with water and ethanol and then dried in a vacuum oven overnight before being used in Na-O$_2$ cells.

6.2.2 Physical characterizations

Morphological studies were performed by Hitachi S-4800 field-emission scanning electron microscope (SEM) operated at 10 kV, respectively. X-Ray diffractograms were obtained using a Bruker D8 Advance (Cu-K$_\alpha$ source, 40 kV, 40 mA). For the XRD measurements, the Na-O$_2$ cells were dissembled in the Ar-filled glove box after testing and the positive electrode materials were placed into an air-sensitive XRD sample holder. XAS measurements were obtained at the Canadian Light Source (CLS) on the spherical grating
monochromator (SGM) beamline. The air electrodes of Na-O\textsubscript{2} cells were washed with the same solvent that was used for preparing the electrolyte. Afterward, the electrodes were dried and sealed inside the glove box and then moved to the analysis place, where the samples were opened in the second glove box and directly introduced to the XAS vacuum chamber. The samples were kept under pure argon atmosphere before the analytical measurements, without any exposure to the atmospheric air. The vacuum during the XAS experiments was around 10\textsuperscript{-8} Torr.

### 6.2.3 Electrochemical Measurements

Swagelok type cells comprised of sodium foil anode, Celgard 3500 separator (5/8 inches in diameter), different air electrode and a stainless steel mesh as current collector were used to carry out electrochemical measurements. The air electrodes were cut into circular pieces (3/8 inches in diameter) with the geometric surface area of 0.71 cm\textsuperscript{2}. A fresh sodium foil was prepared with the aid of a homemade press machine using the sodium metal stick (from Aldrich) as starting sodium metal and cut into circular pieces (3/8 inches in diameter) inside the argon-filled glove box. The electrolytes used in this study was 0.5 M sodium triflate (NaSO\textsubscript{3}CF\textsubscript{3} 98%, Aldrich) dissolved in triethylene glycol dimethyl ether (TEGDME, reagent grade 99%, Aldrich); diethylene glycol diethyl ether (DEGDME, reagent grade \(\geq 98\%\), Aldrich) and 1-Methylimidazole (MeIm, reagent grade 99%, Aldrich). Sodium triflate electrolyte salt was dried at 80°C under vacuum for 48 hours and the water content of the solvents was removed using molecular sieves for at least 10 days. The amount of electrolyte in the cell was \(\sim 200 \mu l\). The assembled Na-O\textsubscript{2} cells were placed into a homemade testing box inside the glove box and then transferred to the testing room. The argon content of testing box was moderately vacuumed out and then pure oxygen (purity 4.3) purged into the box. The pressure of testing box was kept at 1.0 atm during the electrochemical tests. Discharge/charge characteristics were performed using an Arbin BT-2000 battery station at room temperature (25 °C). All the cells were discharged and charged under the constant current density of 0.1 mA cm\textsuperscript{-2}.
6.3 Results and discussion

Figure 6.1 demonstrate full discharge curves of Na-O₂ cells using a plain CC air electrode with different electrolytes. The cells were discharged to the cut-off potential of 1.8 V vs. Na/Na⁺. Na-O₂ cell using TEGDME electrolyte shows the lowest discharge capacity, while the capacity in the case of MeIm is the highest. The observed trend in the discharge capacity of the cells is in accordance with the increase of DN from TEGDME (16.6) to DEGDME (24) and MeIm (47).

![Figure 6.1: Full discharge curves of Na-O₂ cells using plain CC air electrode with different electrolytes.](image)

Limited discharge and charge cycles of Na-O₂ cell using a plain CC air electrode with different electrolytes are shown in Figure 6.2. Multiple charge plateaus can be distinguished during the charge cycle of the cells. As we discussed in chapters 3 and 4, the low potential charge plateau can be correlated to the decomposition of NaO₂ phase, while the higher potential plateaus are related to decomposition of Na₂O₂ and/or carbonate side-products. As can be seen in Figure 6.2, the charge capacity related to the low potential plateau increases with increase of solvent DN. Such an increase in the capacity of low
potential charge plateau suggests that the superoxide content in the discharge product of the cell increases with increasing the solvent DN.

![Figure 6.2: Limited discharge and charge cycles of Na-O₂ cell using a plain CC air electrode with different electrolytes.](image)

In order to determine the composition of discharge products of Na-O₂ cell with different electrolytes, the discharge air electrodes were examined with XRD. The resulted diffractograms are depicted in Figure 6.3. No obvious peak was detected in the case of TEGDME which is probably related to the amorphous nature of the products. Most of the detected peaks in the XRD spectrum of discharged air electrode using DEGDME can be related to Na₂O₂ phase. In addition, a weak peak around 32.3° is related to NaO₂ phase. In the case of MeIm electrolyte however, both NaO₂ and Na₂O₂ phases were detected with comparable quantities. The XRD results are in good agreements with electrochemical response of the cells shown in Figure 6.2, confirming the increase of NaO₂ content in the discharge products along with increase of solvent DN.
Figure 6.3: XRD pattern of discharged air electrodes in Na-O₂ cells using different electrolyte with various DN.

To further confirm the increase of NaO₂ content with increase of solvent DN, the discharge products was also analyzed with synchrotron XAS. As we showed earlier in chapter 4, XAS exhibits both selectivity and sensitivity toward the various sodium oxide phases presented in the discharge product of the cell. The normalized O K-edge XANES spectra of discharged air electrode in Na-O₂ cells using different electrolytes are depicted in Figure 6.4. All discharged electrodes exhibit a feature around 534 eV in the O K-edge XANES spectra relating to the excitation of the 1s electrons to empty 3σ_u (σ*) molecular orbital of Na₂O₂. However, a weak feature around 532 eV appears in the spectra of discharged electrode using DEGDME. The intensity of this feature, which is related to the excitation of the 1s electrons to a semifilled 1π_g (π*) molecular orbitals of superoxide molecules, increases in the case of MeIm electrolyte. The XAS data confirms that the NaO₂ content of the discharge product increases with increase of solvent DN.
The air electrode of Na-O₂ cells with different electrolytes were also examined by XAS after cycling to determine the relative stability of the electrolytes. Normalized O K-edge XANES spectra of the air electrodes after cycling along with a standard Na₂CO₃ sample are shown in Figure 6.5. As can be concluded from XANES spectra, all the air electrodes show a feature similar to standard Na₂CO₃ sample, indicating the formation of carbonate based side products in Na-O₂ cell. These results are in agreement with recent findings toward instability of ether based electrolytes in Na-O₂ cells. The electrochemical results combined with XRD and XAS suggest that solvent DN has a strong influence on choosing the reaction path toward forming NaO₂ or Na₂O₂. Solvents with higher DN can stabilize the superoxide intermediate and hence increase the sodium superoxide content in the discharge products. On the other side, low thermodynamic stability of superoxide intermediate in low DN solvents results in conversion of superoxide intermediate into more thermodynamically preferred peroxide ion.
The air electrode surface may also play an important role on the electrochemical reaction mechanism of Na-O₂ cells. To determine the influence of air electrode surface in Na-O₂ cells, two types of air electrodes with hydrophobic and hydrophilic surfaces were prepared. Commercial plain carbon cloth (CC) was used as the air electrode with hydrophobic surface. A piece of CC was oxidized in an acidic permanganate solution to make the electrode surface hydrophilic. Oxidation of the carbon cloth surface provide carboxyl (COOH) and/or hydroxyl (OH) functional groups which can form hydrogen bonds with water molecules and make the surface hydrophilic. The electrochemical behavior as well as the morphology of the discharge products in Na-O₂ cells using these two air electrodes were studied.

Figure 6.6 shows the full discharge curves of both the hydrophilic and hydrophobic air electrodes in Na-O₂ cells to a cut-off potential of 1.6 V vs. Na/Na⁺. The hydrophobic air electrode displays a flat discharge plateau, while the discharge voltage of hydrophilic air electrode gradually decreases to the cut-off value. In addition, the discharge capacity of
Na-O$_2$ cell using the hydrophobic air electrode is more than twice time higher than that of with hydrophilic air electrode.

![Discharge curves of Na-O$_2$ cells using DEGDME electrolyte and CC air electrode with different hydrophobic and hydrophilic surfaces.](image)

Figure 6.6: Discharge curves of Na-O$_2$ cells using DEGDME electrolyte and CC air electrode with different hydrophobic and hydrophilic surfaces.

The morphology of discharge product of Na-O$_2$ cells using DEGDME electrolyte and CC air electrodes with different hydrophobic and hydrophilic surfaces were inspected using SEM. The SEM micrographs with different magnifications of the discharged air electrodes are displayed in Figure 6.7. An obvious difference can be observed in the morphology of discharge products on different surfaces. A crystalline discharge products are formed on the hydrophobic electrode surface. In addition, the carbonaceous electrode surface seems to be still accessible. On the hydrophilic electrode surface, however, a very uniform film-like discharge product covers the whole electrode surface. Direct observation of the product formation on different electrode surfaces reveals that the mechanism of product formation is strongly dependent on the surface properties of the air electrode. Similar results were also observed using MeIm electrolyte which is displayed in Figure 6.8.
Figure 6.7: Morphology of the discharge product of Na-O$_2$ cells using DEGDME electrolyte and CC air electrodes with different hydrophobic and hydrophilic surfaces.
As we discussed in chapter 5, two distinct growth mechanisms have been proposed for the formation of discharge products in alkali metal-O$_2$ cells. On one side, the surface-mediated electrochemical mechanism forms a conformal surface coating with a thicknesses dictated by charge transport through the product film. On the other side, the solution-mediated growth mechanism involves partial solvation of O$_2^-$ in non-aqueous electrolytes and produces micron-sized products.\textsuperscript{6,7} Direct observation of the discharge products on different electrode surfaces indicates that a solution-mediated growth mechanism is responsible for the formation of crystalline product on the hydrophobic electrode surface, while a surface-mediated growth mechanism is occurring on the hydrophilic electrode surface.
surface. This conclusion is in good agreement with the electrochemical discharge profile observed for both electrodes. Larger discharge capacity was observed for the hydrophobic electrode surface, since a solution-mediated growth mechanism results in formation of larger discharge products. In addition, produced crystalline products do not block the air electrode surface for mass and electron transfer, leading to larger discharge capacities. On the other side, a surface-mediated growth mechanism on the hydrophilic surfaces results in formation of film-like products which gradually block the electrode surface and limits the discharge capacity. Furthermore, gradual reduction of the discharge voltage in the case of hydrophilic electrode surface is likely due to the increased mass and/or charge transfer resistance imposed by discharge products.

Electrochemical discharge/charge curves of Na-O₂ cells using DEGDME electrolyte and CC air electrodes with hydrophobic and hydrophilic surfaces limited to a discharge capacity of 0.1 mAh cm⁻² are shown in Figure 6.9. The Na-O₂ cell using hydrophobic air electrode exhibits lower charging overpotential compared with the hydrophilic electrode. Higher charging overpotential in the case of hydrophilic air electrode is likely due to the increased mass/charge transfer resistance at the electrode/electrolyte surface as a result of film-like discharge product.

![Electrochemical discharge/charge curves of Na-O₂ cells using DEGDME electrolyte and CC air electrodes with hydrophobic and hydrophilic surfaces.](image)

Figure 6.9: Electrochemical discharge/charge curves of Na-O₂ cells using DEGDME electrolyte and CC air electrodes with hydrophobic and hydrophilic surfaces.
6.4 Conclusion

Effect of solvent DN as well as surface properties of air electrode on the composition and morphology of discharge products in Na-O$_2$ cells were studied in this chapter. Three different electrolytes covering a wide range of DN were examined in Na-O$_2$ cells. Electrochemical discharge/charge curves displayed an increasing trend for low potential charging plateau with increase of solvent DN. XAS analysis of the discharge products indicated a direct correlation between NaO$_2$ content of the cell products with solvent DN. However, formation of carbonate side-products was shown to limit the cycleability of Na-O$_2$ cell using all examined electrolytes. Studying the effect of air electrode surface on the morphology of the discharge products in Na-O$_2$ cells revealed that hydrophobic surfaces lead to formation of crystalline discharge products. However, hydrophilic air electrodes alter the growth mechanism to a surface-mediated one, resulting in formation of film-like discharge products. These results help to understand the effective parameters for controlling the morphology and composition of discharge products in Na-O$_2$ cells. More studies are needed to fully understand the chemistry of Na-O$_2$ cells.
References


Chapter 7

7 Conclusion and future remarks

7.1 Summary of the results

A series of studies were conducted aiming to better understand the electrochemical mechanism governing on Na-O\textsubscript{2} and Li-O\textsubscript{2} cells. Various air electrode architectures were designed and synthesized in this regard and the correlation between the electrode architecture and the cell performance was studied in detail. Multiple synthesis strategies were employed to synthesize the desired air electrodes and several analytical techniques were applied to study the underlying electrochemical mechanism. The results described in this thesis can be divided into two major subcategories: i) materials synthesis and characterization; ii) electrochemical mechanism studies.

In the first part, the correlation between the surface area and pore size of the air electrode materials with its electrochemical behavior in Na-O\textsubscript{2} cells was studied. We used a specifically designed electrode materials in this study. The electrode materials employed here were prepared using a heat-treatment procedure under various corrosive atmospheres (such as NH\textsubscript{3} and CO\textsubscript{2}) using non-precious carbon black as starting materials. Heat-treatment of carbon black enables a precise control over the surface area and porosity of the air electrode material. The heat-treated carbon materials allowed us to understand correlations between discharge capacity, surface area and porosity of the cathode materials. Heat-treatment of carbon black removed disordered carbon, resulting in a highly porous structure. Micropore boundaries grew with increasing treatment time and eventually resulted in the formation of mesopores. Then the synthesized carbon materials with different surface area and pore-size distribution was used as the air electrode of Na-air cell. It was found that discharge capacity in Na-air cell is linearly correlated with mesoporous surface area while morphology of the solid discharge product is strongly dependent on specific surface area and pore size. As a results, the discharge capacity of Na-air cells can
be increased by increasing the surface area of the air electrode materials via increasing the porosity of the electrode. These findings help us to design and develop more efficient air electrodes for Na-air cells which consequently leads to improved Na-air batteries.

Kinetics and rechargeability of Na-air cells were also studied using a variety of analytical techniques including XRD, Raman, FTIR and XPS. The results indicated that both sodium peroxide and superoxide are produced during discharge cycles of the cell and decomposed at different charge steps. In addition, the formation of a deficient phase sodium peroxide (Na$_{2-x}$O$_2$, 0 < x < 1) was shown to be likely. We also found that the cells discharged at different current densities exhibited different charge profiles accompanied by a different chemical composition for the discharge product. In other words, by increasing the discharge rate, more superoxide phase was found in the discharge products of the cell. These results indicated that the chemical composition as well as the charge overpotential of Na-air cells can be controlled by kinetic parameters of the cell such as discharge current density.

In the second part, a binder-free three-dimensional (3D) nano-structured air electrode composed of vertically grown nitrogen doped carbon nanotubes on carbon paper (NCNT-CP) was designed and developed for Na-O$_2$ cells. The 3D architecture of the air electrode resulted in increased discharge capacity by optimizing the utilized area of the electrode material. The chemical and electrochemical reaction mechanisms of the cell were also explored with the use of synchrotron-based X-ray absorption spectroscopy (XAS). Investigation of the discharge product of Na-O$_2$ cells during discharge and charge cycles using X-ray absorption near-edge structure (XANES) indicates that both sodium superoxide and peroxide are produced under various physicochemical conditions and can be subsequently decomposed with different overpotentials. Furthermore, formation of carbonate-based parasitic products is also shown to restrict the cyclability of the cell.

Based on the results from previous parts, the desired air electrode of Na- and Li-O$_2$ batteries was defined as a 3D structured electrode with high mesoporous surface area without direct carbon/discharge products interface. Therefore, in third part of this study, an air electrode composed of a light-weight carbonaceous framework mounted with mesoporous
manganese oxide as both the carbon protective layer and the ORR catalyst was designed. Then, palladium nanoclusters were deposited on the manganese oxide layer as OER catalyst. Electrochemical investigations demonstrated a synergetic effect between mesoporous Mn$_3$O$_4$ and Pd nanoclusters toward reducing charging overpotential in both Na- and Li-O$_2$ cells. The prepared air electrode showed more than 100 consecutive discharge/charge cycles with low charging overpotential. In order to understand the origin of the synergetic effect, the electronic state of Mn and Pd species during discharge and charge cycles of Na-O$_2$ cell was monitored using synchrotron based hard X-ray absorption technique. A dynamic charge transfer was observed between Mn and Pd during discharge and charge cycle of the cell. Accordingly, the observed synergetic effect between Mn$_3$O$_4$ and Pd was correlated to the ability of charge transfer between Mn 3d and Pd 4d orbitals through the O 3p bridging orbitals. Furthermore, higher content of superoxide was found in the discharge products of both cells, revealing the role of solid state catalyst in reducing the charging overpotential of the cells via stabilizing the superoxide intermediate. The results of this study highlight the correlation between the ability of solid state catalyst for oxygen bonding with its electrocatalytic activity.

In the final part of this thesis, the effect of oxygen-containing functional groups at the carbon surface on the morphology and composition of the discharge products in Na-O$_2$ cells was studied. The initial results revealed that the presence of oxygen-containing functional groups may results in formation of film-like discharge products via a surface mediated mechanism. While on a hydrophobic carbon surface, the discharge products are formed as crystalline products through a solution mediated mechanism. In addition, chemical composition of the products as well as charging overpotential of the cell were shown to be affected by the properties of carbon surface. The results of this study may explain the inconsistency seen between reported results on composition of discharge products of Na-O$_2$ batteries by different research groups. More systematic studies are ongoing for this part to fully understand the role of functional groups in the control of composition and morphology of discharge products in alkali metal-O$_2$ cells.

The results presented in this thesis provide an extensive understanding towards the electrochemical reaction mechanism of Na-O$_2$ cells. In addition, the air electrode designs
developed in this thesis can be practically employed in order to increase the discharge capacity and cycling performance of alkali metal-O\textsubscript{2} cells. Furthermore, the mechanism studies on the role of solid state catalysts in alkali metal-O\textsubscript{2} cells will help other researchers to develop more effective catalyst systems. It is expected that these results positively contribute to develop alkali metal-O\textsubscript{2} cells with higher energy efficiency and longer cycle life.

7.2 Future perspective

Na-O\textsubscript{2} battery system has been developed as an alternative high energy density storage system with potential application in electric transportation. State of the art studies on Na-O\textsubscript{2} cell brought a great deal of promises to achieve a high energy efficient battery system due to lower charging overpotential of Na-O\textsubscript{2} compared to Li-O\textsubscript{2} cell. However, there are also several challenges that should be addressed to further develop a long-life Na-O\textsubscript{2} rechargeable battery system.

Chemical composition of the discharge product in Na-O\textsubscript{2} cell is shown to be highly dependent on physicochemical conditions of the cell. Controlling the chemical composition of the Na-O\textsubscript{2} cell products is critically important, since the charging overpotential of the cell is dependent on the type of sodium oxides formed during the discharge cycle. Chemical composition of the Na-O\textsubscript{2} cell products can be manipulated by controlling the kinetic parameters of the cell. Reviewing the key studies on the Na- and Li-O\textsubscript{2} battery systems reveals that an oxygen-rich metal oxide phase may be produced by discharging the cells under a deficient oxygen condition. Higher discharge current density along with a high surface area air electrode and lower oxygen partial pressure is one route toward forming oxygen-rich metal oxide phases as the discharge products of Na- and Li-O\textsubscript{2} cells. In addition, finding a high-DN solvent with a relatively low HOMO level and a high pK\textsubscript{a} is proven to be beneficial for Na-O\textsubscript{2} cells in terms of stabilizing the highly oxidative oxygen-rich discharge products produced in the cell. Further, recent studies on the cell chemistry revealed that Na-O\textsubscript{2} cells undergo less parasitic reactions compared to Li-O\textsubscript{2}. Nevertheless, formation and accumulation of parasitic side products as a result of
decomposition of the electrolyte by highly oxidative discharge products in the cell still limits cycle life. Besides, sodium metal negative electrode and sodium oxide discharge product are more sensitive against trace amounts of moisture and carbon dioxide in the cell environment compared to the lithium counterparts which add more complexity to the cell design. Meanwhile, the critical role of proton in the reversibility of Na-O₂ batteries makes the precise control on the concentration of water or other proton donor in electrolyte even more challenging.

Morphology of the discharge products is another critical factor which can also be controlled by kinetics. Higher discharge current density and lower oxygen concentration in the electrochemical active sites may result in higher local overpotential during the discharge reaction. Higher local overpotential makes more nucleation sites energetically accessible and will result in amorphous as well as smaller particle size of the discharge products. More studies on the role of kinetics in alkali metal-O₂ cells are needed in order to truly understand the relation between the morphology of discharge products with kinetic parameters of the cell.

At the time of writing this thesis, the cycling performance of Na-O₂ cells is still generally poor, which can be attributed to a number of reasons including electrolyte decomposition. On one side, the cell with Na₂O₂ as the discharge product suffers from high charging overpotential, similar to Li-O₂ cells. On the other side, the dissolving/precipitation mechanism of crystal growth in the case of NaO₂ results in the formation of micron-sized insulating cubes which may remain partially undecomposed following consecutive cycles. Future efforts on Na-O₂ cell should be conducted toward controlling the composition and morphology of the discharge product. The charging overpotential of the cell can be managed by preventing electro/chemical conversion of NaO₂ to Na₂O₂. Meanwhile, precise control over the nucleation and particle size of NaO₂ product may also be achieved by manipulating the kinetic parameters of the cell.
Curriculum Vitae

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EDUCATION

**PhD** in Mechanical and Materials Engineering  
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**BSc** in Chemistry  
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EXPERIENCE

Research Experiences

**Western University**  
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*PhD researcher*

- Illustrated the mechanism of catalytic activity in Na- and Li-O$_2$ cells using synchrotron based soft and hard X-ray absorption spectroscopy.
- Designed and developed a hierarchical 3D electro-catalyst based on atomically deposited Pd on mesoporous Mn$_3$O$_4$ mounted on 3D NCNT/graphene foam substrate for Na- and Li-O$_2$ cells, characterized and explored its electrochemical behavior.
- Designed and developed a hierarchical 3D air electrode for Na-O$_2$ cells, characterized the air electrode using variety of techniques such as SEM, TEM, BET, TGA and XRD.
- Used synchrotron-based soft X-ray absorption spectroscopy to study the reaction mechanism of Na-O$_2$ cells on cathode electrode.
- Studied the electro/chemical reaction mechanism of Na-O$_2$ cells using various analytical techniques including SEM, XRD, XPS, FTIR and Raman.
K. N. Toosi University     (Sep 2008 – Jun 2012)

PhD researcher

- Developed LiCoO$_2$ nanoparticles and LiV$_3$O$_8$ nanosheets as cathode and anode electrode materials of aqueous Li-ion batteries and determined detailed electrochemical behavior using cyclic voltammetry (CV), chronoamperometry (CA), chronopotentiometry (CP) and electrochemical impedance spectroscopy (EIS).
- Designed and developed poly(ortho-phenylenediamine)/graphene and poly(ortho-aminophenol)/graphene nanocomposites for supercapacitor applications (synthesis, characterization and electrochemical responses).
- Employed various electrochemical and analytical techniques to characterize the synthesized electrode materials.

K. N. Toosi University     (Sep 2005 – May 2007)

MSc researcher

- Developed nanoflakes of the cobaltous oxide for electrocatalysis applications such as methanol oxidation.
- Designed and developed sensors and actuators based on carbon nanotubes (CNT)-modified electrodes for electroanalysis of various medicines and biological compounds.
- Carbon nanotubes (CNT); Nitrogen doped carbon nanotubes (NCNT); Graphene; Tungsten oxide nanowires; Tungsten carbide nanowires; Tin oxide nanowires; Mesoporous Mn$_3$O$_4$, Electrochemical deposition of transition metal oxide

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