Electrochemical and Surface Compositional Studies on Uranium Dioxide

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Graduate Program in Chemistry  
A thesis submitted in partial fulfillment of the requirements for the degree in Doctor of Philosophy  
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(Thesis format: Integrated Article)

by

Mayuri Razdan

Graduate Program in Chemistry

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy

The School of Graduate and Postdoctoral Studies
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THE UNIVERSITY OF WESTERN ONTARIO
ABSTRACT

This thesis describes electrochemical and surface compositional studies performed on a number of simulated nuclear fuel (SIMFUEL) materials under conditions relevant to permanent disposal of spent nuclear fuel in a geologic repository. This is important since a number of critical issues have been identified in the event of waste container failure. The research performed was mainly focused in three areas: (i) the influence of low pH on the surface chemistry of UO₂, since acidity could develop within corrosion product deposits and flaws in the fuel; (ii) the combined influence of dissolved H₂ and H₂O₂ (H₂ and H₂O₂ are key reducing and oxidizing agents) in the presence of HCO₃⁻/ CO₃²⁻ (the key ground water species) on the fuel corrosion process (iii) the influence of rare earth (RE³⁺) fission product doping on the fuel corrosion process (since matrix doping process with RE³⁺ influences the fuel bulk properties, it is expected to influence both anodic and cathodic kinetics under natural corrosion conditions).

The influence of H₂O₂ on 1.5 at% SIMFUEL in acidic (pH 1-4) conditions was studied voltammetrically using a rotating disk electrode (RDE), X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) to determine the composition and morphology of the oxidized UO₂ surface. The H₂O₂ reduction mechanism is shown to occur on either a U⁵⁺-containing surface layer of composition U⁴⁺₁₋₂ₓU⁵⁺₂ₓO₂⁺ₓ or on an adsorbed U⁵⁺ surface intermediate, depending on the surface composition which is determined by solution pH and H₂O₂ concentration. The U⁴⁺₁₋₂ₓU⁵⁺₂ₓO₂⁺ₓ catalytic surface lattice layer, if formed is more stable and supports H₂O₂ reduction up to the diffusion-controlled limit. By contrast, the U⁵⁺ adsorbed surface
intermediate is unstable which prevents significant H\textsubscript{2}O\textsubscript{2} reduction. The simultaneous occurrence of both reduction mechanisms demonstrates the influence of locally established surface compositions and the switch from one to the other appears to be controlled by the diffusive transport conditions at the electrode surface.

In addition to H\textsubscript{2}O\textsubscript{2}, the influence of the dominant reducing species, H\textsubscript{2}, anticipated inside a failed waste container was investigated at different [H\textsubscript{2}O\textsubscript{2}] in the presence of the key ground water species (HCO\textsubscript{3}⁻/CO\textsubscript{3}²⁻). Their combined influence on the redox behavior of UO\textsubscript{2} was followed using open circuit corrosion potential measurements (E\textsubscript{CORR}), cathodic stripping voltammetry (CSV) and XPS. The presence of HCO\textsubscript{3}⁻/CO\textsubscript{3}²⁻ in solution inhibits UO\textsubscript{2} oxidation at lower [H\textsubscript{2}O\textsubscript{2}]. The influence of dissolved H\textsubscript{2} in suppressing surface oxidation under ambient conditions depends primarily on chemically added [H\textsubscript{2}O\textsubscript{2}] and was evident in the presence of carbonate for H\textsubscript{2}O\textsubscript{2} concentrations \(\leq 10^{-5}\) mol L\textsuperscript{-1}.

A second goal of the thesis was to study the effect of fission products (metallic particles and rare earth (RE\textsuperscript{3+})) on UO\textsubscript{2} oxidation. These studies were conducted on 0.3 wt% Yttrium-doped UO\textsubscript{2} (Y-UO\textsubscript{2}), 6 wt% Gadolinium doped UO\textsubscript{2} (Gd-UO\textsubscript{2}), 12.9 wt% Dysprosium doped UO\textsubscript{2} (Dy-UO\textsubscript{2}) and 1 wt% Palladium-doped UO\textsubscript{2} (Pd-UO\textsubscript{2}) electrodes. The electrodes were characterized using Raman Spectroscopy and SEM/EDX and their anodic oxidation studied electrochemically and by XPS.

Voltammetric experiments on Y-doped UO\textsubscript{2} electrodes containing noble metal particles showed the presence of a current at sub-thermodynamic potentials consistent with a lattice containing a mixture of stoichiometric and non-stoichiometric domains. Their presence was verified by Raman and XPS analyses. Electrochemical investigations
on homogeneously RE\textsuperscript{III} doped electrodes demonstrated a clear doping influence on both stages of the anodic oxidation process; i.e., on the initial matrix oxidization step (UO\textsubscript{2} \rightarrow UO\textsubscript{2+x}) and on its further oxidation to soluble U\textsuperscript{VI} (as UO\textsubscript{2}\textsuperscript{2+}). Doping appears to influence the kinetics of the second step more than that of first step. Raman spectroscopy shows that an increase in doping level leads to the formation of RE\textsuperscript{III}-Oxygen vacancy (O\textsubscript{V}) clusters which decreases the number of the O\textsubscript{V} sites required for oxidation.

The influence of carbonate/bicarbonate (the key groundwater constituents likely to influence fuel dissolution) on the electrochemical oxidation process of RE-doped UO\textsubscript{2} (Gd-UO\textsubscript{2}) was examined using CV, potentiostatic polarization and XPS. While CV scans show that carbonate has a significant catalytic effect on the oxidative dissolution of UO\textsubscript{2}, a stable surface layer (UO\textsubscript{2+x}) is present irrespective of carbonate concentration. Potentiostatic experiments in the potential range -0.5 to 0.5V also show that the oxidation/dissolution currents are increased in the presence of carbonate. XPS analyses showed the electrode to be free of U\textsuperscript{VI} species. This indicates that the slow step in the overall anodic dissolution process is the electrochemical formation of U\textsuperscript{VI} not its chemical dissolution.

\textbf{Keywords:} Uranium dioxide, Hydrogen peroxide, Reduction mechanism, Corrosion potentials, Hydrogen, Rare earth, Defects
This thesis includes published data (Chapter 4). For the published results I was the experimental investigator and writer.
ACKNOWLEDGEMENTS

First and foremost, I would like to express my deep and sincere gratitude to my advisor Professor David Shoesmith whose expertise and understanding added considerably to my graduate experience. His open-door policy and willingness to discuss on any matter was invaluable to me. He patiently provided the encouragement and advice necessary for me to proceed through the doctoral program and complete my dissertation. I am grateful to him for carefully reading and commenting on countless revisions of this thesis.

Besides my advisor, I am thankful to the rest of my thesis committee members, Dr. Zhifeng Ding, Dr. Keith Griffiths, Dr. Michael Freund and Dr. Denis O'Carroll for their time and co-operation.

Special thanks to Dr. Mark Biesenger from Surface Science Western (SSW) for providing training and assistance on a surface analytical instrument used in this research, which helped me collecting worth of data. I would also like to thank Ms. Heather Bloomfield, Mr. Brad Kobe and Ms. Mary Jane Walzak from SSW for assistance with other analytical instruments when needed.

I appreciate and extend my thanks to Dr. Jiju Joseph for helping me in conducting hydrogen peroxide analysis in the Radiolysis laboratory at Western.

I would also like to thank my fellow lab-mates, both past and present at Western for making my graduate school experience memorable.

A huge thank to my husband, Ajit. His constant support, practical advice and optimism has helped to keep me going.
Most importantly, I wish to thank my parents for their endless support and encouragement in all aspects of my life. I know that I would not have made it this far without their support. This thesis is dedicated to them.
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SYMBOLS AND ACRONYMS

Ag Silver
Am Americium
Ar Argon
Ba Barium
Ce Cerium
Cu Copper
Dy Dysprosium
Gd Gadolinium
H₂ Hydrogen
Hg Mercury
La Lanthanum
Mo Molybdenum
Nd Neodymium
Np Neptunium
Pt Platinum
Pu Plutonium
Rh Rhodium
Ru Ruthenium
Pd Palladium
Sr Strontium
Tc Technetium
Th Thorium
U Uranium
Y Yttrium
Zr Zirconium
α Alpha
β Beta
γ Gamma
h Planks Constant (m² kg s⁻¹)
<table>
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<tbody>
<tr>
<td>$\nu$</td>
<td>Frequency (Hz or s$^{-1}$)</td>
</tr>
<tr>
<td>$O', O''$</td>
<td>Oxygen Interstitials</td>
</tr>
<tr>
<td>$O_h$</td>
<td>Octahedral</td>
</tr>
<tr>
<td>CuSO$_4$</td>
<td>Copper Sulfate</td>
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<td>SHE</td>
<td>Standard Hydrogen Electrode</td>
</tr>
<tr>
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Chapter 1

Introduction

1.1. Project Background

Nuclear power represents a low-cost, clean and safe form of energy generation and many countries rely on electricity produced from this resource. However, with the use of nuclear power, comes the responsibility for dealing with radioactive waste disposal. The main form of high level nuclear waste available for disposal in Canada is the used fuel bundle discharged from reactor [1]. These bundles which consist mainly of uranium dioxide (UO$_2$) need to be disposed in a way which safeguards human health and minimizes the impact on the environment.

A deep geological repository is one of the approaches being considered for long-term management of nuclear fuel waste in Canada [2]. In this approach, the engineered repository would be a network of horizontal tunnels and emplacement rooms constructed 500 m to 1000 m deep in the stable crystalline rock of the Canadian Shield (Fig. 1.1). Used nuclear fuel in the form of CANDU (CANada Deuterium Uranium) fuel bundles would be sealed in a steel vessel with a corrosion resistant copper shell, surrounded by a compacted buffer material i.e. bentonite clay which swells as it comes in contact with water to fill any spaces or gaps retarding water migration around container. Each room from access tunnels would be sealed with clay/crushed rock backfill material. Copper is chosen as a container material due to its thermodynamic stability when exposed to the
anoxic environment, anticipated in the repository, while the steel provides strength and rigidity.

Figure 1.1 Illustration of the deep geological repository concept showing the container, emplacement room, and tunnel layout. Image source: www.curriculum.cna.ca

While the prospects for containment with waste containers are good, exposure of the used fuel to ground water in the event of failure would have a significant impact on the safety assessment of the repository [3]. Since, the majority of the radionuclides in used fuel (UO₂) are located within the oxide grains, their release rate to the environment would be dictated by the fuel corrosion/dissolution rate. Therefore, it is important to
investigate the surface reactivity of the UO$_2$ in order to understand fuel dissolution mechanisms and to determine its ability to retain individual radionuclides. The most important parameter in determining the fuel corrosion rate is the redox condition inside a failed waste container. The solubility of UO$_2$ is extremely limited under reducing conditions, but increases greatly under oxidizing conditions as shown in Fig. 1.2 [4].

![Figure 1.2 Solubility of uranium dioxide (UO$_2$) and schoepite (UO$_3$.2H$_2$O) as a function of pH at 25°C[4]](image)

**Figure 1.2** Solubility of uranium dioxide (UO$_2$) and schoepite (UO$_3$.2H$_2$O) as a function of pH at 25°C[4]
Generally, reducing conditions can be expected under granitic conditions (in repositories under consideration in Canada, Sweden, and Finland) in a nuclear waste repository, since environmental oxidants (i.e. dissolved O\textsubscript{2} trapped in the porous sealing materials) will be relatively rapidly consumed by waste container (Cu) corrosion and mineral/biochemical oxidation processes in the clay and backfill materials. Therefore, the major source of oxidants to drive fuel corrosion will be water radiolysis.

Figure 1.3 shows the alpha, beta, gamma dose rates calculated at the surface of a fuel bundle of average burn-up. The gamma and beta radiation fields decay markedly over the first 500 years: however, alpha radiation fields will remain significant for periods of $\sim 10^5$ years [5].

**Figure 1.3** Alpha, beta, and gamma radiation dose rates with respect to time for water in contact with a CANDU fuel bundle with a burn up of 721 GJ kg\textsuperscript{-1} U [5]
Hence, if the container fails, the UO$_2$ surfaces could be subject to an oxidizing environment for long periods of time. Radiolytic decomposition of water will generate various oxidants (e.g. O$_2$, O$_2^-$, OH and H$_2$O$_2$) near the surface of the fuel. Since the only source of water is the groundwater, the onset of fuel corrosion will be determined by the performance of the waste container. Canadian waste containers are expected to survive until radiation fields can no longer produce significant oxidizing conditions [6, 7]. However, safety assessments conservatively assume that some containers will be emplaced with undetected defects and the possibility of failure exists. So, it is judicious to assume that containment will not be perfect and that some containers will fail before alpha radiation fields become insignificant. Therefore, considerable effort has been devoted to understanding the influence of alpha radiolysis on the corrosion of UO$_2$ [8-11] and a number of models have been proposed to predict its influence on radionuclide release [12-17].

1.2 UO$_2$ Fuel Composition

1.2.1 Spent Fuel

The fuel (used in CANDU power plants) is fabricated using un-enriched UO$_2$ (\(^{235}\)U = 0.71 \%) by sintering pressed compacts pellets of fine-grained powders at ~1700 °C in a reducing atmosphere [18]. The fuel density is upto 92-99% of the theoretical value (10.96 g cm\(^{-3}\)), with grain sizes of 2-15 \(\mu\)m and an O/M ratio close to stoichiometric (~ 2.001) [3]. These pellets are sealed inside zirconium-tin (Zircaloy-4) tubes; about 0.5 m long, and arranged in a circular array 10 cm in fuel bundles (Fig. 1.4).
This fuel assembly weighs 23.9 kg, of which 21.7 kg is UO$_2$ and 2.2 kg is Zircaloy [19]. The typical burnup range for CANDU fuel is $\sim$ 120 to 320 MWh kg$^{-1}$ U, and a reference value of 220 MWh kg$^{-1}$ U has been used for repository studies.

Figure 1.4 Schematic illustrating the key changes induced by in-reactor fission showing the three general categories of radionuclides [1]

Unlike new unirradiated fuel bundles, spent fuel contains a variety of fission products and actinides ($\sim$2% by mass) created due to in-reactor irradiation. These fission products differ widely in their compatibilities with the fluorite structure of UO$_2$ due to their physical/chemical properties and are grouped into three general categories [20].
(1) Some fission products have very limited solubility in the lattice (e.g; $^{85}$Kr, $^4$He, $^{39}$Ar, $^{99}$Tc, $^{129}$I, $^{14}$C, $^{135}$Cs, $^{125}$Sn, $^{79}$Se) and are volatile at reactor operating temperatures, and migrate to the fuel/sheath gap during reactor operation.

(2) Other fission products are non-volatile and migrate to grain boundaries, and reside in fission gas bubbles, or separate into solid phases such as perovskites ((Ba, Sr)ZrO$_3$) and metallic alloy phases (ε-particles: Mo, Ru, Rh, Pd, Tc).

(3) The majority of fission products and actinides/lanthanides (e.g; $^{238}$Pu, $^{241}$Am and $^{239}$Np) are retained within the UO$_2$ fuel matrix.

**1.2.2 SIMFUEL**

SIMFUEL is a chemically simulated fuel, produced by doping the UO$_2$ lattice with up to 11 non-radioactive elements (Ba, Ce, La, Nd, Sr, Y, Zr, Mo, Pd, Rh, Ru) in order to mimic the chemical effects caused by in-reactor irradiation of CANDU nuclear fuel [21, 22]. SIMFUELs are ideal for laboratory experiments, since it simulates key fuel properties without the associated radiation levels. The microstructure of SIMFUEL is virtually identical to that of typical CANDU fuel pellets with grain sizes of the order 8-15 µm and a density greater than 95% of the theoretical value. Small, spherical (0.5-1.5 µm in diameter) metallic alloy particles are dispersed uniformly throughout the matrix with an average composition of 28 at. % Mo, 47 at. % Ru, 3 at. % Rh and 22 at. % Pd as obtained from EDX/WDX analyses [21]. Perovskite (Ba, Sr)ZrO$_3$ phases (~0.1 µm) are also present as submicron particles on grain boundaries and the additives Y, Ce, Nd, La and Zr are dissolved in the UO$_2$ grains.
The SIMFUEL used in this study replicates spent nuclear fuel with a 1.5 at. % burnup (a little low for typical used CANDU fuel). To investigate the effects of dopant concentration for simulated fuels containing 0.1 wt% Y, 1 wt% Pd, 6.0 wt% Gd or 12.9 wt% Dy were also investigated.

1.3 Fuel Properties

1.3.1 Structural Properties

$\text{UO}_2$ is isostructural with other actinide dioxides with a fluorite crystal structure ($\text{CaF}_2$). The unit cell parameter $a = 5.470 \, \text{Å}$, and the ionic radii are $r_{\text{U}^{4+}} = 0.97 \, \text{Å}$ and $r_{\text{O}^{2-}} = 1.40 \, \text{Å}$ [18]. Figure 1.5 shows a $\text{UO}_2$ lattice, with a U atom in each unit cell coordinated to eight neighboring O atoms. This structure is very flexible and capable of generating derivatives due to its ability to accommodate additional O atoms on cubically coordinated interstitial sites without significant distortion. Oxidation of $\text{UO}_2$ to $\text{UO}_{2+x}$ proceeds by the injection of $\text{O}^{2-}$ at interstitial sites followed by oxidation of $\text{U}^{IV}$ to $\text{U}^{V}$ to maintain overall electroneutrality. The fluorite structure can accommodate oxide ions up to a limiting composition of $\text{UO}_{2.33}$ which has a tetragonally distorted fluorite structure [23]. Further oxidation would require structural rearrangement from the fluorite to a more open, layer-like configuration [24, 25].
Neutron diffraction and X-ray photoelectron spectroscopic studies have shown that when UO$_2$ is extensively oxidized (UO$_{2.13}$ to UO$_{2.25}$), the interstitial sites become displaced [23, 25, 27-31]. Oxygen occupies a newly identified interstitial positions, termed O’ and O”, displaced from the cubically coordinated sites by ~ 1 Å in the (110) and (111) directions with no apparent effect on the U sublattice. Figure 1.6 shows the positions of these interstitial sites in relation to the main UO$_2$ lattice. The occupation numbers of the O’ and O” sites, as well as the O vacancies are approximately the same, and this structure is termed a 2:2:2 cluster.
Figure 1.6 Illustration showing the 2:2:2 cluster in UO$_{2+x}$, with relation to the parent fluorite lattice [25]

It has been claimed that the configuration of the defect complex in UO$_{2.13}$, is a 2:2:2 cluster which contains two O' atoms, two O vacancies and two O" atoms. As the O content increases to U$_4$O$_9$ (UO$_{2.25}$), an alternative 4:3:2 cluster, (Fig. 1.7) was proposed comprised of four O' atoms, three O vacancies and two O" atoms [32]. At this oxygen content the fluorite lattice is distorted with an increase in density.
1.3.2 Electrical Properties

Uranium dioxide can be considered as a Mott-Hubbard insulator [33-37], due to its partly filled cationic shell, which has a sufficiently narrow energy bandwidth that the mobility of the electrons is restricted by their mutual Coulomb interaction. However, electronic conductivity can still result by a small polaron hopping activated process, in which the normally localized electrons can be transferred from one cation to the next by a series of thermally assisted jumps.
Figure 1.8 shows a schematic energy level diagram for UO$_2$ where a narrow U 5f band, containing 2 electrons per U atom lies in the gap between the filled valence band and the empty conduction band. The valence band consists predominantly of O 2p states, with some contribution from U 6d and 5f orbitals (filled U 5f level). The conduction band is a mixture of overlapping U 7s, 6d and 5f states (empty U 5f level). The respective

Figure 1.8 Band structure diagram for UO$_2$, and its relationship to important energy scales (from electrochemical and spectroscopic data) [38]
occupied and unoccupied U 5f levels are termed as the lower and upper Hubbard bands. For stoichiometric UO₂, electronic conductivity requires promotion of an electron from the lower to the upper Hubbard band, a process with a low probability at room temperature ($E_A \sim 1.1$ eV) [37]. However, fabricated UO₂ pellets possess a slight excess of O present as interstitial O²⁻ ions, and charge balance is maintained by ionization of U⁴⁺ ions to the U⁵⁺ and/or U⁶⁺ valence state [33, 35, 39, 40]. This oxidation process creates holes in the occupied U 5f Hubbard band, which then migrate by the polaron hopping mechanism with a lower activation energy of $\sim 0.2$ eV [33, 35, 39, 40]. Thus, hyperstoichiometric UO₂ can be treated as a p-type semiconductor which is able to conduct an electric current for electrochemical reactions occurring at its surface [41]. While SIMFUEL is expected to be very close to stoichiometric, its conductivity is enhanced by the RE⁢⁺⁺ dopants in the UO₂ matrix.

1.3.3 Thermodynamic Properties

The predominant soluble uranium species as a function of potential and pH for a solution with uranium concentration of $10^{-9}$ mol L⁻¹ are shown in Fig. 1.9, demonstrating, rich aqueous electrochemistry of UO₂. Though a range of U oxide phases are thermodynamically possible within the water stability region, only UO₂ and U₄O₉ are stable. At this U concentration ($10^{-9}$ mol L⁻¹), which is close to the solubility of UO₂ in neutral solutions, U₄O₉ would be thermodynamically stable on the surface of UO₂ over the pH range $6 \leq$ pH $\leq 9$. As dissolved U concentration increases this stability range expands to cover the range $5 \leq$ pH $\leq 10.5$, Fig. 1.10. For the pH (8 to 10) conditions
expected within a geological disposal site, UO₂ would be highly insoluble as U⁴⁺ (Fig. 1.2). However, in oxidizing conditions its solubility would increase by many orders of magnitudes, and UO₂²⁺ (soluble form of U⁴⁺) would be the dominant soluble form for pH ≤ 6 [4, 42-44].

![Potential-pH diagram for the uranium/water system at T 25°C. Uranium concentration is 10⁻⁹ mol L⁻¹ [44]](image)

**Figure 1.9** Potential-pH diagram for the uranium/water system at T 25°C. Uranium concentration is 10⁻⁹ mol L⁻¹ [44]

Both these ions UO₂²⁺ and U⁴⁺ are extensively hydrolyzed in aqueous solutions to form species such as Uₓ(OH)ₙ⁺ for U⁴⁺ at pH > 1, and (UO₂)ₓ(OH)ᵧ⁻ for UO₂²⁺ at pH > 4 [4, 42, 44]. Stabilization of these soluble U species can be achieved in aqueous solution by complexation with a wide variety of organic and inorganic anions, such as
Cl⁻, SO₄²⁻, HPO₄²⁻ and HCO₃⁻/CO₃²⁻ [4, 42-45]. Complexation constants for these ions indicate that the solubility of UO₂²⁺ increases significantly when carbonate and phosphate anions are present, while the solubility of U⁴⁺ is influenced much less by these species, and would remain preferentially hydrolyzed [45].

**Figure 1.10** Isosolubility lines for the uranium/water system with various uranium concentrations, at 25°C [44]

### 1.4 Redox Chemistry of Uranium Dioxide

Figure 1.11 shows the composition of a UO₂ surface as a function of surface redox condition (expressed as a corrosion potential, E_{CORR}). The range of corrosion potentials
predicted by the Mixed Potential Model (described in the subsequent section) is indicated by an arrow A. The association between composition and potential shown in this figure has been determined by a combination of electrochemical and surface analytical experiments (voltammetry, photothermal deflection spectroscopy, photocurrent spectroscopy, and X-ray photoelectron spectroscopy) [3, 46]. The vertical dashed line shown at -0.4 V (vs. SCE), represents the threshold for the onset of fuel corrosion.

**Figure 1.1** Composition and corrosion behavior of UO₂ as a function of the UO₂ corrosion potential [3, 46]

For potentials greater than the threshold value fuel corrosion occurs at a rate controlled by the concentration of radiolytically produced oxidants and below this threshold, radionuclides can only be released by chemical dissolution of the fuel. Since
the solubility of UO$_2$ in the groundwater conditions (in a deep geological repository) is extremely low ~ $10^{-9}$ mol·L$^{-1}$ (Fig. 1.2) [47-49], the only mechanism for significant release of radionuclides is via corrosion. Figure 1.11 also shows the potential ranges for the important electrochemical surface oxidation and dissolution processes on UO$_2$.

The corrosion of the fuel can be influenced by factors which affect the redox conditions developed at the fuel surface. In an anaerobic environment, the steel liner will corrode on contact with groundwater. Therefore, two corrosion fronts exist within a failed waste container, one at the spent fuel surface and the other at the steel surface. The essential electrochemical reactions expected within a failed waste container are illustrated in Fig. 1.12.

Figure 1.12 Illustration of possible electrochemical/chemical interactions within a failed copper nuclear waste container
The difference in corrosion potential, which is the driving force between these two fronts, can be 0.9 V. Local oxidizing conditions at the fuel surface leading to corrosion will be maintained due to the α-radiolysis of water producing H2O2 and O2. Radiolytic oxidants produced in the near-field within ~ 25 μm of the fuel surface, will actively drive the corrosion/dissolution of the UO2 surface. Among the several oxidants produced, H2O2 is considered the most likely to cause fuel corrosion and the potential effects of this oxidant have been studied in detail [2, 3, 12, 50-56]. H2O2 reduction on UO2 surfaces occurs via a coupled chemical-electrochemical process in which UIV–UV donor–acceptor sites are first chemically created on the UO2 surface by H2O2 and subsequently destroyed electrochemically,

\begin{align*}
2\text{U}^{IV} + \text{H}_2\text{O}_2 & \rightarrow 2\text{U}^{V} + 2\text{OH}^- \\
2\text{U}^{V} + 2e^- & \rightarrow 2\text{U}^{IV}
\end{align*}

(1.1)

(1.2)

Under natural corrosion conditions, reaction (1.2) is coupled to the oxidation and dissolution of UO2 as UO22+

\begin{align*}
\text{UO}_2 & \rightarrow \text{UO}_2^{2+} + 2e^- \\
\text{H}_2\text{O}_2 & \rightarrow \text{O}_2 + 2\text{H}^+ + 2e^- \\
\text{Fe} + 2\text{H}_2\text{O} & \rightarrow \text{Fe}^{2+} + 2\text{OH}^- + \text{H}_2 \\
3\text{Fe} + 4\text{H}_2\text{O} & \rightarrow \text{Fe}_3\text{O}_4 + \text{H}_2
\end{align*}

(1.3)

(1.4)

(1.5)

(1.6)
The low concentration of Fe$^{2+}$ produced is expected to have only a small influence on preventing oxidation of the UO$_2$ surface via reaction with radiolytic H$_2$O$_2$ oxygen [16]. However, in sealed repositories, hydrogen gas generation may result in significant pressures, leading to dissolved hydrogen concentrations in the range of $10^{-2}$ to $10^{-1}$ mol.L$^{-1}$ [57]. Experimental studies have shown that the H$_2$ produced by the corrosion of steel scavenges the H$_2$O$_2$ generated by $\alpha$-radiolysis of water at the fuel surface and produces H$_2$O. Consequently, H$_2$ is expected to have a significant effect on the corrosion of spent fuel, thereby delaying radionuclide release.

However, redox conditions at the fuel surface are expected to change over the repository lifetime considering many environmental factors like temperature, dissolved O concentration, pH and groundwater species. The composition of the fuel surface should, therefore, evolve with the accumulation of corrosion/dissolution product deposits. This accumulation could have a number of distinct effects: (i) it could block the fuel surface reducing the area exposed to the solution thereby suppressing fuel corrosion; (ii) it could restrict the diffusion of solution species to (e.g. Fe$^{2+}$, H$_2$) and from (e.g., H$_2$O$_2$, UO$_2$(OH)$_y$(2-$y$)$^+$) the reacting surface leading to the accumulation of H$_2$O$_2$ within the pores of the deposits creating local acidity; (iii) it could also trap $\alpha$-emitting radionuclides which would modify the yield and distribution of $\alpha$-radiolysis products.

1.5 Previous Approaches and Modelling----The Mixed Potential Model (MPM)

Presently, a world wide effort is underway to develop performance assessment (PA) models to understand the fuel behavior in a nuclear waste repository. As a part of
this effort, Shoesmith et al developed a Mixed Potential Model (MPM) which is presently used in the Canadian Nuclear Waste Management program to guide experimental programs [58]. A range of different processes are included in this model: adsorption/desorption, precipitation/dissolution, and homogeneous redox reactions involving various species in the groundwater. The model consists of corrosion fronts on the fuel and steel liner surfaces, interconnected by diffusion processes in the groundwater assumed to flood the container on failure.

A number of critical issues were identified and need to be investigated for the development of this, and other, PA models. These include; (i) the reactivity of the fuel surface; (ii) the composition of the fuel surface as a function of redox conditions; (iii) the influence of corrosion product deposits on the fuel surface; (iv) the kinetics of hydrogen peroxide reduction in support of fuel corrosion; (v) the scavenging of radiolytic oxidants (H$_2$O$_2$, O$_2$), and/or the inhibition of their reaction with the fuel, by the products of steel corrosion (Fe$^{2+}$/H$_2$). With these concerns in mind, we have focused our studies on issues such as the influence of corrosion product deposits on the corrosion of fuel surface since this would directly impact the expected radionuclide release. In addition, the effect of rare-earth fission products on the fuel oxidation process and how it is influenced in the presence of carbonate complexing agent (the key groundwater constituent expected to influence fuel dissolution/corrosion process) has been studied.
1.6 Research Goal

The overall goal of this project is to develop the mechanistic understanding required to understand radionuclide release from fuel inside a failed waste container. Thus, the specific goals of this research are:

(1) To study the kinetics of H₂O₂ reduction in low pH conditions, since there is a possibility of forming acidic conditions within surface flaws in the fuel and/or pores in corrosion product deposits. This is important since the dissolution rate of the fuel is very dependent on pH for values ≤ 5.

(2) To determine the influence of rare-earth (RE³⁺) lattice doping on the overall reactivity of UO₂ specimens.

(3) To investigate the effect of trivalent rare earth doping on the electrochemical reactivity of UO₂ in carbonate.

(4) To explore the catalytic effect of H₂ on UO₂ in the presence of H₂O₂ and carbonate
1.7 References


2.1 UO₂ Fuel Corrosion

The expected conditions for the Canadian repository will only be oxidizing for a short period (upto a few hundred years) after it has been sealed. Consequently by the time container failure is predicted to occur, the groundwater entering the container, and contacting the fuel, will be anoxic. Under these conditions, the driving force for fuel dissolution would be proportional to the solubility of UO₂ in the ground water, and its rate of dissolution controlled by the conditions established inside the failed container.

2.1.1 Factors Affecting UO₂ Corrosion/Dissolution

Numerous factors such as water radiolysis (particularly α-radiolysis), pH, temperature, groundwater composition and the fission product content of the fuel could influence its corrosion/dissolution [1-6]. The radiation fields emanating from the fuel surface can produce oxidants. The influence of these on UO₂ corrosion have been reviewed in detail elsewhere [1] and will only be briefly discussed here. Figure 2.1 illustrates some of the key influences expected for UO₂ dissolution.
2.1.1.1 Effect of α-Radiolysis

Alpha radiolysis of water will produce both oxidizing (H₂O₂, O₂) and reducing (H₂) species in equal amounts: however, the overall effect will depend on the relative reactivity of these species in the aqueous environment. Oxygen is a kinetically slower oxidizing agent than H₂O₂, and H₂ is an inert molecular reducing species below 100 °C [7]. Consequently, the effect of α-radiolysis on fuel oxidation/dissolution is expected to be dominated by the production of the molecular oxidant H₂O₂, and its decomposition to O₂ and H₂O.

In recent years, two experimental approaches have been used; chemical and electrochemical, with many studies concentrated on the dissolution/leaching of α-doped UO₂ [8]. Measurements conducted on these materials provide little information on the influence of spent fuel properties like composition and microstructure. In some of these studies, doping levels of upto 5 and 10 % (with ²³³U: 32 and 63 MBq.g⁻¹(UO₂)) did not show any effect on dissolution rates of the fuel in anoxic solutions and an increase in U dissolution was observed only when high α-activity levels were used [9].

Based on such studies on α-doped materials an activity threshold of 18-33 MBq.g⁻¹(UO₂) was proposed for carbonate solution (10⁻³ mol.L⁻¹) under anoxic conditions (O₂ < 0.1 ppm) [10]. However, this threshold value was dependent on environmental conditions and in the presence of H₂ (1 bar) increased to 385 MBq.g⁻¹(UO₂). Wren et al used electrochemical methods to study α-radiation effects (using external α-sources ≥ 250 μCi in activity). They proposed that UO₂ corrosion in the presence of α-radiolysis products is controlled by redox buffering of the fuel surface as a result of H₂O₂
decomposition to $\text{O}_2$ and $\text{H}_2\text{O}$ [11]. For sufficiently low $\alpha$-dose rates, the low rate of production of radiolytic oxidants would be expected to control the overall corrosion rate.

**Figure 2.1** Schematic illustration of the major processes involved at the fuel/water interface in the radiolytic dissolution of spent fuel. First, $\alpha$-radiolysis of water (1) produces oxidants which subsequently oxidize U in the spent nuclear fuel matrix (2). Then, uranium is released to solution aided by complexation through aqueous ligands, and finally (3) the U can re-precipitate on the fuel surface as a secondary phase [12].

King et al. have developed a mixed potential model (MPM) to predict the effects of $\alpha$-radiolysis on fuel dissolution kinetics [13]. Based on the $\alpha$-dose rates of Garisto et al [14] who calculated the $\alpha$-dose rates as a function of radiation decay times from 10 to $10^7$ years after discharge from reactor while assuming that the radionuclides are uniformly distributed within the fuel. Subsequently, Garisto et al [14] updated this calculation and Wu et al [15] implemented these values in a model for the $\alpha$-radiolytic corrosion of spent
fuel (burnup 220 MWh kg.U\(^{-1}\)): Unlike the MPM this model included the influence of H\(_2\) which was found to be the dominant redox controlling agent.

### 2.1.1.2 Effect of β/γ-Radiolysis Products

Since 100-year old spent fuel is not available, it is not possible to avoid β and γ-radiolysis effects in studies conducted on spent fuel and on the corrosion rates derived from such studies. Early experimental work showed high β/γ-radiation field resulted in the generation of powerful radiolytic oxidizing species (OH\(^{●}\), H\(_2\)O\(_2\)) which rapidly oxidize UO\(_2\). The influence of β/γ radiolysis on the corrosion rate of UO\(_2\) in aerated and oxygenated solutions shows a power law dependence of the dissolution rate on the dose rate \([1, 16]\).

Nielsen & Jonsson \([17]\) developed a mathematical model based on the geometrical and energetic properties of radiation and found that within the range of α-dose rates expected, the β contribution to the total dose was very small. This was attributed to the fact that at the fuel/water interface, β/γ-radiation field is not as intense as the alpha field \([18]\). Shoesmith et al. \([1]\) argued against using rates of reaction measured on relatively fresh used fuel for performance assessment calculations, since corrosion tests on fresh spent fuel (less than 30 years out of reactor) overestimate the corrosion rates expected to prevail in the long term. Other authors, who have compared the corrosion rates of unirradiated UO\(_2\) and spent nuclear fuel, have not found any significant difference under air-saturated groundwater conditions \([1, 16, 19]\).
2.1.1.3 Effect of Oxygen

Oxygen-driven UO$_2$ corrosion in aqueous solution has been determined to be a kinetically slow reaction process due to the necessity to break the strong O=O bond. A range of reaction orders have been reported (0.1 to 1) which depend on both the dissolved oxygen concentration and temperature [1, 16, 20]. The reaction was first order at low dissolved O$_2$ concentrations, and lower at higher concentrations, which was attributed to the adsorption of dissolved O$_2$ being the rate-limiting step in the overall corrosion process [1]. This leads to a fractional reaction order as surface coverage varies.

In order to break the strong O-O bond on a UO$_2$ surface, catalysis is required by mixed oxidation states (U$^{IV}$, U$^{V}$) available in the surface of the oxide [21]. These sites work as donor-acceptor sites. This catalysis is based on the theory of Presnov and Trunov [22], who explained the reduction kinetics of O$_2$ on transition metal oxides with p-type semiconductivity. Measured Tafel slopes (180-240 mV), and the variation of this slope with potential, suggest that the kinetics of O$_2$ reduction change with surface composition (i.e., the number of available U$^{IV}$/U$^{V}$ or U$^{V}$/U$^{VI}$ sites) making the reaction sensitive to solution redox conditions [23].

2.1.1.4 Effect of pH

The groundwater anticipated in the proposed Canadian repository is expected to be in the pH range 5-10 [24] making it important to investigate the redox behavior of UO$_2$ in this range. The influence of pH on the corrosion rates of UO$_2$ have been studied
by a number of authors [25-27]. These studies show that the corrosion rate increases with a decrease in pH below ~5 and exhibits a power law dependence (exponent equal to ~0.4) on the [H⁺]. The fractional order indicates that other ionic species may be involved as complexants in the dissolution process. Also, experiments have indicated the absence of an oxidized surface layer (i.e., UO₂⁺ₓ) suggesting the rate of proton-mediated transfer of U⁶⁺ species to solution is too fast to allow incorporation of O²⁻ species into the UO₂ lattice [26]. Figure 1.2 shows that, at these low pH values, the solubility of UO₂²⁺ increases by several orders of magnitude which prevents its precipitation and the blockage of the fuel corrosion process.

There is no significant influence of pH on the rate of dissolution of UO₂ in neutral to alkaline solutions (5 < pH < 10) [1], since in this pH range, the solubility of the U⁶⁺ corrosion product is at a minimum and independent of pH [28, 29].

2.1.1.5 Effect of Groundwater Species

Various ions (HCO₃⁻/CO₃²⁻, PO₄³⁻, Ca²⁺, SiO₄⁴⁻) are common in natural environments and could affect the rate of UO₂ corrosion. The uranyl ion is complexed by carbonate and phosphate over the neutral to alkaline pH range [25, 30]. Kim et al [31] reported that the dissolution rate of U increases with a decrease of pH in carbonate solution. The effect of carbonate concentration on UO₂ dissolution has been discussed by Shoesmith [1]. At low concentrations of carbonate, UO₂²⁺ solubility increases due to its complexation and its deposition on the corroding surface is reduced. For intermediate concentrations (10⁻³ to 10⁻¹ mol.L⁻¹), HCO₃⁻/CO₃²⁻ prevents the formation of the oxygen
rich surface layer (UO$_{2+x}$) on the UO$_2$ surface leading to a further acceleration of dissolution. At high carbonate concentrations, formation of a surface layer of UO$_2$CO$_3$ limits the dissolution rate which becomes less dependent on [CO$_3^{2-}$]. Later, Hossain et al [32] reported a similar influence of carbonate. For [HCO$_3^-$] ≤ 10$^{-3}$ mol.L$^{-1}$, the rate constant for oxidant consumption increases linearly with HCO$_3^-$ concentration and the dissolution reaction is the rate limiting step. When [HCO$_3^-$] > 10$^{-3}$ mol.L$^{-1}$; this rate constant becomes independent of [HCO$_3^-$] and the rate limiting step switches to the surface oxidation step.

Interestingly, phosphate also plays an important role even when present in very small amounts in the aqueous phase [33]. Rey et al [34] reported that the dissolution of UO$_2$ in a phosphate medium (10$^{-6}$ - 10$^{-4}$ mol.L$^{-1}$) occurs faster in the presence of carbonate at similar concentrations. Also, the presence of both phosphate and carbonate in solution restricts the precipitation of any secondary solid phase.

When cations are present in the groundwater, they are not expected to affect the corrosion rate of UO$_2$ directly but may affect the stability and rate of formation of secondary phases formed on the fuel surface. Further, formation of these phases may accelerate or inhibit dissolution. However, it is more likely that they will inhibit the corrosion rate by reducing the transport of oxidant to, or dissolved U from, the oxidized UO$_2$ surface. Calcium and silicate ions were found to reduce the rate of corrosion by forming a layer of stable corrosion products with low solubilities [1, 35]. Electrochemical studies suggest that, while these groundwater species may form thin protective corrosion product films which significantly reduce the rate of the oxidative dissolution, this effect can be counteracted by the presence of carbonate [36, 37].
2.1.1.6 Effect of Dopants in the UO$_2$ Matrix

The composition of the fuel matrix itself can influence the corrosion behavior of the fuel. The effect of dopants on the air oxidation of UO$_2$ has been studied extensively in order to determine the effect of fission-product impurities present in solid solution in used fuel. Their presence was found to enhance the stability of the cubic fluorite structure (U$_4$O$_9$-type structure with respect to U$_3$O$_8$-type) to higher temperatures and higher O/M ratios as compared to undoped UO$_2$ [38-40].

Park and Olander [41], attempted to explain this increase in oxygen potential/stability of the cubic phase on the basis of a RE(III)-doped defect model which included both intrinsic point defects and defect clusters. They explained that as the RE dopant content increased the dopant cations were stabilized by the formation of dopant-oxygen vacancy clusters (O$_V$) clusters. This led to a reduction in availability of the interstitial sites required for fuel oxidation to occur. McEachern speculated that the enhanced stability of the cubic phase (the appearance of a U$_4$O$_9$ intermediate rather than U$_3$O$_7$) for the doped materials was due to the dopants disrupting the defect-cluster ordering assumed to be responsible for the tetragonal distortion of the fluorite lattice. This observation was based on studies on simulated fuel which showed that increasing simulated burn-up stabilizes the cubic instead of tetragonal structure [42]. However, the reasons for the stability of the fluorite phase in doped materials remains unclear.

The phase-relationships between rare-earth-oxides and uranium oxide suggest that the solubility of rare-earth elements in UO$_{2+x}$ decreases with an increase in x and that
these elements are insoluble in the U$_3$O$_8$ phase. However, a kinetically metastable state (rare earth doped U$_3$O$_8$ phase) is possible by oxidation of rare-earth doped UO$_2$ [43].

2.1.2 Surface Composition and the Presence of Deposits

Over the repository lifetime, redox conditions at the fuel surface will be primarily controlled by water radiolysis, and as radiation fields decay, the composition of the fuel surface and, hence, the relative kinetics of fuel corrosion/peroxide decomposition will evolve. It has been shown that the anodic oxidation of UO$_2$ in slightly alkaline solutions occurs in stages [1, 30, 44-50].

\[
\text{UO}_2 \rightarrow \text{UO}_{2+x} \rightarrow (\text{UO}_2^{2+})_{\text{sol}} \rightarrow \text{UO}_3 \cdot y\text{H}_2\text{O}
\] (2.1)

where UO$_3 \cdot y$H$_2$O is a corrosion product deposit on the fuel surface. This oxidation process (reaction 2.1) proceeds through a UO$_{2+x}$ stage containing U$^{V}$, produced when O$^{2-}$ ions are incorporated into interstitial sites in the UO$_2$ fluorite lattice (Fig. 1.5). This process is accompanied by oxidation of U$^{IV}$ atoms in adjacent sites to U$^{V}$ [51-53] to balance the charge due to the excess oxygen. In these studies, XPS was employed to determine the relative amounts of U$^{IV}$, U$^{V}$ and U$^{VI}$ oxidation states in the electrode surface [54]. The creation of a U$^{V}$ state involves the formation of “electron holes” in the U 5f energy level. This lowers the activation energy barrier for U matrix oxidation and could have a considerable effect on the fuel corrosion rate.
Formation of the final corrosion product (UO$_3$·yH$_2$O) is expected to block dissolution sites on the UO$_{2+x}$ surface. For pH < 6 this phase undergoes chemical dissolution (as UO$_2^{2+}$) and the solubility of U and dissolution rate increase significantly with decreasing pH (Fig. 1.2). Literature suggests that, at low pH values, the presence of H$_2$O$_2$ at sufficient concentrations can lead to the formation of uranyl peroxides, such as studtite (UO$_4$·4H$_2$O), a dominant secondary phase over schoepite (UO$_3$·2H$_2$O) [55-61]. Even after the formation of secondary phases, the redox conditions at the fuel surface will change over the repository lifetime, and the composition of the fuel surface is expected to further evolve.

Besides blocking the fuel surface and impeding its corrosion, the corrosion product deposits could also restrict the transport of species to (e.g. Fe$^{2+}$, H$_2$ from corrosion of the steel vessel) and from (e.g., H$_2$O$_2$, UO$_2$(OH)$_{(2-y)^+}$) the reacting surface. Although neutral to slightly alkaline conditions (pH 6–9.5) are expected to prevail under repository conditions, this effect could lead to localized chemistries within pores/flaws in the deposits such as the accumulation of radiolytically-produced H$_2$O$_2$ and/or the development of acidic locations by UO$_2^{2+}$ hydrolysis, reaction 2.2 [11, 62-67],

\[ n\text{UO}_2^{2+} + y\text{H}_2\text{O} \rightarrow (\text{UO}_2)n(\text{OH})_{(2n-2y)^+} + y\text{H}^+ \]  \hspace{1cm} (2.2)

Generally, surface acidification would not be expected since OH$^-$ produced by the cathodic reaction (H$_2$O$_2 + 2\text{e}^- \rightarrow 2\text{OH}^-$) should neutralize most of the H$^+$ produced by UO$_2^{2+}$ hydrolysis. However, the spent fuel surface contains noble metal particles and surface non-homogeneity can create the separation of anodes and cathodes (Fig. 2.2). If
this occurs, experiments on used fuel have shown that the development of acidity could be a possibility [2]. Thus, a complete understanding of long term disposal of spent nuclear fuel requires a knowledge of fuel corrosion under acidic, as well as neutral conditions.

Figure 2.2 Illustrations showing the development of acidity within pores in a corrosion product deposit. The left panel shows that acidity can develop at the anodic dissolution site if it is separated spatially from the cathodic site. The right panel shows that if the two sites are not separated spatially, then the alkalinity produced by H$_2$O$_2$ reduction should be, at least partially, neutralized by the acidity created due to UO$_2^{2+}$ hydrolysis [2].
2.2 Influence of H$_2$ on UO$_2$ (SIMFUEL) Corrosion

The role of H$_2$ has been observed to be very important under radiolysis conditions. Dissolved H$_2$ concentrations from the anaerobic corrosion of iron are expected to reach $10^{-2}$ to $10^{-1}$ mol.L$^{-1}$ in the solution inside a failed container [68] and despite the expectation that H$_2$ will be kinetically hindered at anticipated repository temperatures (< 100ºC), a range of studies have demonstrated that dissolved H$_2$ suppresses UO$_2$ corrosion.

Experiments with spent fuel and alpha-doped UO$_2$ materials have shown that dissolved H$_2$ suppresses the oxidation and dissolution of UO$_2$. Rollin et al [69] conducted leaching studies on spent fuel in the presence of H$_2$ (1 bar, $8\times10^{-4}$ mol.L$^{-1}$), and showed that the concentrations of U and redox-sensitive radionuclides (Pu, Tc, Mo, Np) were significantly decreased and remained very low throughout the leaching period, indicating the absence of any oxidative dissolution (corrosion) of the spent fuel matrix. In their studies the steady-state concentrations of U, Pu, Np and Am were up to four orders of magnitude lower than those measured under oxidizing conditions. This significant decrease in fuel dissolution rate and the release rate of redox sensitive elements was attributed to a catalytic effect of the UO$_2$(s) surface on the reactivity of H$_2$. Other leaching studies on spent fuel (PWR fuel) showed a complete suppression of UO$_2$ dissolution at H$_2$ pressures ($\sim$ 50 bar $\equiv 4.3\times10^{-2}$ mol.L$^{-1}$) which simulate those anticipated under repository conditions [68, 70]. Two possible explanations for the activation of H$_2$ were suggested; either it is activated by the fuel (UO$_2$) surface matrix and/or the metallic particles in the fuel surface, or it is activated by the influence of $\alpha$ /$\beta$ /$\gamma$-radiation fields.
through reactions with radiolytic radicals. However, it was not possible to separate these two possible reactions in experiments on actual spent fuel.

Subsequently, experiments on high-burnup spent fuel (67 GWd/tHM) in the presence of H₂ (10⁻² mol.L⁻¹) also yielded low dissolution rates with dissolved U concentrations as low as 10⁻¹⁰ mol.L⁻¹ [71]. Carbol et al reported similar results on irradiated MOX fuel (47 GWd/tHM) in the presence of H₂ [72]. Even lower U concentrations (10⁻¹² mol.L⁻¹) were measured in corrosion tests conducted on 10 % ²³³U-doped UO₂ (α-doped) [73]. Based on these studies, a H₂ concentration of ~10⁻⁵ mol.L⁻¹ was reported to be the required threshold concentration to completely inhibit corrosion [68].

A tentative explanation for the decreased U concentration in the presence of dissolved H₂ was given by Fors [71] and Carbol et al. [5] (Fig. 2.3). They suggested that a U⁴⁺ atom in the UO₂ surface is oxidized by OH⁺ or H₂O₂ to form a U⁵⁺ site (Fig. 2.3). This site can either be further oxidized to U⁶⁺ by OH⁺, H₂O₂ or O₂, or reduced by H⁺ or H₂. With the carbonate present in the solution, U⁶⁺ would be expected to quickly dissolve but if reduction occurs, the uranium returns to its tetravalent state. If the reduction occurs by reaction with H₂ then an extra reductive species (H⁺) is formed. Since, the amount of dissolved H₂ is large compared to the concentration of oxidants, the reduction of U⁶⁺ sites to U⁴⁺ is much more probable than further oxidation and dissolution. However, no clear explanation of how a U⁴⁺-U⁵⁺ site would activate H₂ to initiate the reduction of U⁵⁺ was offered.
Figure 2.3 A proposed mechanism for the possible reactions between H₂ and potential oxidants on the fuel surface [5, 71]

Later, Nilsson and Jonsson [74] investigated the possible catalytic effects of UO₂ and noble metal particles (Pd) on the reaction between H₂O₂ and H₂. These studies were conducted on UO₂ powders containing 0.1 to 2 wt% of Pd and showed an increase in the rate of the reaction with increasing amounts of Pd. They suggested the possibility that noble metal particles catalyze the reduction of U⁶⁺ to U⁴⁺ by H₂. However, their results did not demonstrate that a UO₂ surface could catalyze the reaction between H₂O₂ and H₂.

The effects of H₂ on the oxidation and dissolution of UO₂ have also been studied using electrochemical methods [75-78]. King et al. [75] performed a series of electrochemical experiments to determine the extent of oxidation on unirradiated UO₂ due to γ-radiolysis in the presence of H₂ (5 MPa) at room temperature. Based on corrosion potential (E₉₉) measurements it was reported that H₂ not only suppressed the oxidation of UO₂(s) by radiolytic oxidants, it also produced more reducing conditions.
than observed when H$_2$ or Ar were present in the absence of radiation. A similar suppression in E$_{\text{CORR}}$ of UO$_2$ by H$_2$ was reported in the absence of radiation [76, 77]. Experiments conducted on SIMFUEL specimens with and without noble metal (ε) particles indicated that these particles acted as catalytic electrodes for H$_2$ oxidation (to H$^+$), and that the galvanic coupling of these particles to the conductive, rare-earth doped UO$_2$ matrix was responsible for the suppression of E$_{\text{CORR}}$ (Fig 2.4) [77].

![Diagram](image)

**Figure 2.4** Schematic of the galvanic coupling between the fuel matrix and noble metal (ε) particles leading to the suppression of fuel corrosion by H$_2$ oxidation [77].

Electrochemical studies [78] on SIMFUEL specimens with different levels of simulated burn-up (1.5, 3 and 6 at. %) have shown that, the extent of oxidation of the fuel surface (determined by XPS) decreases in the order oxic > anoxic > reducing. Under oxic and anoxic conditions neither E$_{\text{CORR}}$ nor the surface composition varied with ε-particle number and size. However, in reducing conditions, E$_{\text{CORR}}$ was suppressed to the
thermodynamic oxidation threshold of -400 mV (vs. SCE) as the number density and size of metal-particles increased, and the absence of $\text{U}^{\text{V}}/\text{U}^{\text{VI}}$ states in the surface confirmed that no oxidation occurred [3]. At such low $E_{\text{CORR}}$ values corrosion would be completely inhibited and radionuclide release could only proceed at a rate controlled by the negligible chemical dissolution rate of the fuel.

Grambow [79] modelled the effect of H$_2$ using an electrochemical radiolysis model for the dissolution of the fuel. The model considered transport processes at the fuel surface, the effects of pH, H$_2$O$_2$ and carbonate concentrations, as well as the partial pressures of H$_2$ and O$_2$. He compared the modelling results with the measured dissolution rates of 0, 5 and 10 % $^{233}\text{U}$-doped UO$_2$ fragments under reducing conditions [80] and found that measured dissolution rates were close to the calculated rate curve for the $10^{-4}$ mol.L$^{-1}$ H$_2$ content.

A key result obtained from the modelling studies was that H$_2$ concentrations from container corrosion will remain as high at the fuel surface as in the overall near field. Also, the consumption of H$_2$ by radiolytic or catalytic reactions will not be able to compete with the transport rates of H$_2$ from the near field to the fuel surface. Recently, Wu et al calculated the critical [H$_2$] concentrations required to completely suppress fuel corrosion as a function of $\alpha$-dose rate for various spent fuel ages. The [H$_2$]$_{\text{crit}}$ calculated for the highest $\alpha$-dose rates (anticipated after ~100 years of disposal) was $\leq 1.5 \times 10^{-5}$ mol.L$^{-1}$ consistent with previous predictions.
2.3 Influence of Rare-Earth Doping on UO\textsubscript{2} Corrosion

The effect of fission products (~1 at.% fission products are created in the fuel for each 10 MW d/kg U of burnup [81]) on the corrosion of fuel are expected to be important, in particular the rare earths which significantly influence the properties of the UO\textsubscript{2} matrix. In general, the fuel (doped/undoped) air oxidation process (reaction 2.1) involves two stages (reaction 2.3). The intermediate products, U\textsubscript{4}O\textsubscript{9} and U\textsubscript{3}O\textsubscript{7}, are derivatives of UO\textsubscript{2} and involve a slight volume reduction [42],

\[
\text{I} \quad \text{II}
\]

\[
\text{UO}_2 \rightarrow \text{U}_3\text{O}_7/\text{U}_4\text{O}_9 \rightarrow \text{U}_3\text{O}_8
\]  \hspace{1cm} (2.3)

These oxidation steps have been shown to be influenced by the type and the amount of dopants. Oxidation experiments on UO\textsubscript{2} doped with rare earths and other trivalent ions, higher actinides, and fission product simulants (such as Y\textsuperscript{3+}, La\textsuperscript{3+}, Pu\textsuperscript{3+}, Pu\textsuperscript{4+}, Th\textsuperscript{4+}, Gd\textsuperscript{3+}, Zr\textsuperscript{2+}) showed an enhanced stability of the fluorite structure with respect to U\textsubscript{3}O\textsubscript{8} formation at large dopant concentrations (≥ 4 to 10 wt%) [40, 82, 83]. This kinetic stability appeared to be due to the formation of a U\textsubscript{4}O\textsubscript{9+y} intermediate (reaction 2.4) which accommodates excess O beyond the nominal stoichiometry of UO\textsubscript{2.25} [40],

\[
\text{UO}_2 \rightarrow \text{U}_4\text{O}_{9+y} \rightarrow \text{U}_3\text{O}_8
\]  \hspace{1cm} (2.4)

Campbell et al [83] studied the effect of 5 and 10 wt% Gd\textsubscript{2}O\textsubscript{3} doping on UO\textsubscript{2} oxidation and found that the initial rate of oxidation was faster for UO\textsubscript{2} pellets containing Gd\textsubscript{2}O\textsubscript{3} compared to undoped ones at 200 °C. That, Gd-doping inhibited the formation of
U₃O₈ was indicated by a decrease in lattice parameter (5 wt %: 5.455 to 5.425 Å, 10 wt%: 5.445 to 5.425 Å) which is consistent with the filling of vacant lattice sites with oxygen.

Later, You et al. [43] investigated the kinetics of air-oxidation of unirradiated UO₂ fuel with various Gd₂O₃ concentrations i.e. (2, 5, 10 and 15 wt %) at 350 °C. The doped fuel oxidized faster than the undoped fuel (Fig. 2.5) in the initial stage of oxidation, as observed by Campbell et al [83]. Interestingly, the weight gain of oxidized Gd-doped UO₂ decreased with the increasing Gd content. After 12 hours of oxidation, the 2 % Gd₂O₃ doped showed the specimen was completely converted to powdered U₃O₈ while the 5 % specimen experienced only a local oxidation to powdered U₃O₈. XRD results revealed that, at a 15 % dopant level, the formation of U₃O₈ on the surface of UO₂ was completely inhibited.

Figure 2.5 Oxidation of Gd₂O₃ doped UO₂ at 350 °C [43]
The results of Kim et al. [84] on the oxidation of UO$_2$ containing various Gd$^{3+}$ contents, obtained using thermogravimetry and X-ray diffraction, showed contrasting behavior. Their results showed that the slowdown in the oxidation reaction due to increasing Gd doping occurred mainly in the first step UO$_2$ $\rightarrow$ U$_4$O$_9$. Consistent with previous results, the second step was also inhibited, the degree of oxidation to U$_3$O$_8$ decreasing linearly with increasing Gd content (Fig. 2.6).

**Figure 2.6** Thermogravimetric measurements on powdered (U$_{1-y}$Gd$_y$)$_2$O$_2$ showing gradients of weight gain by O (O/(U+Gd)) as a function of temperature from 50 to 540 °C at a heating rate of 1 °C.min$^{-1}$. The value of the O/U ratio (2.25) at the first plateau corresponds to U$_4$O$_9$ and the value at the second plateau (2.67) corresponds to U$_3$O$_8$[84].
Thomas et al [40] compared the oxidation behavior of undoped UO$_2$ to specimens doped with 4 and 8 wt% Gd$_2$O$_3$ and 0.4 wt% NbO$_2$ at temperatures < 600 °C. XRD analysis on the Gd-doped UO$_2$ showed two reaction products, U$_4$O$_9$ and U$_3$O$_8$ at intermediate weight gains but formation of U$_3$O$_8$ required a higher onset temperature with increasing dopant level. By contrast, NbO$_2$ doped material oxidized to U$_3$O$_7$. Analysis of partially oxidized material (oxidized to the same degree of weight gain) revealed higher amounts of U$_3$O$_8$ were formed in materials doped with lower amounts of NbO$_2$.

In all these studies, a longer induction time for U$_3$O$_8$ powder formation was observed for doped compared to undoped material, indicating that the impurities inhibited the U$_3$O$_8$ nucleation and growth process. This correlation between U$_3$O$_8$ powder formation time and burnup is related to the large amounts of fission-product dopants in spent fuel. This conclusion is supported by the results of Choi et al [85] who replicated the burnup dependence using simulated fuel (SIMFUEL) with a dopant content similar to used fuel. They investigated the oxidation behavior of five SIMFUEL specimens with various simulated burnups (1.5, 3.0, 4.0, 6.0 and 8.0 at %). An increased simulated burnup resulted in longer U$_3$O$_8$ formation times at 250 °C. Similar results have been obtained for UO$_2$ doped with Pu or Th and for used LWR fuel. Studies have also shown that the kinetics of oxidation of other oxides with the fluorite structure (such as CeO$_2$) when doped with rare earths (Y$^{3+}$ and Dy$^{3+}$) decreases with dopant content [86].

These results show that the appearance of the intermediate U$_4$O$_{9+x}$ rather than U$_3$O$_7$ for RE doped materials is indicative of enhanced stability of the cubic phase. Janeczek et al [87] described two possible mechanisms to account for the retention of cubic phases during uraninite oxidation. They suggested that impurities present in the
sample inhibited deviation from cubic symmetry by limiting the number of Os that can fit into interstitials in the fluorite-type structure. They also suggested that radiation-induced point defects, such as O interstitials, may inhibit oxidation by limiting the rate of O diffusion into the lattice. However, since interstitials are the diffusing species that control the oxidation mechanism, it is difficult to visualize how their generation would inhibit oxidation.

Additional ideas have been put forward to explain the stability of the cubic phases and recent theoretical studies have made good progress towards describing the O potential and other properties of UO$_2$ in terms of the defects therein. However, a detailed theoretical understanding has not yet been achieved. Ultimately, the stability of the doped material will need to be explained in terms of a model that takes into consideration the relative energy of formation of various defects (impurity ions, interstitial O, etc.) as well as the rates of diffusion and phase transformation [41, 42, 88, 89].

2.4. Defects

The absence or excess of atoms or ions in an ideal crystal structure and the misalignment of unit cells in real crystals are termed crystal defects. These are often classified in terms of a dimensionality and occur as points, along lines, or in the form of a surface, and are called point, line, or plane defects respectively.
2.4.1 Point Defects

Point defects are atomic scale, ‘zero-dimension’ defects in a crystal structure, as shown schematically in a 2-D representation in Fig. 2.7. A number of point defects can arise; (i) a vacancy which occurs when an atom is not present on the site that it should occupy in a perfect crystal; (ii) a self-interstitial which arises if an atom is present in a space between lattice sites; (iii) a substitutional impurity resulting from the replacement of a bulk atom at a lattice site by a different type of atom; (iv) an interstitial impurity present due to atoms in non-lattice locations.

Figure 2.7 Types of point defects in an elemental crystal. Image source: http://www.ndt-ed.org
Defects can be categorized as intrinsic or extrinsic. Intrinsic defects, such as *vacancies* and *self-interstitials*, are formed spontaneously in the lattice without any external intervention and do not involve changes in the overall composition. Extrinsic defects are formed due to the presence of impurities and involve changes in the overall composition.

2.4.1.1 Intrinsic defects: Schottky and Frenkel defects

There are two main types of intrinsic defects which preserve the stoichiometry of a compound, the Schottky and the Frenkel defect illustrated in Fig 2.8.

![Schottky defect](image1.png) ![Frenkel defect](image2.png)

Figure 2.8 Schottky (left) and Frenkel (right) defects in a MX-type ionic crystal, where the square denotes a vacancy.
The Schottky Defect

This defect arises when an ion is removed from its lattice site, leaving a vacancy. There are generally equal numbers of vacancies on the cation and anion lattice points, to preserve charge neutrality, and so the overall stoichiometry remains unchanged. In general, Schottky defects are found when the metal cations can exist in more than one oxidation state. In this case the number of accompanying anion vacancies is that amount required to maintain overall charge balance.

The Frenkel Defect

This kind of defect occurs when an ion is removed from its lattice site, leaving a vacancy, and moved into an interstitial site. It is favoured in crystals with readily available interstitial sites large enough to accommodate the displaced ion. Frenkel defects may occur on either the anion or cation sublattice, but cation Frenkel defects are more common than anion defects. Schottky and Frenkel defects are created independently, and in any particular crystal, if one dominates then the other will either be absent or have a minor contribution. In UO$_2$, for example, Frenkel defects are common while Schottky defects occur to a lesser extent
2.4.1.2 Extrinsic defects

As mentioned above, extrinsic point defects occur due to the presence of impurity or dopant atoms (e.g. O, C, and metals) and are more critical than intrinsic point defects. Real crystals contain both intrinsic and extrinsic defects, but the dominant defect type depends upon temperature, doping or degree of nonstoichiometry. The presence of point defects is important in the kinetics of diffusion and oxidation since the rate at which the diffusion of dopants occurs is dependent on the concentration of vacancies.

2.4.2 Point Defects in UO$_2$

Defects are of key importance for several properties of UO$_2$ since they drive diffusion properties, provide insertion sites for fission products, and accommodate variations in stoichiometry. Point defects such as vacancies, interstitials (at octahedral sites), Frenkel pairs (1 vacancy + 1 interstitial) and Schottky defects (1 U vacancy + 2 O vacancies) are possible in stoichiometric UO$_2$, with the Frenkel pair being dominant. To understand the stability of particular point defects or defect clusters, atomistic scale modelling methods (Density Functional Theory and Molecular Dynamics) [90-95] have been widely used. Despite these studies, the formation energies of point defects in UO$_2$ are a matter of debate due to the significant discrepancies between the various published studies [92, 96-98]. Importantly, these studies have enabled the determination of parameters inaccessible to experiment either due to their small length scale or to the
impossibility of isolating one contribution from another on the physical properties of the matrix [90].

Figure 2.9 shows the calculated [99-101] and experimental [102-104] formation energies for various point defects in UO$_2$. Comparison shows the formation energies for O interstitials and vacancies are lower than those for U defects, in agreement with neutron diffraction data [105-109]. This suggests that the majority of defects in UO$_2$ will be present in the O sublattice.

**Figure 2.9** Point defect formation energies in UO$_2$ [110]

The O-vacancy formation energy is nearly half of that of the U-vacancy formation energy. Most notably, the formation energy of an O-interstitial in an octahedral site is negative indicating its formation should be spontaneous. Consequently, UO$_2$ oxidation
should occur by the incorporation of additional O atoms at interstitial sites rather than by
the creation of U vacancies, giving UO$_2$ an inclination to be hyper-stoichiometric. These
interpretations are supported by experimental data [110].

### 2.4.3 Association of Point Defects

Point defects are often assumed to be independent of each other and randomly
distributed in the structure. However, in principle this is only applicable for small defect
conzentations, i.e. typically when the fraction of defects (relative to the number of
normal atoms in the crystal) is smaller than 0.001-0.01, although this depends on
temperature [111].

For larger defect concentrations (~ 1 mol %), the defects begin to interact either
coulombically or mechanically. These interactions may change the activity coefficients
and formation enthalpies leading to associations between defects. In particular, this
attraction may result in an overall lowering of energy for defect formation and clustering.
This is especially important in nonstoichiometric oxides such as UO$_{2+x}$ [112].

### 2.4.4 Defect clusters in UO$_2$

As described previously, UO$_2$ has the fluorite structure and may have a deficit or
excess of O depending on the temperature and O activity [111]. Investigations on the
clustering of point defects in non-stoichiometric uranium dioxide (UO$_{2+x}$) have been
mostly carried out using density functional theory (DFT) [95]. These calculations suggest
that defect clustering is unavoidable for \( x \geq 0.03 \), compatible with experimental observations. They also confirm the predominance of O over U defects at any composition.

The maximum value of \( x \) in \( \text{UO}_{2+x} \) should be 0.25. Since a substantial amount of excess O interstitials can be accommodated in \( \text{UO}_2 \), there is a high probability that, at this composition, the predominant point defects are O interstitials. Experimentally, Willis [107] used neutron diffraction to investigate the positions of O interstitials in \( \text{UO}_{2.12} \) and concluded that they interact strongly among themselves and with the host fluorite lattice resulting in aggregation into larger clusters. There are multiple propositions for the structure of these clusters, of which the so-called 2:2:2 Willis cluster [107, 113] and the cuboctahedral cluster [114, 115] are the most prominent. Bevan and Willis [114] conducted neutron diffraction experiments to investigate the structures of O interstitial clusters in \( \beta\text{-U}_4\text{O}_{9-y} \). Their data fit well to the cuboctahedral cluster model. In this model, 4 excess O interstitials displace 8 original O lattice ions in the fluorite unit cell to form a large cluster consisting of 12 O ions. The center of the cluster may or may not be filled with a 13th O ion [109, 114, 115].

Recently, He and Shoesmith [116] conducted studies on a \( \text{UO}_2 \) specimen of similar stoichiometry (\( \text{UO}_{2.1} \)) using X-ray diffraction, Raman spectroscopy, and electron microscopy to investigate the relationship between microstructure and structural defects. They concluded that the O interstitials can form isolated interstitials, 2:2:2 Willis clusters, cuboctahedral clusters, or mixtures of these defects, depending on the local stoichiometry in individual grains. Desgranges et al [109] used neutron diffraction to study the crystalline structures of different phases during \( \text{UO}_2 \) oxidation and for the \( \text{U}_4\text{O}_9 \) phase,
their results agree well with the cuboctahedral model. Geng et al [94] conducted DFT calculations to investigate the stability of cuboctahedral clusters. Their results showed that O interstitials prefer to form cuboctahedral clusters with an additional O atom in the cluster center (COT-o) at low temperatures and isolated interstitials at high temperatures. However, some researchers have suggested different cluster models [117].

Although, considerable effort has been expended in the investigation of the structure and behavior of these clusters, the composition and detailed location of the individual point defects in the clusters are still an issue for discussion.

### 2.5 Defect Structures: The Cuboctahedral Cluster (U₄O₉ / U₃O₇)

The crystalline phases with an elemental composition O/U between 2.23 and 2.38, which have been frequently reported as products of the first stage of UO₂ air oxidation below 400 °C, are seen as ordered phases (since there is clear evidence for defect clusters). The UO₂-like ordered phases are usually categorized into two types of oxide: U₄O₉ and U₃O₇, and have been regarded as cubic and tetragonal, respectively [110].

#### 2.5.1 U₄O₉ Structure

U₄O₉ is known to be a nonstoichiometric compound whose O/U ratio can vary from 2.23 to 2.25. It has three distinct stability regions as a function of temperature: rhombohedral α-U₄O₉ stable below 65 °C, cubic, β-U₄O₉ stable between 65 °C and 530 °C, and cubic γ-U₄O₉ stable at higher temperatures. The majority of U₄O₉ studies focus
on β-U₄O₉, given its wide stability range and its relevance to the long-term storage of spent fuel with the exact ratio of β-U₄O₉ being 2.234375 [118]. This difference in the O content could create different local concentrations. As the number of O defects increases, the U sublattice is only slightly affected while the O sublattice is strongly disturbed. It is believed that the transition from UO₂ₓ to U₄O₉ involves conversion of the anion cube to a square-antiprism accompanied by long-range ordering of O defects and interstitials, leading to a unit-cell dimension that is roughly four times the size of the original UO₂ unit cell [94, 95, 119, 120].

Early diffraction studies, conducted to determine the location of O interstitials (O_{int}) and to refine the U₄O₉ structure, suggested that O_{int} atoms were displaced from the centers of the vacant cubic sites [121]. Other studies showed that O_{int} atoms occupy sites along the z perpendicular bisector and the body diagonal of the cubic sites [122]. Willis and co-workers [107, 123] performed experiments on near-stoichiometric U₄O₉ (U₄O₉₋₀.₃) and found that the cuboctahedral cluster model [114] fits well to the bond lengths measured in neutron diffraction experiments. A schematic illustration of the formation of a cuboctahedral cluster is shown in Fig. 2.10.
Figure 2.10  Schematic illustration of the formation of a cuboctahedral cluster. Left figure: the small blue spheres indicate U lattice atoms and small red spheres O lattice atoms; Right figure: large red spheres indicate displaced O atoms (interstitials) and small purple spheres indicate vacant O lattice sites (vacancies) [117].

Later, Cooper et al also described U₄O₉ as an intricate arrangement of cuboctahedral clusters, and there is evidence to show that the cuboctahedral cluster is the most appropriate structural description of U₄O₉, in which, the defect is composed of (13 O interstitial atoms) 12 O’ atoms situated in the cuboctahedron vertices and one additional O ion slightly displaced from the central position. However, it is still debated whether or not the central site in the cuboctahedral is occupied by an additional 13th O [124] and whether this 13th O site is really displaced along the O” direction [114, 115]. The cuboctahedral cluster represents the densest and most close-packed defect cluster with five excess anions compared to only two for the Willis (2:2:2) cluster.
2.5.2 U$_3$O$_7$ Structure

U$_3$O$_7$ refers to the product of the first stage of air oxidation of UO$_2$ and was first postulated by Jolibois [42, 125]. Early experiments confirmed the existence of several similar phases, including the $\alpha$-U$_3$O$_7$, $\beta$-U$_3$O$_7$ [126, 127] polymorphs, which can be described by a deformed structure including the tetragonal phases [124, 128]. The main structural difference between $\alpha$ and $\beta$-U$_3$O$_7$ is their $c/a$ ratio, which is 0.989 and 1.031 [127], respectively. Typically, $\alpha$-U$_3$O$_7$ is considered the normal oxidation product at temperatures $< 200$ °C [42], whereas $\beta$-U$_3$O$_7$ appears at temperatures $> 200$ °C [42, 127].

Based on neutron diffraction studies [124], when UO$_2$ is oxidized to U$_3$O$_7$ the primary changes occur in the O sublattice where excess O atoms occupy two kinds of sites, O and O'. The O atoms occupy normal fluorite positions while the O' atoms occupy non-fluorite cuboctahedron positions, located 310 pm along the (1 1 0) directions from the center of the lattice [124]. The composition of U$_3$O$_7$ can also be expressed as U$_4$O$_{8-m}$O'$_n$, where m is the number of empty O sites and n is the number of interstitial O' sites. The excess O atoms in U$_3$O$_7$ are also accommodated in cuboctahedral clusters.

So, the defect structure of U$_3$O$_7$ is related to that of U$_4$O$_9$ in the sense that they both incorporate excess O anions interstitially in the cuboctahedral clusters and parabolic kinetics is observed for the formation of both the intermediate products [109, 124, 128]. However, in U$_4$O$_9$ the clusters are sufficiently far apart and maintain cubic symmetry but in U$_3$O$_7$ the cluster concentration is higher than in U$_4$O$_9$ and, in order to accommodate, additional clusters, the lattice is distorted from cubic to tetragonal symmetry.
Only a few attempts have been made to solve the crystal structure of U$_3$O$_7$ [124, 129] of which that by Desgranges et al [129] is probably the most ambitious. All existing U$_3$O$_7$ models are extensions of the cuboctahedral structure model proposed for U$_4$O$_9$. Compared to U$_4$O$_9$ the most prominent feature of the U$_3$O$_7$ crystallography is a highly variable tetragonal symmetry reduction. The main difference between the two structural models is that the U$_4$O$_9$ structure possesses 12 cuboctahedra, each made of 13 O atoms, with six neighbouring U atoms sharing the normal cation sublattice of the fluorite structure with a square antiprism coordination instead of the normal cubic coordination. By contrast, U$_3$O$_7$ consists of 16 cuboctahedra, which are noticeably tilted and deformed within the fluorite structure [109].
2.6 References


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This chapter briefly reviews the principles of the experimental techniques employed in this project. Also, general details on electrode preparation, experimental arrangements and procedures are included. However, more specific information on the electrochemical procedures and experimental parameters used in individual studies are provided in the subsequent chapters.

3.1 Electrochemical Experimental Details

3.1.1 Experimental Cell and Equipment

All the experiments were conducted in a jacketed three-electrode, three-compartment cell made of Pyrex shown schematically in Fig. 3.1. The cell contained one central chamber with two side arms separated by glass frits to minimize the contamination of the working electrode compartment. A commercial saturated calomel reference electrode (SCE, Fischer Scientific) was placed in one side arm and connected to the central chamber of the cell via a Luggin capillary to minimize IR (I-current; R-solution resistance) drop within the cell. All potentials were measured against the saturated calomel reference electrode (SCE) (+0.242 V, 25ºC vs. SHE). The counter electrode, a Pt foil (99.9% purity, Alfa Aesar) with a surface area of ~ 6 cm² and spot-welded to a Pt wire, was placed in the other side arm. A gas dispersion tube with a frit on
the end was used to de-aerate the solution using ultra high purity Ar/H₂. When required, the rotation rate of the working electrode (WE) was controlled by an ASR analytical rotator (Pine Instrument Company). The cell was housed in a grounded Faraday cage to minimize external noise. A Solartron model 1287 potentiostat was used to control applied potentials and record current responses. Corrware™, version 3.0, software (Scribner and Associates) was used to analyze the data. The current interrupt method was employed to compensate for any potential drop due to the electrode and solution resistances.

![Figure 3.1 Schematic diagram of the standard three-compartment electrochemical cell](image)

**Figure 3.1** Schematic diagram of the standard three-compartment electrochemical cell used
3.1.2 Electrode Material and Preparation

Electrochemical experiments were performed on a variety of simulated spent fuel materials such as 1.5 at \% SIMFUEL, Gadolinium (6 wt\%) doped UO$_2$ (Gd-UO$_2$), Dysprosium (12.9 wt\%) doped UO$_2$ (Dy-UO$_2$), Pt (1 wt\%) and Yttrium (0.3 wt\%) doped UO$_2$ (Pt-UO$_2$, Y-UO$_2$) fabricated by Atomic Energy of Canada Limited (Chalk River, ON (SIMFUEL, Dy-UO$_2$)), Cameco Corporation (Port Hope, ON (Gd-UO$_2$)), and the Royal Institute of Technology (Stockholm, Sweden (Pt-UO$_2$, Y-UO$_2$)). Electrodes \~2-5 mm thick and 12 mm in diameter were prepared from these specimens.

One face of the specimen was electroplated with a thin layer of Cu to provide good electrical contact to an external measuring circuit. Prior to electroplating, the surface was polished with 600 grit SiC paper to create a rough surface to ensure good adhesion of the Cu. The disc was then fitted into the end of a piece of rubber tubing and placed in a 0.1 mol.L$^{-1}$ CuSO$_4$ solution. Electronic grade Hg was poured into the tubing, and a Ag wire used to facilitate electrical contact between the UO$_2$ sample and the power supply. A Cu metal counter electrode was employed. This cell is shown schematically in Fig. 3.2 (a). A 10 mA current was applied between the two electrodes for 10 minutes using a DC power supply (GPR-30H10D) to produce a thin and evenly distributed layer of Cu on the UO$_2$ surface.

The Cu-plated side of the electrode was then glued to a stainless steel post with a conductive Ag epoxy (MG Chemicals 8331). The disc was then encased in a moulding compound (Hysol EE4190, Henkel Loctite) and placed first in a vacuum chamber for 20 minutes to remove any air bubbles, and subsequently cured in an oven at 60 °C for 4
hours. The excess resin on the electrode surface was then removed by polishing to expose only a flat circular face, Fig. 3.2 (b).

Figure 3.2 Schematic of the (a) experimental arrangement employed to electroplate Cu onto one face of UO$_2$ electrode; and (b) the prepared electrode

Prior to each experiment, the electrode was polished (wet) with 1200 grit SiC paper and rinsed with distilled de-ionized water. Subsequently, it was ultrasonically cleaned with distilled de-ionized water for 2 min to remove any residual SiC and UO$_2$ debris from the fuel surface before emplacement in the electrochemical cell.
3.1.3 Solution Preparation

All solutions were prepared using distilled deionized water (ρ = 18.2 MΩ cm) purified using a Millipore milli Q plus unit to remove organic and inorganic impurities. Electrolytes were prepared with 0.1 mol.L⁻¹ reagent grade NaCl (Caledon, >99%) and purged with Ar, or 5% H₂/95% Ar gas (Praxair) for at least one hour prior to, and throughout, each experiment. This prevents interfering cathodic reactions, such as O₂ reduction. The solution pH was adjusted to the desired value using either HCl or NaOH. All chemicals used were analytical grade. The solution pH was monitored with an Orion model 720A pH meter. The H₂O₂ concentration used was determined by an ultraviolet/visible spectrophotometric technique.

3.2 Electrochemical Experimental Techniques

3.2.1 Corrosion Potential (E_{CORR}) Measurements

The corrosion of UO₂ in aqueous solution is an electrochemical reaction in which the oxidative dissolution of UO₂ is coupled with the reduction of an available soluble oxidant,

\[
\text{UO}_2 + \text{Ox} \rightarrow \text{UO}_2^{2+} + \text{Red}
\]  

(3.1)

where Ox is an oxidizing agent, and Red is its reduced form. Since this reaction is electrochemical, the rate can be expressed as a corrosion current, \( i_{\text{CORR}} \). Since a corrosion
reaction is a short-circuited electrochemical reaction, conservation of charge requires that
\[ i_{\text{CORR}} = \Sigma i_a = -\Sigma i_c, \]
where \( i_a \) and \( i_c \) represent the anodic and cathodic currents, respectively,

The basis for considering a reaction to be electrochemical is that it may be separated into two half-reactions, each of which can be studied individually [1]. In the case of reaction (3.1), the two half-reactions are:

\[ \text{UO}_2 \rightarrow \text{UO}_2^{2+} + 2e^- \quad (E_e)_{\text{UO}_2^{2+}/\text{UO}_2} \quad (3.2) \]

\[ \text{Ox} + ne^- \rightarrow \text{Red} \quad (E_e)_{\text{Ox}/\text{Red}} \quad (3.3) \]

where \((E_e)_{\text{UO}_2^{2+}/\text{UO}_2}\) and \((E_e)_{\text{Ox}/\text{Red}}\) are the equilibrium potentials for the half-reactions (3.2) and (3.3), given by the Nernst equation, and written, by convention, as reductions.

The thermodynamic requirement for the reaction (3.1) to be spontaneous is:

\[ (E_e)_{\text{UO}_2^{2+}/\text{UO}_2} < (E_e)_{\text{Ox}/\text{Red}} \quad (3.4) \]

Since each half-reaction is an electron transfer reaction, its kinetics can be described by the Butler-Volmer equation [2]:

\[ i = i_o \left[ \exp \left( \frac{2\alpha F}{RT} \eta \right) - \exp \left( - \frac{2(1 - \alpha)F}{RT} \eta \right) \right] \quad (3.5) \]

where \( i_o \) is the exchange current density, \( \alpha \) is the transfer coefficient, \( F \) is Faraday's constant, \( R \) is the gas constant, \( T \) is the temperature and \( \eta \) is the overpotential, defined as:

\[ \eta = E - E_e \quad (3.6) \]

At the equilibrium potential \((E = E_e), \eta = 0\) where no measurable current flows and the equilibrium is dynamic, with \( i_a = -i_c = i_o \).

In a corrosion process, the anodic and cathodic reactions are coupled together. For a spontaneous corrosion process, we consider the Butler-Volmer relationships for
reactions (3.2) and (3.3), and the thermodynamic requirement in equation (3.4). The kinetic scenario is illustrated in Fig. 3.3 for UO₂ being oxidized to the soluble species UO₂²⁺ by the reduction of an oxidant. Since corrosion is a short-circuited reaction, the total anodic current must be equal and opposite in sign to the total cathodic current.

**Figure 3.3** Current-potential relationships for the UO₂ dissolution and the oxidant reduction reactions illustrating their coupling at the corrosion potential (E₉CORR) to yield the corrosion current (i₉CORR)

Inspection of Fig. 3.3 shows that this criterion can only be met at a single potential, termed the corrosion potential (E₉CORR), which must lie between the equilibrium potentials for the two half-reactions:

\[
(E_{\text{e}_{\text{anodic}}} < E_{\text{CORR}} < (E_{\text{e}_{\text{cathodic}}})
\]

\[
\text{(3.7)}
\]
While the $E_{\text{CORR}}$ is thermodynamically restricted according to equation (3.7), its value provides qualitative information on the kinetics of the system, since the shapes of the current-potential curves in Fig. 3.3 determine the value of $E_{\text{CORR}}$. Providing $E_{\text{CORR}}$ is sufficiently far from the equilibrium potentials, the UO$_2$ oxidation and oxidant reduction can be considered to be proceeding irreversibly and the reverse current for both reactions can be ignored. When this is the case the currents in Fig. 3.3 can plotted as the log of current $i$ versus $E$ to yield an Evans diagram, Fig. 3.4, which depicts where the two lines intersect to give $I_{\text{CORR}}$ and $E_{\text{CORR}}$. The two linear portions of the plots yield the Tafel regions for each half reaction with slopes given by:

$$
b_a = \frac{2.303RT}{\alpha nF}$$  \hspace{1cm} (3.8)

$$
b_c = \frac{-2.303RT}{(1-\alpha)nF}$$  \hspace{1cm} (3.9)

The exchange currents for the two reactions can also be determined by extrapolating the Tafel lines back to the respective equilibrium potentials. The overall measurable current can be obtained as the sum of the currents for the two half reactions and yields a modified Butler-Volmer equation

$$
i = i_{\text{CORR}} \left[ \exp \left( \frac{\alpha nF}{RT} (E_{\text{App}} - E_{\text{CORR}}) \right) - \exp \left( -\frac{(1-\alpha)nF}{RT} (E_{\text{App}} - E_{\text{CORR}}) \right) \right]$$ \hspace{1cm} (3.10)

The two polarization curves, Fig. 3.3 and 3.4 are not necessarily symmetrical and the shape of the curves is determined by the two exchange currents and both Tafel coefficients. Also, $E_{\text{CORR}}$ values cannot be predicted from the equilibrium potentials for
the anodic and cathodic half reactions. Figures 3.3 and 3.4 show that the value of $E_{\text{CORR}}$ is determined by the shape of the current-potential relationships for the two half reactions, and so by kinetic parameters ($i_o$, $\alpha$, n) for the two reactions. Since $E_{\text{CORR}}$ is determined by the properties of both half reactions, it is commonly called a mixed potential. The overall rate of corrosion will be controlled by the kinetically slowest reaction (i.e., the one with the smallest exchange current ($i_o$) or largest Tafel coefficient ($b$)) [1].
3.2.2 Rotating Disc Electrode (RDE) Technique

Electrochemical reactions occurring at an electrode surface are two-dimensional, since electron transfer can only occur in the interfacial region. Therefore, there is potentially a contribution from mass-transport (diffusion) to the overall reaction kinetics. The rate of mass transfer (i.e., the flux, $J_a(x,t)$) of substance $a$ is proportional to its concentration gradient according to Fick’s laws of diffusion [2] with

$$-J_a(x,t) = D_a \frac{\partial c_a(x,t)}{\partial x} \quad (3.11)$$

where $D_a$ is the diffusion coefficient of species $a$ and $c_a(x,t)$ is the concentration of $a$ at a distance $x$ from the electrolyte surface and time $t$. The Nernst diffusion layer treatment for steady-state transport assumes a transition point between the bulk solution concentration and the diffusion layer (the region within which a concentration gradient exists). The distance from the electrode surface to the transition point is termed the diffusion layer thickness ($\delta$), as illustrated in Fig. 3.5. Use of a rotating disc electrode (RDE) allows control over the dimensions of the diffusion layer, and hence the concentration gradient, at the electrode surface, according to equation [2]

$$\delta = 1.61 D_i^{2/3} \nu^{1/6} \omega^{-1/2} \quad (3.12)$$

where $\nu$ is the kinematic viscosity of the solution (cm$^2$ s$^{-1}$) and $\omega$ is the rotation rate of the electrode in rad s$^{-1}$. An increase in $\omega$ reduces $\delta$, and increases the flux of species $a$ to the electrode surface, as illustrated in Fig. 3.5.
Figure 3.5 Diagram of the concentration gradients ($dc/dx$) near an electrode/solution interface as the electrode rotation rate ($\omega$) changes. The $\delta$’s represent the Nernst diffusion layer thickness for these values of $\omega$.

For the general electrochemical reaction occurring on an electrode surface:

$$A \pm ne^- \rightarrow \text{Products}$$

(3.13)

the reactant species $A$ must diffuse from the bulk solution to the electrode surface before undergoing reaction. Assuming that $A$ is the only reacting species, and that the reverse reaction is negligible, then the overall current ($i$) can be related to the diffusion limited current ($i_d$) by:

$$i = i_d \frac{(c_b - c_s)}{c_b}$$

(3.14)

where $c_b$ is the bulk concentration of $A$ and $c_s$ is its surface concentration. The current can also be related to the surface concentration by the equation:
\[ i = nFkA c^m \]  

in which \( n \) is the number of electrons transferred, \( F \) is Faraday's constant, \( A \) is the surface area of the electrode and \( m \) is the reaction order with respect to species \( A \). By defining the kinetic current (the current in the absence of any mass transfer limitations) as:

\[ i_k = nFkA c^m \]  

and recognizing that the diffusion limited current at a RDE is given by [2]:

\[ i_d = n\xi FAc D^{2/3} v^{-1/6} \omega^{1/2} = B\omega^{1/2} \]  

where \( \xi \) is a numerical coefficient [3], then equations (3.14) to (3.17) can be combined to yield the Koutečky-Levich (K-L) equation (3.18) [2]:

\[ \left( \frac{1}{i} \right)^{1/m} = \left( \frac{1}{i_k} \right)^{1/m} + \left( \frac{i}{i_d} \right)^{1-1/m} \]  

Equation (3.17) has been used extensively in the analysis of electrochemical reactions at RDEs [4-8], and its strengths and limitations have been discussed [4]. The K-L equation is rather insensitive to the value of \( m \), since straight lines are obtained whether \( m = \frac{1}{2}, 1, \) or 2 [4]. Thus, the K-L equation alone cannot be used to deduce the electrochemical reaction order. An alternative method [4] is to plot data according to the equation:

\[ \log(i) = \log(i_k) + m \cdot \log\left( \frac{1 - \frac{i}{i_d}}{1 - \frac{i}{i_d}} \right) \]  

In order to use equation (3.19), the diffusion-limited current must be measured experimentally or calculated from equation (3.17) providing all the other quantities are accurately known.
3.2.3 Electrochemical Polarization Techniques

3.2.3.1 Potentiostatic Polarization

In potentiostatic polarization experiments a constant potential is applied to the electrode. In this project such experiments were conducted for 30 minutes or up to an hour. Potentials were chosen to cover and exceed the range anticipated on UO$_2$ under natural corrosion conditions. The range used was from -0.5 V to +0.5 V. The measured relationship between current and time at each potential can be used to reveal the characteristics of the film formation and dissolution reactions.

3.2.3.2 Cyclic Voltammetry (CV)

Cyclic voltammetry is a potentiodynamic technique that allows the general electrochemical reactivity of a system to be examined in a fast and simple manner [2]. The potential profile for a typical CV experiment is shown in Fig. 3.6. Starting at a negative potential (the cathodic limit ($E_c$), usually -1.2 V on UO$_2$ electrodes), the potential is scanned in the positive direction at a constant scan rate ($v_s = dE/dt$). At a certain potential (the anodic limit ($E_a$), up to 0.5 V on UO$_2$ electrodes), the potential scan is reversed, and the scan continued in the negative direction until the cathodic limit is reached again.
Figure 3.6 Potential-time profile for a CV in which the potential is scanned twice from $E_c (-1.2 \text{ V})$ to $E_a (0.4 \text{ V})$, and then back to $E_c$.

The CVs give a summary of the oxidation (anodic (forward) scan) and reduction (cathodic (reverse) scan) processes that occur on the electrode surface over the potential range used. The positions of current peaks within the potential range scanned are an indication of various stages of oxidation and help to determine (in the present case) the anodic oxidation mechanism of UO$_2$. The position of peaks in the reverse cathodic scan indicates reduction of oxidized species formed on the electrode surface during the anodic scan. Changing the value of the potential at the anodic limit can control the extent of oxidation and influence the availability of surface species that would be reduced on the reverse scan.
3.2.3.3 Cathodic Stripping Voltammetry (CSV)

A cathodic stripping voltammogram (CSV) can be used to determine the consequences of a period of oxidation at a known applied potential (E_{App'd}) or at E_{CORR} under open circuit corrosion conditions, Fig. 3.7. By scanning the potential from E_{App'd} or E_{CORR} back to the cathodic limit (E_c) and recording the reduction current as a function of potential, the extent of oxidation at E_A or E_{CORR} can be determined providing it leads to reducible surface films or deposits.

![Figure 3.7 Potential-time profile for a typical CSV when the potential is scanned from E_{App'd} or E_{CORR} to E_c](image)

3.2.3.4 Integration of Voltammograms

Integration of the areas under the current peaks in a CV yield values of the charge (Q) consumed by oxidation (Q_a) or reduction (Q_c) which are measures of the total amount
of electrochemical reaction that has occurred. The charge ($Q$) is proportional to the amount of material oxidized or reduced (according to Faraday's Law), and is given by,

$$Q = \int i dt = \int i \left( \frac{dE}{dE} \right) dE = \frac{1}{V_s} \int i dE$$  \hspace{1cm} (3.20)

Figure 3.8 shows a schematic of a CV and the integrated areas between the potential limits $E_i$ and $E_f$ (-1.2V and +0.4V). Note that $Q_A$ also includes the anodic charge accumulated on the reverse scan.

![Schematic of a CV showing the integrated areas $Q_a$ and $Q_c$. The lower limit of integration when determining $Q_c$ is the threshold for the onset of water reduction.]

Figure 3.8

To determine $Q_c$ it is necessary to separate the oxide reduction process from the partially-overlapping water reduction process which occurs for $E \leq -1.2V$. The difference,
Q_D = Q_A − Q_C, can be taken as the amount of oxidized material lost by dissolution and transported to the bulk of the solution, and hence, unavailable for reduction on the cathodic scan.

3.2.4 Linear Polarization Resistance Measurements

Linear polarization resistance is an electrochemical technique that can measure the instantaneous polarization resistance (R_p). A small potential perturbation in the range of ±10 mV (or 20mV) is applied at a scan rate of 0.01mV.sec^{-1} starting below and terminating above E_{CORR}. The slope of the resulting linear current-potential relationship around E_{CORR} yields the R_p (in the absence of ohmic resistances such as the solution resistance), Fig. 3.9, which is inversely related to the uniform corrosion rate;

\[ R_p = \left( \frac{\Delta E}{\Delta i} \right)_{\Delta E \rightarrow 0} \]  \hspace{1cm} (3.21)

It is to be noted that the current-potential relationship plotted in Fig. 3.9 is the sum of the currents from the two opposing (anodic and cathodic) reactions shown in Fig. 3.3, described by the modified Butler-Volmer relationship in equation 3.10. For potentials close to E_{CORR} (at low overpotentials) the exponential relationships can be linearized (i.e. e^\eta = \eta + 1) and the modified Butler-Volmer equation can be simplified to equation 3.22
Figure 3.9 Schematic of a linear polarization curve showing the linear potential used to measure the polarization resistance

\[ i_{\text{CORR}} = 2.303 \left( \frac{b_a b_c}{b_a + b_c} \right) \frac{1}{R_p} \]  
(3.22)

or when the expression is rearranged;

\[ R_p = 2.303 \left( \frac{b_a b_c}{b_a + b_c} \right) \frac{1}{i_{\text{CORR}}} \]  
(3.23)

If the Tafel slopes are known, the measured \( R_p \) can be converted to \( i_{\text{CORR}} \) using equation 3.23. If these values are not known (e.g. when the corrosion mechanism is not known), \( R_p \) can still be used as a quantitative parameter to compare the corrosion resistance of materials using equation 3.21. A high \( R_p \) value implies a high corrosion resistance and vice versa.
3.3 X-Ray Photoelectron Spectroscopy (XPS)

3.3.1 Principles of XPS

XPS was employed in this project to determine the oxidation states of chemical species in the surface of the various UO$_2$ electrodes after electrochemical treatment. XPS is a technique which utilizes irradiation by a fixed low-energy X-ray source to detect and analyze the photoelectrons produced [5]. When a sample is irradiated with x-rays of known energy, $h\nu$, electrons with a binding energy, $E_b$, less than the incident energy ($h\nu$), are ejected from core energy levels with a kinetic energy, $E_k$, Fig. 3.10. The conservation of energy dictates the relationship between the $E_b$ and the $E_k$ of

![Figure 3.10](image-source: wiki.utep.edu)
the emitted photoelectron. The kinetic energy of the photoelectron ($E_k$) is the difference between the energy of the X-ray ($h\nu$) and the binding energy of the electron ($E_b$) plus the work function of the spectrometer, $\phi$;

$$E_k = h\nu - (E_b + \phi)$$  \hspace{1cm} (3.24)

This work function is the difference between the energy of the Fermi level and the energy of the vacuum level and is determined by calibration for the spectrometer used. It is a common practice to use the spectrometer work function since it is very difficult to determine simultaneously a binding energy reference and the work function of the sample. The solution employed in modern spectrometers is to put the sample in good electric contact with the spectrometer, so that the two Fermi levels are aligned (Fig. 3.11) and the zero value for binding energy will be the position of the Fermi Level of both sample and spectrometer.

![Figure 3.11](image.png)

Figure 3.11 Illustration of the Fermi-level alignment of a metallic sample and the spectrometer [7].
Since, electrons escaping from a sample have a low inelastic mean-free path \((\lambda_m)\), XPS can be considered a surface sensitive technique, with most photoelectrons escaping from a depth of between 0.5 and 3.0 nm [6]. Those photoelectrons originating more than 3 to 10 nm below the sample surface are unable to escape from the surface with sufficient energy to be detected due to collisions within the sample.

An XPS consists of a fixed energy radiation source, an electron energy analyzer for the photoelectrons, a high vacuum chamber and an electron detector, Fig. 3.12 [6, 8-11]. Since the photoelectron energy depends on the X-ray energy, the excitation source must be monochromatic.

**Figure 3.12** Schematic diagram of an XPS instrument. *Image source: chemwiki.ucdavis.edu*

X-rays illuminate an area of the surface causing electrons to be ejected with a range of energies and directions. The electron optics, which may be a set of electrostatic
and/or magnetic lens units, collect a proportion of these emitted electrons defined by those rays that can be transferred through the source slit and focused onto the analyzer entrance slit. The electrostatic fields within the concentric hemispherical energy analyzer are set to allow electrons of only a given energy (pass energy) to arrive at the collector slits and enter the detector. Electrons of a specific initial kinetic energy are measured by setting voltages for the lens system (so as to focus the electrons of the required initial energy onto the entrance slit and to retard their velocity) so that the kinetic energy of these electrons, after passing through the transfer lenses, matches the pass energy of the hemispherical analyzer. An XPS spectrum is produced by stepping the voltage on the analyzer spheres to detect photoelectron intensity as a function of kinetic energy. The resultant spectrum is then replotted as a function of binding energy using equation 3.24 with known values for the spectrometer workfunction ($\phi$) and the frequency ($\nu$) of the radiation. A characteristic spectrum generated by XPS, plots the measured photoelectron intensity as a function of $E_b$. For every element, there is a characteristic binding energy associated with each core atomic orbital (K and L in Fig. 3.10); i.e. each element will give rise to a characteristic set of peaks in the photoelectron spectrum at kinetic energies determined by the photon energy and the respective binding energies. Moreover, the intensity of the peaks is related to the concentration of that element within the analyzed region.

Figure 3.13 shows a representative low-resolution survey photoelectron spectrum recorded on a freshly polished Pt-doped UO$_2$ electrode. In the core level region, the Al K$_\alpha$ can excite several characteristic U lines but the principal lines from which most of
the information is extracted, are the U 4f peaks, since these are the most intense. The spectrum is plotted as signal intensity versus binding energy ($E_b$). The labels indicate the electron energy level corresponding to each photoelectron peak. The U 4f, U 4d, and U 5d peaks all appear as doublets, while the O 1s and C 1s peaks are singlets. This is the expected pattern based on spin-orbit splitting. Clearly, only U and O (and the adventitious C) can be seen by the low-resolution XPS scan. The dopant element produces too weak a signal to be seen on the survey scan.

![XPS spectrum](image)

**Figure 3.13** Survey spectrum on a polished Pt-doped UO$_2$ electrode as an example of an XPS spectrum with U lines. The most prominent lines are indicated on the graph.
A valuable feature of XPS is its ability to discriminate between different oxidation states and chemical environments since the binding energy of the electrons depends on the valence state of the atoms. So, the position of the U4f line will vary with the U valence state. A more detailed discussion of the U4f positions will be given when experimental results are discussed.

Additional features are present in close proximity to the U 4f main lines, known as satellite peaks to the high binding energy side. These satellites are commonly interpreted as so-called shake-up satellites, which are the result of a charge transfer process. The photoemission causes a major perturbation on the atom, resulting in substantial reorganisation of the valence electrons. This relaxation may involve excitation of one of these valence electrons to a higher unfilled level, which is called the shake-up process. The energy required for this transition is not available to the primary photoelectron, leading to a discrete structure to the low kinetic energy (high $E_b$) side of the photoelectron peak [12]. The position of the satellite also depends on the U valence and is expected to vary as the oxidation state of the element changes. The position and shape of the satellite structure is always used to confirm the change in oxidation state of the element. Detailed literature values will be given in the discussions of the experimental results.

### 3.3.2 XPS Experimental Details

All XPS analyses in this project were performed on a Kratos Axis NOVA spectrometer equipped with a monochromatic Al $K_\alpha$ ($h\nu = 1486.6$ eV) radiation source.
The instrument work function was set to give a binding energy (BE) of 83.96 eV for the Au 4f$_{7/2}$ line for metallic Au and the spectrometer dispersion was adjusted to give a BE of 932.62 eV for the Cu 2p$_{3/2}$ line of metallic Cu. The instrument charge neutralizer was used on all specimens. Survey spectra were recorded for the energy range 0-1100 eV with an analysis area of ≈ 300 × 700 μm at a pass energy of 160 eV, and high resolution spectra for the U 4f, O 1s, C 1s and the U 5f valence band regions were collected with a pass energy of 20 eV. The C 1s line at 285 eV was used as a standard, when necessary, to correct for surface charging. Spectra were analyzed using CasaXPS software (version 2.3.14).

The procedure used to analyze the U (4f) and O 1s regions involved a fitting routine which was 50% Gaussian and 50% Lorentzian with a Shirley background correction [13, 14]. The proportions of U oxidation states U$^{IV}$, U$^{V}$ and U$^{VI}$ in the electrode surface were determined by fitting the whole U4f spectra. The detailed procedure is described in Chapter 4 which involves the deconvolution of high-resolution spectra (including well-resolved satellites) based on a combination of reference spectra provided in the literature.
3.4 Scanning Electron Microscopy (SEM)/Energy Dispersive X-ray (EDX) Spectroscopy

3.4.1 Principles of SEM/EDX

The Scanning Electron Microscope (SEM) is an instrument that uses electrons rather than light to form an image. High resolution images of surface topography, with excellent depth of field, are produced using a highly-focused, scanning (primary) electron beam. A schematic of a typical scanning electron microscope is shown in Fig. 3.14. The sample surface must be electrically conducting in order to avoid surface charging by an electron beam. An electron source is focused to a fine beam (in a vacuum, $10^{-6}$ Torr) and scanned (rastered) across the sample via magnetic scan coils. A system of electrical and magnetic field optics is used to focus the beam to a spot $< 10$ nm in diameter on the sample surface. The electrons are generated by thermionic emission from a metal filament, and accelerated to 0.5 to 30 keV, and generate many low energy ($< 50$ eV) secondary electrons [15]. The electrons reflected from the surface are collected, amplified, and plotted as a two-dimensional ‘micrograph’ image of the signal intensity.
Three types of images are produced in SEM; secondary electron images, backscattered electron images, and elemental X-ray maps [10, 11, 15]. Secondary and backscattered electrons are conventionally separated according to their energies, as they are produced by different mechanisms. When a high-energy primary electron interacts with an atom, it undergoes either inelastic scattering with atomic electrons or elastic scattering with the atomic nucleus. In an inelastic collision with an electron, some amount of energy is transferred to the other electron. If the energy transfer is very small, the emitted electron will probably not have enough energy to exit the surface. If the energy transferred exceeds the work function of the material, the emitted electron can exit.
the solid. When the energy of the emitted electron is less than about 50 eV, it is referred to as a secondary electron. Most of the emitted secondary electrons are produced within the first few nm of the surface [15]. Secondary electrons produced much deeper in the material, suffer additional inelastic collisions, which lower their energy and trap them in the interior of the solid. The intensity of the emitted secondary electrons is largely governed by the surface topography of the sample and they can leave the surface if their energy is greater than the work function of 2 to 6 eV.

Higher energy electrons are primary electrons that have been scattered without loss of kinetic energy (i.e., elastically) by the nucleus of an atom, although these collisions may occur after the primary electron has already lost some of its energy to inelastic scattering. Backscattered electrons are considered electrons that exit the specimen with energy greater then ~ 50 eV. However, most backscattered electrons have energies comparable to the energy of the primary beam. The higher the atomic number of a material, the more likely it is that backscattering will occur [11]. Thus, as a beam passes from a low-Z (atomic number) to a high-Z area, the signal due to backscattering, and consequently the image brightness, will increase.

An additional electron interaction of major importance in SEM occurs when the primary electron collides with and ejects a core electron from an atom in the solid. The excited atom will decay to its ground state by emitting either a characteristic X-ray photon or an Auger electron. The X-ray emission signal can be sorted by energy in an energy dispersive X-ray detector or by wavelength with a wavelength spectrometer. These distributions are characteristic of the elements that produced them and the SEM
can use these signals to produce elemental images that show the spatial distribution of particular elements in the field of view.

3.4.2 SEM/EDX Experimental Details

SEM images were obtained using an Hitachi S-4500 Field emission scanning electron microscope. Electrodes removed from an electrochemical cell were rinsed with Millipore water and air dried prior to placing in the microscope. A high electron beam voltage 15 kV (or 10 kV) was used resulting in a spatial resolution of < 2 nm. Micrographs were recorded at various magnifications (100 – 5000X).

3.5 Raman Spectroscopy

3.5.1 Principles of Raman Spectroscopy

Raman spectroscopy provides information about molecular vibrations that can be used for sample identification and quantification. Figure 3.15 shows a schematic of a Raman microscope build from a standard optical microscope, by adding an excitation laser, a monochromator, and a sensitive detector (such as a charge-coupled device (CCD), or photomultiplier tube (PMT)).
The technique involves shining a monochromatic light source (i.e. laser) on a sample and detecting the scattered light. This scattering arises from a change in polarizability in the molecule which means that symmetric stretches, vibrations involving multiple bonds, and vibrations of heavier atoms will give the most intense Raman scattering. This is in complete contrast to infrared absorption where a dipole change in the molecule gives intensity and, at a very simple level, this means asymmetric rather than symmetric vibrations will be intense. Raman spectroscopy offers several advantages for microscopic analysis and spectra can be collected from a very small volume (< 1 μm in diameter) which allows the identification of species present within that volume.

Though the majority of the scattered light is of the same frequency as the excitation source, and is known as Rayleigh or elastic scattering (Fig. 3.16), it does not contain significant information on the structure of molecular states. A very small amount of the scattered light (ca. $10^{-5}$ % of the incident light intensity) is shifted in energy from
the laser frequency due to interactions between the incident electromagnetic waves and the vibrational energy levels of the molecules in the sample. It is this shift in wavelength of the inelastically scattered radiation that provides the chemical and structural information [16].

![Energy level diagram](image-source)

**Figure 3.16** Energy level diagram showing the states involved in a Raman signal. The line thickness is roughly proportional to the signal strength from the different transitions. *Image source: University of Cambridge, Teaching and Learning Package Library.*

Raman shifted photons can be of either higher or lower energy, depending upon the vibrational state of the molecule under study. When the energy of the scattered radiation is less than the incident radiation it is called Stokes radiation (red shift) and when it is higher than the incident radiation it is called anti-Stokes radiation (blue shift) (Fig. 3.16). Plotting the intensity of this "shifted" light versus frequency results in a
Raman spectrum of the sample which is very specific, and chemical identification can be performed by using digital databases. Figure 3.17 shows an example of a Raman spectrum recorded on a 1.5 at% SIMFUEL electrode indicating two characteristic bands at ~ 450 (O-U stretching mode) and 1150 cm$^{-1}$ along with a broad peak between 500 and 700 cm$^{-1}$. The significance and influence of these Raman bands will be discussed in detail in Chapter 7.

![Figure 3.17 Characteristic Raman spectrum obtained on a polished 1.5 at% SIMFUEL electrode](image)

**3.5.2 Raman Experimental Details**

Raman active vibrations were excited on samples by a HeNe laser with a wavelength of 632.8 nm which produces a focused beam of ~ 2 µm diameter at the
sample surface. The Raman spectrometer was calibrated using a Si crystal standard at room temperature. The laser beam was focused onto the sample mounted on a Leica DMLM microscope with a 50x uncoated objective lens. Each spectrum was measured for an exposure time of ~45 sec over the wavenumber range 120 to 1400 cm\(^{-1}\). Repeated measurements were conducted at different locations on the electrode to ensure that bands do not show any shifts in vibrational frequencies. After the measurement, the Lorentzian peak model and a Shirley baseline correction were used to fit the Raman peaks, as will be discussed in chapter 6 and 7 in more detail.

3.6 UV-vis Spectrophotometry

3.6.1 Principles of UV-vis Spectrophotometry

Ultraviolet and visible (UV-Vis) absorption spectroscopy is the measurement of the attenuation of a beam of light by passage through a sample or after reflection from a sample surface. This absorption spectroscopy uses electromagnetic radiation between 200 nm and 800 nm and is divided into the ultraviolet (UV, 200-400 nm) and visible (VIS, 400-800 nm) regions.

Figure 3.18 shows an illustration of a UV-vis spectrophotometer consisting of a light source, a holder for the sample, and a diode array detector which allows the instrument to simultaneously detect the absorbance at all wavelengths. A beam of light generated in the source lamp travels through a small transparent container (cuvette) containing the solution requiring analysis. The intensity of the beam is measured before
(Io) and after (I) passage through the sample and the absorbance is calculated using the formula,

\[ A = \log \frac{I_0}{I} \]

(3.25)

The absorption is plotted as a function of the wavelength in an absorption spectrum and the molar absorptivity (corrected absorption value) is calculated by using the Beer-Lambert law (Equation 3.26) which gives the relationship between absorbance and concentration,

\[ A = \varepsilon c l \]

(3.26)

In equation 3.26 A is the absorbance, \( \varepsilon \) is the molar absorptivity expressed in units of \( \text{L.mol}^{-1} \text{cm}^{-1} \), \( c \) is the concentration of the sample expressed as \( \text{mol.L}^{-1} \), and \( l \) is the optical path length of the cuvette expressed in cm [17].

Figure 3.18 Illustration of a diode array UV-Vis spectrophotometer. Image source: http://cnx.org/content/m34525/latest/
This technique is based on the ability of a molecule to absorb ultraviolet and visible light due to the excitation of electrons from the outer shells to a higher energetic level. Electrons close to the atomic nucleus do not absorb the UV/Vis radiation since the input energy is insufficient to overcome local electrostatic interactions. Though the radiation initiates the excitation of $\sigma$- and $n$-electron transitions, such as $\sigma \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$, $n \rightarrow \sigma^*$ and $n \rightarrow \pi^*$ transitions (Fig 3.19), the characteristic transition always takes place from the Highest Occupied Molecular Orbital (HOMO) to the Lowest Unoccupied Molecule Orbital (LUMO) [17]. Consequently the input energy absorbs at different

![Energy Levels Diagram](image)

**Figure 3.19** Possible electronic transitions of $\sigma$, $\pi$ and $n$ electrons [18]

frequencies which are characteristic of the chemical and electronic structure of the absorbing species. An optical spectrometer records the wavelengths at which absorption occurs, together with the degree of absorption at each wavelength. The resulting spectrum is presented as a graph of absorbance (A) versus wavelength. The concentration of the
absorbing species is then obtained from calibration curves which obey the Beer-Lambert law, equation 3.26. Fig 3.20 shows an example of characteristic UV-Vis spectra recorded for increasing H$_2$O$_2$ concentrations (10$^{-7}$ -10$^{-3}$ mol.L$^{-1}$), where absorbance peaks were detected in the low 400 nm range [19]. A calibration plot (in the inset) shows an increase in absorbance with a gradual increase in peroxide concentration following the Beer-Lambert law.

![Figure 3.20 UV-Vis spectra for H$_2$O$_2$ over the concentration range 10$^{-7}$ to 10$^{-3}$ mol.L$^{-1}$. The inset shows a calibration plot [19].]

**3.6.2 UV-vis Experimental Details**

All spectrophotometric measurements were performed using a diode array spectrophotometer (BioLogic Science Instruments). The H$_2$O$_2$ concentration was determined by the Ghormley tri-iodide method in which I$^-$ is oxidized to I$_3^-$ by H$_2$O$_2$ in
the presence of ammonium molybdate as a catalyst [20]. I$_3^-$ has a maximum absorption at 350nm with a molar extinction coefficient of 25,500 mol L$^{-1}$ cm$^{-1}$ [21]. Calibration curves indicate that the detection limit for H$_2$O$_2$ is 3 x 10$^{-6}$ mol L$^{-1}$. The uncertainties in the measurement arising from sampling and instrumental errors were estimated to be ±0.2% at the lower end of the measured concentration range to ±0.05% at the higher end of the measured range. The H$_2$O$_2$ analysis was performed immediately upon termination of an experiment to minimize any decomposition of H$_2$O$_2$ in the sample vials. The final concentration for each sample was calculated by averaging the [H$_2$O$_2$] value obtained from three separate analyses.
3.7 References

Chapter 4

Electrochemical Reduction of Hydrogen Peroxide on SIMFUEL (UO₂) in Acidic pH Conditions

4.1 Introduction

While nuclear power represents a clean and safe form of energy generation it comes with the responsibility of managing the radioactive fuel waste. Internationally deep geologic disposal is the primary option for long term nuclear waste management. In the Canadian approach, used nuclear fuel bundles would be sealed in corrosion resistant containers, emplaced in a vault excavated deep underground in a stable geologic formation [1, 2]. Safety assessments conservatively assume that some containers will be emplaced with undetected defects which could allow groundwater to contact the fuel waste form and initiate its corrosion/dissolution.

Assuming that the containers remain unbreached until the β and γ-radiation fields have decayed to insignificant levels (a process which will take a few hundred years [3]) , then the primary source of oxidants will be the α-radiolysis of water,

\[ 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{H}_2 \] (4.1)

Among the several oxidants produced, H₂O₂ is considered the most likely to cause fuel corrosion, and the potential effects of this oxidant have been studied in detail [3-20]. H₂O₂ reduction on UO₂ surfaces occurs via a coupled chemical-electrochemical process
in which U$^{IV}$ − U$^{V}$ donor-acceptor sites are first chemically created on the UO$_2$ surface by H$_2$O$_2$ and subsequently destroyed electrochemically,

\[ 2U^{IV} + H_2O_2 \rightarrow 2U^{V} + 2OH^- \]  \hspace{1cm} (4.2)

\[ 2U^{V} + 2e^- \rightarrow 2U^{IV} \]  \hspace{1cm} (4.3)

Under natural corrosion conditions, reaction 4.3 is coupled to the oxidation and dissolution of UO$_2$ as UO$_2^{2+}$

\[ UO_2 \rightarrow UO_2^{2+} + 2e^- \]  \hspace{1cm} (4.4)

although it could also lead to the oxidation of H$_2$O$_2$

\[ H_2O_2 \rightarrow O_2 + 2H^+ + 2e^- \]  \hspace{1cm} (4.5)

resulting in its overall decomposition.

Based on an original suggestion by Nicol and Needes [21], Keech et al. [12] proposed that, for the low pH region (pH < 3), H$_2$O$_2$ reduction is catalyzed by a surface adsorbed U$^{V}$ species (U$^{V}$O$_2$OH$_{ads}$) created by the chemical reaction (4.2). In less acidic solutions (pH ~ 5 to 9) the U$^{V}$ state is created within the UO$_2$ matrix by incorporation of O$^{2-}$ anions at interstitial sites creating a U$^{IV}_{1.2x}$U$^{V}_{2x}$O$_{2+x}$ surface layer. This layer is considerably more stable than the adsorbed state formed in acidic solutions and can sustain H$_2$O$_2$ reduction at the diffusion-controlled limit [6, 12].

Further oxidation of this surface layer can lead to the formation of a corrosion product deposit (UO$_3$.yH$_2$O), but for pH < 6 this phase undergoes chemical dissolution (as UO$_2^{2+}$) and the UO$_2$ dissolution rate increases considerably [22]. The literature suggests that the presence of H$_2$O$_2$ at sufficient concentrations can also lead to the formation of uranyl peroxides, such as, studtite (UO$_4$.4H$_2$O) which can be the dominant secondary phase rather than schoepite (UO$_3$.2H$_2$O) [23-29]. Calorimetric calculations
[24] indicate that stutite can form in the presence of [H$_2$O$_2$] as low as 10$^{-14}$ mol/L, and it is reported to inhibit H$_2$O$_2$ reduction on fuel surfaces leading to steady-state uranium concentrations during leaching experiments [30]. However, HCO$_3^-$/CO$_3^{2-}$ can influence the stability of these phases by complexing UO$_2^{2+}$ [22], and Hanson has reported their solubility in acidic solutions [31]. In addition, these peroxy hydrates are reported to be unstable in the presence of ionizing radiation ~10$^6$ Gy (total absorbed dose) which leads to their partial amorphization and decomposition [32].

Although neutral to slightly alkaline conditions (pH 6 to 9.5) are expected to prevail under repository conditions, the possibility of producing acidic locations by UO$_2^{2+}$ hydrolysis

$$n\text{UO}_2^{2+} + y\text{H}_2\text{O} \rightarrow (\text{UO}_2)_n (\text{OH})_{y}^{(2n-y)^+} + y\text{H}^+$$  \tag{4.6}

within corrosion product deposits and flaws in the fuel surface has been considered [10-15]. While unlikely, such a possibility is difficult to rule out on a spent fuel surface which will contain noble metal particles able to enforce the separation of anodes and cathodes.

With this possibility of local acidification in mind the electrochemical reduction of H$_2$O$_2$ has been studied over the pH range 1 to 9 [12]. While this study identified a change in mechanism with pH, the details remained obscure. In the study presented here a wider range of H$_2$O$_2$ concentrations have been studied over a narrower range of pH (1 to 4). The primary goal of the study is to identify the details of this change in mechanism with pH and how it is influenced by, or dictates, the composition of the UO$_2$ surface.
4.2 Experimental

4.2.1 Electrode material

Experiments were performed on a simulated nuclear fuel (SIMFUEL). SIMFUEL is a chemical analogue of spent nuclear fuel fabricated by Atomic Energy of Canada Limited (Chalk River, Ontario, Canada). The pellets are produced by doping the UO$_2$ matrix with a series of stable elements (Ba, Ce, La, Mo, Sr, Y, Rh, Pd, Ru, Nd, Zr) in the proportions required to simulate fuels of different in-reactor burn-up [33]. In this case the matrix was doped to simulate a burn-up of 1.5 at% [33]. Doping leads to the substitution of trivalent rare-earth species for U$^{IV}$ atoms in the fluorite lattice and the creation of a corresponding number of U$^{V}$ species to maintain the charge balance. The noble metal dopants (Pd, Mo, Ru, Rh) separate as metallic particles uniformly distributed in the UO$_2$ matrix as spherical precipitates [33]. The electrodes were approximately 2 mm thick and 1.2 cm in diameter and were cut from a SIMFUEL pellet using a previously published procedure [34].

4.2.2 Electrochemical cell and equipment

All experiments were carried out in a standard three-electrode, three-compartment cell. The cell compartments were separated by glass frits to minimize contamination of the working electrode compartment. The working electrode was screwed on to the shaft of a Pine Instruments model AFASR analytical rotator and the rotation rates were varied
from 5 to 33 Hz. All potentials were measured and are quoted against a saturated calomel reference electrode (SCE, Fischer Scientific). The counter electrode was a ~ 6 cm² Pt sheet spot-welded to a Pt wire (99.9% purity, Alfa Aesar). The cell was housed in a grounded Faraday cage to minimize external sources of noise. A Solartron model 1287 potentiostat was used to record current responses as a function of applied potential and Corrware™, version 3.0, software was used to control the instrument and analyze the data. The current interrupt method (IR) was employed to compensate for potential drop due to the electrode and solution resistances.

4.2.3 Electrode polishing and solution preparation

Electrodes were prepared by polishing on wet 1200 SiC paper and rinsed with distilled deionized water. Subsequently, they were electrochemically cleaned at two different potentials, -1.5 V and -1.2 V for 5 min each (vs. SCE). This procedure removed any air formed oxides or organic contaminants. X-ray photoelectron spectroscopy (XPS) was used to investigate the chemical composition of the fuel surface after electrochemical measurements. On extraction from the cell, the electrode surface was immediately rinsed with Millipore water and air dried before loading into the XPS vacuum chamber.

Solutions used were prepared with distilled deionized water (resistivity ($\rho$) = 18.2 MΩ·cm) purified using a Millipore milli-Q-plus unit to remove organic and inorganic impurities. All experiments were performed in a 0.1 mol L⁻¹ NaCl (Caledon, >99%) solution purged with Ar gas (Praxair). The solution pH was adjusted to the desired values using a 0.1 mol L⁻¹ HCl solution, and monitored with an Orion model 720A pH
meter. Hydrogen peroxide (Fisher Scientific, 3% w/v) was added to the electrochemical cell before the start of an experiment.

4.2.4 UV/VIS spectrophotometry

The H$_2$O$_2$ concentration in the cell was determined by ultra-violet/visible spectrophotometry. All spectrophotometric measurements were performed using a BioLogic Science Instruments MOS 450 diode array UV/VIS spectrophotometer. H$_2$O$_2$ concentrations were determined using the Ghormley tri-iodide method in which ammonium molybdate is used to catalyze the oxidation of I$^-$ to I$_3^-$ by H$_2$O$_2$. The maximum absorption of I$_3^-$ was taken to occur at 350 nm with a molar extinction coefficient of 25,500 mol L$^{-1}$cm$^{-1}$ [35, 36]. The detection limit for H$_2$O$_2$ was 3 x 10$^{-6}$ mol L$^{-1}$.

4.2.5 Scanning electron microscopy (SEM)

SEM micrographs were obtained using a Hitachi S-4500 Field emission scanning electron microscope. Immediately following experimentation, samples were rinsed with Millipore water and placed into the microscope. During image collection, the electron beam potential was maintained at 10.0 kV and the working distance was 10 mm.
4.2.6 X-Ray photoelectron spectroscopy (XPS)

XPS analyses were performed on a Kratos Axis NOVA spectrometer. Spectra were collected using Al Kα-monochromatic radiation (15 mA, 14 kV) to bombard the surface with high energy monochromatic X-rays ($h\nu = 1486.6$ eV). The instrument work function was set to give a binding energy (BE) of 83.96 eV for the Au 4f$_{7/2}$ line for metallic gold and the spectrometer dispersion was adjusted to give a BE of 932.62 eV for the Cu 2p$_{3/2}$ line of metallic copper. The instrument charge neutralizer was used on all specimens. Survey spectra were recorded for the energy range 0-1100 eV with an analysis area of ~300 x 700 microns at a pass energy of 160 eV, and high resolution spectra for the U 4f, O 2p, C 1s and the U 5f valence band regions were collected with a pass energy of 20 eV. The carbon 1s line at 285 eV was used as a standard, when necessary, to correct for surface charging. Spectra were analysed using CasaXPS software (version 2.3.14).

In many previous studies, researchers have opted to deconvolute the U4f$_{7/2}$ peak to avoid the complications due to overlap of the U5f$_{7/2}$ peak with a shake-up band associated with the U4f$_{7/2}$ satellite peak [34, 37-39]. In this study, we have fitted both the two spin-orbit split peaks and the associated satellite structures following the procedure and recommendations of Schindler et al. [40] and Ilton et al [41, 42]. As discussed recently, there are advantages and disadvantages to both procedures consistent with the observations of Ilton et al. [43]: a 10-15% higher U$^{VI}$ content is observed when ignoring the satellite structures in the fitting procedure. Acknowledging these ambiguities we have
resolved the 4f spectrum into contributions from $U^{IV}$, $U^{V}$, and $U^{VI}$. Table 4.1 summarizes the fitting parameters used, where the separation between the $U4f_{7/2}$ and $U4f_{5/2}$ and

**Table 4.1** Peak binding energies used for $U$ ($4f_{7/2}$) and satellite peak positions associated with $U$ ($4f_{7/2}$)

<table>
<thead>
<tr>
<th></th>
<th>$U; 4f_{7/2}; (eV)$</th>
<th>$U; 4f_{5/2}; (eV)$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>$UO_2; Main; Peaks$</strong></td>
<td>379.9 - 381.0</td>
<td>390.8 - 391.9</td>
<td></td>
</tr>
<tr>
<td><strong>Main peak FWHM (eV)</strong></td>
<td>1.55</td>
<td></td>
<td>[44]</td>
</tr>
<tr>
<td></td>
<td>1.38</td>
<td></td>
<td>[40]</td>
</tr>
<tr>
<td></td>
<td>1.65</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Separation between $U_{7/2}$ and $U_{5/2}$ peaks (eV)</strong></td>
<td>10.9</td>
<td></td>
<td>[40]</td>
</tr>
<tr>
<td></td>
<td>10.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Peak separation between primary peaks (eV)</strong></td>
<td>$U(IV)$-$U(V)$</td>
<td>$U(V)$-$U(VI)$</td>
<td>$U(IV)$-$U(VI)$</td>
</tr>
<tr>
<td></td>
<td>0.85</td>
<td>0.85</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>0.8</td>
<td>1.0</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>0.9</td>
<td>0.8</td>
<td>1.7</td>
</tr>
<tr>
<td><strong>Separation between main peak and satellite (eV)</strong></td>
<td>$U(IV)_{5/2}$</td>
<td>$U(V)_{5/2}$</td>
<td>$U(VI)_{5/2}$</td>
</tr>
<tr>
<td></td>
<td>6.3-7.0</td>
<td>8.1</td>
<td>4, 10</td>
</tr>
<tr>
<td></td>
<td>6.3</td>
<td>8</td>
<td>4, 10</td>
</tr>
<tr>
<td></td>
<td>6.6</td>
<td>8.1</td>
<td>4, 10</td>
</tr>
</tbody>
</table>

between the deconvoluted peaks under the main 4f peak are adopted from the literature [40-43]. Following a Shirley background correction, Gaussian-Lorentzian peak shapes were used: 50% Lorentzian for the main $4f_{7/2}$ and $4f_{5/2}$ peaks and 30% Lorentizian for the satellite peaks.
4.3 Results and Discussion

4.3.1 Voltammetry

A series of voltammograms recorded in H$_2$O$_2$ – containing solutions with various pH values ranging from 1 to 3 are shown in Fig. 4.1. The various stages of reduction are numbered and the features present are consistent with previous observations [12]. The reduction current observed in region 1 (at the most negative potentials) can be attributed to H$^+$ reduction catalyzed on noble metal particles in the SIMFUEL matrix [45, 46] and therefore, as the pH is decreased, the current density increases. However, in very acidic conditions the H$^+$ reduction current is large and the hysteresis observed between the forward and reverse scans obscures the current for H$_2$O$_2$ reduction. The enhanced H$^+$ reduction current observed on the reverse scan at pH 1.0 and 1.4 indicates a sensitization of the UO$_2$ surface by the formation (forward scan) and reduction (reverse scan) of oxidized species. At pH 3, the reduction current observed in region 2 is characteristic of H$_2$O$_2$ reduction on a U$^{IV}_{1-2x}$U$^{V}_{2x}$O$_{2+x}$ surface layer formed by the injection of O$^{2-}$ anions into the UO$_2$ lattice accompanied by the creation of a U$^V$ surface species, reaction 4.2. The kinetics of H$_2$O$_2$ reduction on such a layer have been investigated in detail [6-9].
Figure 4.1 Voltammograms recorded on a 1.5 at.% SIMFUEL at 10 mV s\(^{-1}\) at an electrode rotation rate of 16.7 Hz in 0.1 mol L\(^{-1}\) NaCl containing 5 \times 10^{-3} \text{ mol L}^{-1} \text{ H}_2\text{O}_2\) at different pH values. The scans are offset by 15 mA cm\(^{-2}\).

Rotating disc studies have shown that \text{ H}_2\text{O}_2 reduction on this surface can achieve mass transport control at sufficiently negative potentials (\(\leq 0.8\text{V vs. SCE}\)) [7]. However, at pH 3 the formation of such a layer is unexpected, since it should be thermodynamically unstable in solutions with a pH < 5 [47]. Its presence would be consistent with the elevation of the pH at the electrode surface by OH\(^{-}\) production, reaction 4.2.
A separate H$_2$O$_2$ reduction pathway was observed in region 3 for pH ≤ 2.60, Fig. 4.1, attributed to H$_2$O$_2$ reduction catalyzed by the adsorbed U$^\text{V}$ surface species, (U$^{\text{V}}$O$_2$OH)$_{\text{ads}}$, formed by surface coordination with OH$^-$ [12]. It was claimed that this intermediate is unstable to electrochemical reduction, which prevents the H$_2$O$_2$ reduction current from increasing to the diffusion-controlled value. At pH 2.6, both reduction processes occur suggesting localized surface regions of low and high pH. As will be shown below, the surface of the electrode is rough allowing the convective/diffusive conditions to vary with surface location.

In support of this argument, Fig. 4.2 shows CVs recorded with and without H$_2$O$_2$ at pH = 2.6. The low background current (A) shows that any contribution from H$^+$

![Figure 4.2](image-url)

**Figure 4.2** Voltammograms recorded on a 1.5 at.% SIMFUEL at 10 mV s$^{-1}$ at an electrode rotation rate of 16.7 Hz in 0.1 mol L$^{-1}$ NaCl at pH 2.6 containing H$_2$O$_2$: (A) 0 mol L$^{-1}$; (B) 1.5 x 10$^{-3}$ mol L$^{-1}$ and (C) 5 x 10$^{-3}$ mol L$^{-1}$. The arrows indicate scan direction.
reduction is very small at this pH and confined to very negative potentials. The CV recorded at the lower [H$_2$O$_2$] shows only the current associated with region 3 while at the higher [H$_2$O$_2$] current was observed in both regions 2 and 3. The observation of a current in region 2 only at the higher [H$_2$O$_2$] is consistent with the need for a high [OH$^-$] to stabilize the catalytic U$^{IV}_{1-2x}$U$^{V}_{2x}$O$_{2+x}$ layer.

Figure 4.3 (a, b) shows background-corrected H$_2$O$_2$ reduction curves recorded at pH = 4 for two slightly different [H$_2$O$_2$] as a function of electrode rotation rate. At both concentrations, a well-developed, rotation rate-dependent, current density plateau is observed at high overpotentials suggesting H$_2$O$_2$ reduction is diffusion-controlled when the local pH becomes sufficiently high to stabilize a U$^{IV}_{1-2x}$U$^{V}_{2x}$O$_{2+x}$ surface layer. However, comparison of the plateau currents to the theoretical diffusion-limiting currents, calculated using the Levich equation [48] and a diffusion coefficient adopted from Goldik et al. [7], show deviations from the limiting current values which depend both on electrode rotation rate and [H$_2$O$_2$] (Fig. 4.4 (a, b)). As can be seen in Fig. 4.5, which plots the ratio of the measured currents to the theoretical diffusion-limited values, diffusion control is only achieved at low electrode rotation rates at both concentrations when the flux of OH$^-$ away from, or H$^+$ to, the electrode surface will be at its lowest and the surface pH at its highest. Additionally, even though the difference in [H$_2$O$_2$] in the two experiments is small, the deviation from diffusion control, indicating the onset of a kinetically-limited process, commences at a lower rotation rate and is more significant at the lower [H$_2$O$_2$] (Fig. 4.4 (b)) when the surface disturbance of pH by H$_2$O$_2$ reduction will be less marked.
Figure 4.3 Voltammograms recorded on a 1.5 at.% SIMFUEL RDE at 10 mV s\(^{-1}\) in Ar-purged 0.1mol L\(^{-1}\) NaCl solution at pH 4 in solutions containing H\(_2\)O\(_2\) (a) 6.5 × 10\(^{-4}\) mol L\(^{-1}\) and (b) 4.9 × 10\(^{-4}\) mol L\(^{-1}\). The currents have been corrected for the background current recorded in the absence of H\(_2\)O\(_2\). The arrows indicate scan direction.
Figure 4.4 Levich plots for $\text{H}_2\text{O}_2$ reduction currents recorded on a 1.5 at.% SIMFUEL RDE in Ar-purged 0.1mol L$^{-1}$ NaCl solution at pH 4 in solutions containing $\text{H}_2\text{O}_2$ (a) $6.5 \times 10^{-4}$ mol L$^{-1}$ and (b) $4.9 \times 10^{-4}$ mol L$^{-1}$. The currents have been corrected for the background current recorded in the absence of $\text{H}_2\text{O}_2$. 
The ratio of the background corrected currents ($\Delta i$) to the theoretical diffusion limiting current ($i_L$) recorded as a function of electrode rotation rates at -0.8 V in 0.1 mol L$^{-1}$ NaCl solutions for (a) pH 4; $[\text{H}_2\text{O}_2] = 6.5 \times 10^{-4}$ mol L$^{-1}$ (B) pH 4; $[\text{H}_2\text{O}_2] = 4.9 \times 10^{-4}$ mol L$^{-1}$ (C) pH 3; $[\text{H}_2\text{O}_2] = 8.3 \times 10^{-4}$ mol L$^{-1}$.

A similar set of background-corrected H$_2$O$_2$ reduction curves and a Levich plot, recorded at pH = 3 ($[\text{H}_2\text{O}_2] = 8.3 \times 10^{-4}$ mol L$^{-1}$) as a function of electrode rotation rate, are shown in Fig. 4.6. No diffusion-controlled reduction process is observed in the -0.75V to -1.1V range (Fig. 4.6 (a)) and the H$_2$O$_2$ reduction current only increases towards the diffusion-controlled limit at very negative potentials. Figure 4.6 (b) confirms this behavior, the deviation from theoretical diffusion-limiting current values indicating H$_2$O$_2$ reduction is kinetically inhibited. Although the currents are corrected for the contribution from H$^+$ reduction they will be influenced by the local pH increase associated with this.
reaction occurring in an unbuffered solution (Fig. 4.6 (a)). Thus, the large, but potential-delayed H$_2$O$_2$ reduction currents can be attributed to this pH increase and the eventual stabilization of the U$^{IV}_{1-2x}$U$^{V}_{2x}$O$_{2+x}$ layer. The ratio of the measured (at -0.8V) to the diffusion-limited current for this [H$_2$O$_2$] is included in Fig. 4.5, and it is clear that only a limited current for H$_2$O$_2$ reduction is observed and that it is only marginally-dependent on electrode rotation rate. These observations suggest the H$_2$O$_2$ reduction current is kinetically rather than diffusion-controlled at this pH and [H$_2$O$_2$]. Comparison of the three sets of data, Fig. 4.5, indicates a transition from diffusion control to kinetic control occurs as the [H$_2$O$_2$]/[H$^+$] decreases.

At an intermediate pH of 3.5 and with only slightly different [H$_2$O$_2$] a very distinct hysteresis occurs between the forward and reverse scans and both types of behavior are observed, Fig. 4.7. Comparison of Figs. 4.7 (a) and 4.7 (b) shows the transition between the two reduction mechanisms depends on pH, [H$_2$O$_2$], and the potential on the forward and reverse voltammetric scans. On the forward scan from -1.2V, alkaline conditions are initially established at the electrode surface due to H$^+$ and H$_2$O$_2$ reduction. Under these conditions the catalytic surface layer (U$^{IV}_{1-2x}$U$^{V}_{2x}$O$_{2+x}$) is formed and the H$_2$O$_2$ reduction current approaches the diffusion controlled limit. As the potential becomes more positive, this catalytic layer is destabilized due to the decreased rate of OH$^-$ production and the formation of (U$^V$O$_2$OH)$_{ads}$ occurs, at least on some areas of the electrode surface. As will be shown below, the surface is rough and hence the convective/diffusive conditions will vary somewhat from location to location on the fuel surface. Consequently, the pH will also change slightly from location to location leading
Figure 4.6 (a) Voltammograms and (b) Levich plot for H$_2$O$_2$ reduction current recorded on a 1.5 at% SIMFUEL RDE in Ar-purged 0.1 mol L$^{-1}$ NaCl solutions at pH 3 containing 8.3 x 10$^{-4}$ mol L$^{-1}$ H$_2$O$_2$. The currents have been corrected for the background current recorded in the absence of H$_2$O$_2$. The arrows indicate scan direction.
to some non-uniformity in the transition between processes. The onset of this transition in surface state accounts for the kink ($\sim -0.4V$) in $H_2O_2$ reduction current at the higher $[H_2O_2]$, Fig. 4.7 (a), and the very rapid drop in this current ($E < -0.7V$) at the slightly lower $[H_2O_2]$, Fig. 4.7 (b). This is clearly demonstrated in Fig. 4.8 (a, b) which shows scans to various anodic limits for two different electrode rotation rates in the solution containing the higher $[H_2O_2]$. The observation of hysteresis at the high rotation rate only, confirms that its development is very dependent on surface pH.

As demonstrated previously [10, 12], this $U^{V}$ intermediate becomes unstable at potentials more positive than $\sim -0.2V$ and is electrochemically oxidized and subsequently dissolved.

$$ (U^{V}O_2OH)_{ads} + H_2O \rightarrow (U^{VI}O_2(OH)_2)_{ads} + H^+ + e^- \quad (4.7) $$

$$ (U^{VI}O_2(OH)_2)_{ads} + 2H^+ \rightarrow UO_2^{2+} + 2H_2O \quad (4.8) $$

On the reverse scan from an anodic limit of $-0.1V$ the cathodic current increases slightly for $E \leq -0.2V$; i.e., when the potential becomes too negative for the electrochemical oxidation reaction 4.7. Subsequently, a low potential-independent cathodic reduction current is stabilized over a potential range which depends on $[H_2O_2]$ and electrode rotation rate. At the higher $[H_2O_2]$, Fig. 4.7 (a), once a sufficiently negative potential is achieved, the $H_2O_2$ reduction current rises steeply towards the diffusion limit for all electrode rotation rates. This rise indicates that sufficiently alkaline conditions are established at the electrode surface to stabilize a $U^{IV}_{1-2x}U^{V}_{2x}O_{2+2x}$ layer allowing the $H_2O_2$ reduction current to rise towards the diffusion-controlled limit.
Figure 4.7 Voltammograms for H₂O₂ reduction currents recorded on a 1.5 at % SIMFUEL RDE in Ar-purged 0.1M NaCl solutions at pH 3.5 containing H₂O₂ (a) 7.7 x 10⁻⁴ mol L⁻¹ and (b) 4.4 x 10⁻⁴ mol L⁻¹. The currents have been corrected for the background current recorded in the absence of H₂O₂. The arrows indicate scan direction.
Figure 4.8 Voltammograms to various anodic potential limits for $\text{H}_2\text{O}_2$ reduction currents recorded on a 1.5 at% SIMFUEL RDE in Ar-purged 0.1M NaCl at pH 3.5 containing $7.7 \times 10^{-4}$ mol L$^{-1}$ H$_2$O$_2$: (a) 5.0 Hz (b) 25 Hz. The currents have been corrected for the background current recorded in the absence of H$_2$O$_2$. The arrows indicate scan direction.

While a current close to the diffusion-controlled value is eventually achieved at all electrode rotation rates, the increase towards this value commences at lower potentials the lower the electrode rotation rate; i.e., the lower the diffusive flux of OH$^-$ from, or H$^+$ to, the electrode surface the more rapidly a high pH is established at the electrode surface. That this is the case is more clearly illustrated at the lower [H$_2$O$_2$], Fig. 4.7 (b), when the local pH will be more readily neutralized by OH$^-$/H$^+$ transport. The potential at which
the H₂O₂ reduction current begins to rise is more obviously rotation rate dependent. Additionally, considerably more negative potentials are required for the current to approach the diffusion-controlled limit. For the higher electrode rotation rates, the H₂O₂ reduction current does not approach the diffusion limit within the range of potentials investigated.

That the composition of the electrode surface is dictated by a balance between the rate of OH⁻ production by H₂O₂ reduction and the flux of OH⁻/H⁺ from/to the electrode surface is confirmed by the plot of the ratio of the measured background-corrected currents to theoretically calculated diffusion-limiting currents in Fig. 4.9. The H₂O₂ reduction current only approaches the diffusion limit when its concentration is sufficiently high that the production of OH⁻ cannot be neutralized at that pH.

**Figure 4.9** The ratio of the background corrected currents (Δi) to the theoretical diffusion limiting current (i_L) as a function of [H₂O₂] at -0.8 V in 0.1 mol L⁻¹ NaCl solutions at 3 ≤ pH ≤ 4. The lines in the figure are not fits to the data points.
4.3.2 XPS Analyses

The evidence presented above clearly demonstrates two distinct pathways for the cathodic reduction of H$_2$O$_2$ depending on the pH at the electrode surface. The kinetics and mechanism of this reaction on the U$^{IV}_{1-2x}$U$^V_{2x}$O$_{2+3x}$ surface stabilized at pH $\geq$ 5 have been studied in detail [6-9] but only a preliminary mechanism developed for the mechanism in more acidic solutions [12]. The constant current for H$_2$O$_2$ reduction observed over a wide potential range, Figs. 4.2 and 4.6, is consistent with the presence of the proposed (U$^V$O$_2$OH)$_{ads}$ surface intermediate which can either be further oxidized to soluble UO$_2^{2+}$ via reactions 4.7 and 4.8 or reduced back to the substrate UO$_2$ via reaction (9)

$$\text{(U}^V\text{O}_2\text{OH)}_{ads} + e^- \rightarrow \text{UO}_2 + \text{OH}^- \quad (4.9)$$

To investigate this mechanism in acidic solutions in more detail, potentiostatic experiments were performed at -0.2V in 0.1 mol L$^{-1}$ NaCl (pH 3.5) solution with and without added H$_2$O$_2$. The electrode was subsequently analyzed by XPS to determine the relative abundances of the three oxidation states of U (U$^{IV}$, U$^V$, U$^{VI}$) in the electrode surface.

Fig. 4.10 shows the background-corrected steady-state currents recorded over the [H$_2$O$_2$] range from 0 to 8x10$^{-3}$ mol L$^{-1}$. Steady-state was achieved in a few minutes at all
Figure 4.10 Background corrected H$_2$O$_2$ reduction currents ($\Delta i$) as a function of [H$_2$O$_2$] at pH 3.5 after applying a constant potential of -0.2 V for 1 hour concentrations. The dependence of the current on [H$_2$O$_2$] confirms that the reduction current is due to H$_2$O$_2$ reduction. The current measured in the absence of H$_2$O$_2$ is insignificant suggesting only minor anodic oxidation and dissolution of the electrode surface.

Figure 4.11 shows the high resolution XPS spectra recorded after potentiostatic oxidation in the absence and presence of H$_2$O$_2$. In the absence of H$_2$O$_2$, U$^{IV}$ is the dominant oxidation state present in the electrode surface as clearly demonstrated by the location of the satellite peak at a binding energy of 7.0 eV higher than the U 4f$_{5/2}$ peak. This confirms that little electrochemical oxidation of the UO$_2$ surface occurs at this
potential. At the intermediate [H$_2$O$_2$] the fraction of oxidized states, in particular the U$^V$ state, in the surface is significantly increased. The presence of U$^V$ is confirmed by the development of the satellite peak at a binding energy 8.1 eV above the U 4f$_{5/2}$ peak. At the higher [H$_2$O$_2$], U$^{VI}$ becomes the dominant oxidized state in the electrode surface as indicated by both the deconvolution of the two main peaks and the development of additional satellite peaks at binding energies of 4.0 eV and 10.1 eV above the U 4f$_{5/2}$ peak consistent with the literature [49-51].

Figure 4.12 shows the fractions of the individual oxidation states determined after the full range of potentiostatic experiments. While the exact amounts of individual oxidation states may be slightly suspect due to the inevitable difficulties involved in transferring electrodes from aqueous solution to the spectrometer vacuum chamber, our many previous studies have demonstrated that the trends are significant. In addition, since the analytical sampling depth is in the range of ~3nm and the oxidized surface layer will be thinner than this, the fractions should be considered illustrative rather than quantitative. The increase in extent of oxidation of the electrode surface on adding H$_2$O$_2$ is consistent with the chemical oxidation of the surface to produce adsorbed oxidized states (reaction 4.2). Additionally, the constant composition of the surface and the dominance of U$^V$ over U$^{VI}$ as the H$_2$O$_2$ reduction current increases (Fig. 4.9) can be attributed to the balance between the chemical production of the (U$^V$O$_2$OH)$_{ads}$ state, its catalysis of H$_2$O$_2$ reduction, and eventual destruction by either electrochemical reduction or further chemical oxidation to (U$^{VI}$O$_2$(OH)$_2$)$_{ads}$ and dissolution as soluble UO$_2$$^{2+}$. As noted above, the electrochemical oxidation of the chemically formed U$^V$ intermediate should be minimal at -0.2V [34]. The increased U$^{VI}$ content of the surface at the highest
Figure 4.11 Representative U 4f XPS spectra recorded on a 1.5 at% SIMFUEL electrode in pH 3.5 solution under constant potential at -0.2V for 1 h: (a) without H$_2$O$_2$ (b) with $2\times10^{-3}$ mol L$^{-1}$ and (c) $8\times10^{-3}$ mol L$^{-1}$ H$_2$O$_2$. The arrows indicate the separation between satellites and the U 4f$_{5/2}$ peak.
[H₂O₂] may indicate the increased rate of oxidation of (U⁴⁺O₂OH)ads to (U⁶⁺O₂(OH)₃)ads by H₂O₂ prior to its dissolution.

![Graph showing the fraction of surface oxidation (%) as a function of [H₂O₂] in mmol L⁻¹.](image)

**Figure 4.12** Relative percentages of the three U oxidation states as a function [H₂O₂] in 0.1 mol L⁻¹ NaCl solutions at pH 3.5 at a potential of -0.2 V for 1 hour

### 4.3.3 Scanning Electron Microscopy (SEM)

Figure 4.13 shows SEM micrographs of the freshly polished electrode surface and the electrode surface after the one hour potentiostatic treatment in solutions containing 2 x 10⁻³ and 8 x 10⁻³ mol L⁻¹ H₂O₂; i.e., at a low [H₂O₂]/[H⁺] ratio when acidic conditions will prevail at the electrode surface. The surface roughness shown in Fig. 4.12 (a) is characteristic for a polished SIMFUEL electrode surface. After potentiostatic oxidation in
Figure 4.13 SEM images collected at a magnification of 1000x on a 1.5 at.% SIMFUEL after a 1 h potentiostatic treatment in 0.1 mol L\(^{-1}\) NaCl solution at pH 3.5 containing [H\(_2\)O\(_2\)] (a) freshly polished surface (b) 2 \(\times\) 10\(^{-3}\) mol L\(^{-1}\) and (c) 8 \(\times\) 10\(^{-3}\) mol L\(^{-1}\)
the solution containing the low \([H_2O_2]\) there is no visible change in the morphology of the surface supporting the claim that at this concentration chemical dissolution is minimal and the chemical formation of \((U^{V}O_2OH)_{ads}\) is primarily balanced by its electrochemical reduction. At the higher concentration the electrode surface is considerably rougher and unevenly etched or pitted. This indicates that at this higher concentration the further oxidation/dissolution of the \((U^{V}O_2OH)_{ads}\) state occurs. The lateral variations in surface etching and pitting would be consistent with an uneven distribution of the oxidation/dissolution reaction which, at \([H_2O_2]/[H^+] \leq 1\), could lead to the coexistence of acidic and alkaline surface locations as suggested by the results in Figs. 4.2 and 4.6.

### 4.3.4 Summary

Figure 4.14 attempts to illustrate schematically the mechanisms for \(H_2O_2\) reduction operating in the two \([H_2O_2]/[H^+]\) regimes. If this ratio is > 1, then \(H_2O_2\) reduction proceeds through the chemical formation of a \(U^{IV}_{1-2x}U^{V}_{2x}O_{2+x}\) surface layer (1) in which \(O^{II}\) ions are injected into the readily-available interstitial sites in the fluorite \(UO_2\) lattice. Subsequently, this layer is reduced electrochemically (2) which involves the ejection of these \(O^{II}\) ions (3). At the neutral to alkaline conditions prevailing at the electrode surface and the potentials required for the overall \(H_2O_2\) reduction reaction to occur, the formation of \(U^{VI}\) species, which could lead to the oxidative dissolution of the \(UO_2\), does not occur. Consequently, this layer is relatively stable and, for sufficiently high \([H_2O_2]\), the current for its reduction can approach the diffusion-controlled limit.
When the $[\text{H}_2\text{O}_2]/[\text{H}^+]$ ratio is $<1$, Fig. 4.13 (b), this $\text{U}^{\text{IV}}\text{O}_{2-2x}\text{U}^{\text{V}}\text{O}_{2+x}$ layer is not stable and $\text{H}_2\text{O}_2$ reduction proceeds via the chemical formation (1) and electrochemical reduction (2) of a $(\text{U}^{\text{V}}\text{O}_2\text{OH})_{\text{ads}}$ surface intermediate. However, this intermediate can also be further chemically oxidized (3) and dissolved (4). This instability to both electrochemical reduction and chemical oxidation prevents the $\text{H}_2\text{O}_2$ reduction current from achieving the diffusion-controlled limit.

**Figure 4.14** Proposed mechanism for the reduction of $\text{H}_2\text{O}_2$ with $\text{UO}_2$ surfaces in acidic solutions (a) $[\text{H}_2\text{O}_2] \geq [\text{H}^+]$ (b) $[\text{H}_2\text{O}_2] < [\text{H}^+]$
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Chapter 5

Influence of Carbonate on the Surface Oxidation of SIMFUEL (UO$_2$) in the Presence of Dissolved Ar or 5% H$_2$/95% Ar

5.1 Introduction

The Canadian concept to ensure the long term safe disposal of used nuclear fuel is based on multiple barriers: the used fuel bundles, durable metal containers, a clay buffer which seals around the container, and a deep stable geologic environment [1]. While it can be reasonably assumed that long term containment will be achieved [2], it is judicious to assume container failure leading to the exposure of the fuel to groundwater.

The groundwater entering a failed container would be anoxic since oxidants (mainly dissolved O$_2$) trapped in the repository on sealing will be rapidly consumed by minerals (e.g., iron oxides) and biochemical reactions in the surrounding clays, and by minor corrosion of the copper container [3]. However, radiolysis of the groundwater caused by the radioactivity in the fuel can produce oxidizing conditions at the fuel surface. Under these conditions the solubility of the fuel increases by many orders of magnitude [4, 5] and fuel corrosion would be expected to accelerate.

The fuel corrosion process involves a sequence of oxidation, dissolution, and possibly, deposition reactions,

\[
\text{UO}_2 \rightarrow \text{UO}_{2+x} \rightarrow \text{UO}_2^{2+} \rightarrow \text{UO}_3.y\text{H}_2\text{O} \quad (5.1)
\]
where $\text{UO}_2^{+x}$ is a thin intermediate oxide layer [6] and $\text{UO}_3.y\text{H}_2\text{O}$ is a $\text{U}^{\text{VI}}$ deposit formed due to local super-saturation with dissolved $\text{UO}_2^{2+}$ at the fuel surface. Since, the anticipated ground water pH will be between 6 and 9 when $\text{U}^{\text{VI}}$ is at a solubility minimum, corrosion product deposits would be expected to form and to influence the corrosion rate [7-9]. In Canadian groundwater, the key constituent likely to influence fuel dissolution is $\text{HCO}_3^-/\text{CO}_3^{2-}$ ($10^{-4}$ to $10^{-3}$ mol L$^{-1}$) [10], which increases the solubility of $\text{UO}_2^{2+}$ by complexation [11] and buffers the pH.

In the presence of $\text{HCO}_3^-/\text{CO}_3^{2-}$, the rate of oxidative dissolution increases, deposition of $\text{UO}_3.y\text{H}_2\text{O}$ is prevented, and the overall corrosion reaction becomes limited by the rate of surface oxidation (to $\text{UO}_2^{+x}$). For $[\text{CO}_3^{2-}] \geq 10^{-3}$ mol L$^{-1}$, both electrochemical [6, 12, 13] and chemical studies [14-16] show that both deposition and formation of the underlying $\text{UO}_2^{+x}$ layer are prevented [14, 15] and oxidative dissolution becomes strongly promoted [13].

Within a failed and groundwater-flooded container two corrosion fronts exist, the one on the fuel surface and a second on the inner surface of the carbon steel vessel where steel corrosion is sustained by reaction with water to produce $\text{Fe}^{2+}$ and $\text{H}_2$. This introduces the possibility that the products of steel corrosion will scavenge the radiolytic oxidants (primarily $\text{H}_2\text{O}_2$) responsible for fuel corrosion. Many studies on the influence of Fe and Fe corrosion products on fuel corrosion have been published ([17] and references therein) and inevitably show that the presence of Fe suppresses fuel corrosion and radionuclide release.
There is now a considerable amount of evidence to show H$_2$ has a much larger effect on the suppression of fuel corrosion than Fe$^{2+}$ [H$_2$], and large H$_2$ pressures could develop within a failed container emplaced in a sealed repository [18, 19]. Investigations of the influence of H$_2$ on a range of used fuels (high burnup, MOX, PWR fuel), alpha-doped UO$_2$, simulated spent fuels, and undoped UO$_2$ specimens have been reviewed [20, 21]. Experiments conducted on high burnup fuel did not exhibit any enhanced fuel dissolution in the presence of H$_2$ [20, 22]. Initially, on the basis of a number of leaching studies [20, 23, 24] carried-out in the presence of H$_2$, it was proposed that the decrease in corrosion rate of UO$_2$ could be attributed to the scavenging of radiolytic oxidants by radioactively activated H$_2$. Later, Broczkowski et al. [21, 25, 26], on the basis of electrochemical studies on SIMFUEL specimens with a range of simulated burnups, demonstrated that H$_2$ oxidation on noble metal ($\epsilon$) particles galvanically coupled to the UO$_2$ matrix prevented UO$_2$ oxidation. There is also published evidence suggesting dissolved H$_2$ (4 MPa) can reduce dissolved uranyl carbonate species present in solution for T > 70°C (74 -100°C) [27, 28]. By contrast, model simulations [29, 30] indicate that HCO$_3^-$ reduces the ability of H$_2$ to inhibit fuel oxidation.

In this paper we present results on the influence of HCO$_3^-$/CO$_3^{2-}$ on the corrosion of 1.5 at% SIMFUEL in H$_2$O$_2$-containing solutions, using electrochemical methods and X-ray photoelectron spectroscopy (XPS).
5.2 Experimental Details

5.2.1 Electrode Materials

Experiments were conducted on a 1.5 at% SIMFUEL fabricated by Atomic Energy of Canada Limited (Chalk River, Ontario). SIMFUEL is a simulated chemical fuel, produced by doping UO$_2$ with eleven stable elements (Y, La, Ce, Mo, Sr, Ba, Rh, Zr, Ru, Nd, Pd) in the proportions required to simulate spent fuel of a specific burnup. The noble metal dopants (Mo, Rh, Pd, Ru) are unstable as oxides and uniformly distributed in the UO$_2$ matrix as noble metal ($\varepsilon$) particles [31]. The microstructure of the material is typical of CANDU fuel with grains 8-15 $\mu$m in size and a density $\sim 97\%$ of the theoretical value. The electrodes used were $\sim 2$ mm thick and 1.2 cm in diameter and were prepared from pellets using a procedure described in detail elsewhere [9].

5.2.2 Electrochemical Cell and Equipment

A standard three compartment glass cell was employed in all experiments. The compartments were separated by fine glass frits to minimize contamination of the working electrode from the counter and the reference electrodes. The working electrode was a 1.5 at% SIMFUEL disc, set in resin to expose only one flat face to the solution. A Luggin capillary was used to minimize any ohmic potential drop between the working and reference electrodes. The reference electrode was a commercially available saturated calomel electrode (SCE, Fischer Scientific). The counter electrode was a Pt foil,
with a surface area of ~ 6 cm$^2$, spot-welded to a Pt wire (99.9% purity, Alfa Aesar). All potentials were measured, and are quoted, against the SCE scale. The cell was housed in a grounded Faraday cage to minimize interference from external sources of noise. A Solartron Model 1287 potentiostat was used to control experiments and record electrochemical data. Corrware™ software (supplied by Scribner and Associates) was used to control instrumentation.

5.2.3 Electrode Polishing and Solution Preparation

Electrodes were manually polished (wet) with 1200 grit SiC paper and polishing residue was removed by sonication with deionized water before each experiment. Any air-formed oxides were reduced at a cathodic potential of -1.5 V (vs. SCE) applied for 5 min before each experiment. On removal from the electrochemical cell, the electrode was rinsed with deionized water and air dried prior to analyzing by X-ray photoelectron spectroscopy (XPS).

Solutions were prepared using distilled deionized water purified using a NANOpure Diamond UV ultrapure water system from Barnstead International which removes organic and inorganic impurities ($\rho = 18.2$ MΩ cm). Experiments were carried out in a 0.1 mol L$^{-1}$ NaCl (Caledon, > 99%) solution purged with UHP Ar or 5% H$_2$/95% Ar gas (Praxair) with and without added HCO$_3^-$ /CO$_3^{2-}$. Solutions were purged for a minimum of an hour prior to the start of an experiment to minimize dissolved O$_2$ levels. The 5 x 10$^{-2}$ M HCO$_3^-$ /CO$_3^{2-}$ solution was prepared with Na$_2$CO$_3$ and NaHCO$_3$ (Caledon, > 99%) and the pH adjusted to ~9 (when required) using NaOH and an Orion Model
720A pH meter. Stock solutions of H$_2$O$_2$ were prepared using an appropriate amount of 3% w/v solution (Fisher Scientific) and the desired cell concentration ($10^{-8}$ to $10^{-3}$ mol L$^{-1}$) was achieved by adding the required amount of this solution into the electrolyte. The H$_2$O$_2$ concentration used was determined by ultra-violet/visible spectrophotometry.

### 5.2.4 Experimental Procedure

The corrosion potential ($E_{CORR}$) measurements were performed at ambient temperature either on a bench top in a grounded Faraday cage or in a grounded Ar-purged anaerobic chamber (Canadian Vacuum Systems Ltd.). This chamber is maintained at a positive pressure (2-4 mbar) with [O$_2$] < 1 ppm, analyzed with an oxygen probe. $E_{CORR}$ was monitored continuously, except for brief periods during which linear polarization resistance ($R_p$) measurements were conducted. $R_p$ scans were performed by sweeping the potential ±10 mV from $E_{CORR}$ at a scan rate of 0.1 mV s$^{-1}$ with IR compensation. This method was used to follow the trends in the corrosion rates as a function of [H$_2$O$_2$]. Each measurement required around 10 minutes.

When the analysis of any contribution of analyte diffusion was required, forced convection was introduced by placing the cell on an external magnetic stirrer and stirring at a constant rate.
5.2.5 UV/VIS spectrophotometry

Spectrophotometric measurements were carried out using a BioLogic Science Instruments MOS UV/VIS spectrophotometer. The \( \text{H}_2\text{O}_2 \) concentrations were analyzed using the Ghormley tri-iodide method in which ammonium molybdate catalyzed the oxidation of \( \Gamma^- \) to \( \text{I}_3^- \) by \( \text{H}_2\text{O}_2 \). The \( \text{I}_3^- \) produced has a maximum absorption at 350 nm with a molar extinction coefficient of 25,500 mol \( \text{L}^{-1}\text{.cm}^{-1} \). Calibration curves indicate that the lower detection limit for \( \text{H}_2\text{O}_2 \) is \( 3 \times 10^{-6} \) mol \( \text{L}^{-1} \) [32, 33].

5.2.6 XPS Surface Analysis

A Kratos Axis Ultra spectrometer was used to record XPS spectra on all the samples. Spectra were excited using an Al \( \text{K}_\alpha \) (15mA, 14 kV) monochromatic high energy \( (h\nu = 1486.6 \text{ eV}) \) radiation source. The spectrometer work function was set to give a value of 83.96 eV for the binding energy (BE) of the Au \( (4f_{7/2}) \) line of metallic gold. The instrument was calibrated to give a BE of 932.62 eV for the Cu \( 2p_{3/2} \) line of copper metal. Survey spectra were collected using a 160 eV pass energy with an X-ray spot size \( \approx 300 \times 700 \text{ microns} \). Core level spectra for U \( 4f \), O \( 1s \), C \( 1s \) and the U \( 5f \) valence band regions were collected at a lower pass energy of 20 eV with a step size of 0.05 eV.

The instrument charge neutralizer was used for all analyses with a filament current of 1.6 A and a charge balance of 2.4 V. The carbon \( 1s \) peak at 285.0 eV was used as a standard, when required, to correct for surface charging. All spectra were analyzed using CasaXPS software (version 2.3.14) and involved a 50% Gaussian and 50%
Lorentzian fitting routine with a Shirley background correction. The procedure used to deconvolute the U4f spectra into contributions from U^{IV}, U^{V}, and U^{VI} has been described elsewhere [34-37]. The satellite structures close to the U4f_{5/2} peak, and the valence band region were used to check the validity of the spectral fit.

5.3 Results and Discussion

The influence of H$_2$O$_2$ on the oxidative dissolution of UO$_2$ was studied in Ar-purged solution with and without added HCO$_3^-$/CO$_3^{2-}$. Prior to the first H$_2$O$_2$ addition $E_{\text{CORR}}$ was allowed to stabilize, and further additions were made only after $E_{\text{CORR}}$ achieved a steady-state value. Following completion of the $E_{\text{CORR}}$ measurement at the final [H$_2$O$_2$], the electrode was transferred to a cell containing no H$_2$O$_2$ and cathodic stripping voltammetry (CSV) performed. A similar set of experiments was performed and the electrode subsequently removed and analyzed by XPS.

In the Ar-purged solution containing HCO$_3^-$/CO$_3^{2-}$ the $E_{\text{CORR}}$ value measured prior to H$_2$O$_2$ addition, Fig. 5.1 (b), was lower than that measured in the solution without HCO$_3^-$ /CO$_3^{2-}$, Figs. 1 ((a) and (b)), suggesting the surface is “chemically cleaned”; i.e., more reduced. The addition of $< 10^{-7}$ mol L$^{-1}$ H$_2$O$_2$ had no observable influence on $E_{\text{CORR}}$, Fig. 5.1 (a). Subsequent additions to higher concentrations lead to increases in $E_{\text{CORR}}$ to higher steady-state values which depended on carbonate concentration. This dependence of $E_{\text{CORR}}$ on [H$_2$O$_2$] suggests the UO$_2$ surface becomes progressively more oxidized as [H$_2$O$_2$] increases. The lack of sensitivity of $E_{\text{CORR}}$ to [H$_2$O$_2$] below $10^{-7}$ mol L$^{-1}$ is in
contrast to previous experiments conducted at 60°C [26] in which $E_{\text{CORR}}$ responded to $\text{H}_2\text{O}_2$ additions in the concentration range $10^{-11}$ to $10^{-10}$ mol L$^{-1}$.

Figure 5.1 $E_{\text{CORR}}$ as a function of time for different $[\text{H}_2\text{O}_2]$ obtained on a 1.5 at. % SIMFUEL electrode in Ar-purged 0.1 mol L$^{-1}$ NaCl (pH ~ 9) (a) without and (b) with 0.05 mol L$^{-1}$ HCO$_3^-$ /CO$_3^{2-}$.
A similar set of experiments in a solution containing 0.05 mol L\(^{-1}\) HCO\(_3\)/CO\(_3^{2-}\), Fig. 5.1 (b), showed little response of E\(_{\text{CORR}}\) up to a concentration of 8.6 x 10\(^{-6}\) mol L\(^{-1}\). This lack of response suggests either the UO\(_2\) is not oxidized in the presence of these low [H\(_2\)O\(_2\)] or, alternatively, oxidized to soluble U\(^{VI}\) species complexed by carbonate (UO\(_2\)(CO\(_3\))\(_x\)(2-x)+) and dissolved, thereby, maintaining the electrode surface unoxidized. Previous studies [6, 26, 38] have shown that the extent of oxidation of the surface (to U\(^{IV}\)1-2xU\(^{V}\)2xO\(_2+x\)) is proportional to the E\(_{\text{CORR}}\) over the potential range -0.4V to ~ 0V in the absence of HCO\(_3\)/CO\(_3^{2-}\).

A second set of experiments in solutions with and without HCO\(_3\)/CO\(_3^{2-}\) was conducted inside an anaerobic chamber to avoid any possible influence of dissolved O\(_2\) which could be present in comparable concentrations to that of H\(_2\)O\(_2\) in bench top experiments. For [H\(_2\)O\(_2\)] ≤ 10\(^{-5}\) mol L\(^{-1}\) similar responses of E\(_{\text{CORR}}\) to H\(_2\)O\(_2\) additions were observed, E\(_{\text{CORR}}\) increasing with [H\(_2\)O\(_2\)] in the absence of HCO\(_3\)/CO\(_3^{2-}\), Fig. 5.2 (a). When HCO\(_3\)/CO\(_3^{2-}\) was present E\(_{\text{CORR}}\) increased only slightly with H\(_2\)O\(_2\) addition, Fig. 5.2 (b), and steady-state was commonly not achieved, which could reflect a slow oxidation of the UO\(_2\) surface. This behavior is perhaps not surprising since the carbonate concentration was only 0.01 mol L\(^{-1}\) in this experiment (compared to 0.05 mol L\(^{-1}\) in the bench top experiment, 5.1 (b)).

In the anaerobic chamber experiments the [H\(_2\)O\(_2\)] was increased to > 10\(^{-4}\) mol L\(^{-1}\), with E\(_{\text{CORR}}\) becoming independent of H\(_2\)O\(_2\) at [H\(_2\)O\(_2\)] ≥ 10\(^{-5}\) mol L\(^{-1}\), irrespective of whether HCO\(_3\)/CO\(_3^{2-}\) was present or not. A similar independence of E\(_{\text{CORR}}\) on [H\(_2\)O\(_2\)] was noted previously [39]. Also Wren et al. [40] observed a similar trend from a dependence on [H\(_2\)O\(_2\)] (produced by \(\alpha\)-radiolysis) at low values to independence at high
Figure 5.2 $E_{\text{CORR}}$ as a function of time for different [H$_2$O$_2$] recorded on a 1.5 at. % SIMFUEL electrode in 0.1 mol L$^{-1}$ NaCl (a) without carbonate (stirred solution); (b) with 0.01 mol L$^{-1}$ HCO$_3^-$ /CO$_3^{2-}$ (unstirred solution) (pH ~ 9.5). These experiments were conducted in an anaerobic chamber.
values. This independence was attributed to a condition of redox buffering in which the surface is oxidized to U$^{VI}$ and both UO$_2$ corrosion and H$_2$O$_2$ decomposition are occurring at rates determined by the rate of release of U$^{VI}$ to solution. In the absence of HCO$_3^-$ /CO$_3^{2-}$ this release would be expected to be slow but accelerated when carbonate is present.

Figure 5.3 summarizes the E$_{CORR}$ values measured in the anaerobic chamber experiments. For [H$_2$O$_2$] in the range 10$^{-6}$ mol L$^{-1}$ to 10$^{-5}$ mol L$^{-1}$ the E$_{CORR}$ values differ depending on whether HCO$_3^-$ /CO$_3^{2-}$ is present but at higher concentrations become independent of the presence of HCO$_3^-$ /CO$_3^{2-}$. Figure 5.4 shows linear polarization resistance (R$_p$) values measured in these experiments. At [H$_2$O$_2$] < 10$^{-6}$ mol L$^{-1}$, for which only data in the presence of HCO$_3^-$ /CO$_3^{2-}$ is available, the increase in E$_{CORR}$, Figure 5.3, is accompanied by a slight decrease in R$_p$, indicating an increase in the rate of interfacial electrochemical reactions. The two feasible reactions are; H$_2$O$_2$-driven corrosion of UO$_2$ and the decomposition of H$_2$O$_2$ to O$_2$ and H$_2$O.

Over the [H$_2$O$_2$] range 10$^{-6}$ mol L$^{-1}$ to ~ 2.5 x 10$^{-5}$ mol L$^{-1}$, the R$_p$ value is significantly lower in the carbonate solution despite the fact E$_{CORR}$ is more positive in the carbonate-free solution. A possibility is that, in the presence of HCO$_3^-$ /CO$_3^{2-}$ the corrosion of UO$_2$ is accelerated leading also to an increased rate of H$_2$O$_2$ decomposition on the less oxidized UO$_2$ surface. The reaction of H$_2$O$_2$ with UO$_2$ in a carbonate-containing solution is complex with a mixed carbonate-peroxide complex (U$^V$O$_2$ (HCO$_3$)(H$_2$O$_2$)$_{ads}$) thought to be involved in H$_2$O$_2$ reduction [13].

The major transition in E$_{CORR}$ to ~ 0.1 V, which occurs both in the presence and absence of HCO$_3^-$ /CO$_3^{2-}$ is accompanied by a major decrease in R$_p$ to a value which does
**Figure 5.3** $E_{\text{CORR}}$ as a function of $[\text{H}_2\text{O}_2]$ recorded on a 1.5 at % SIMFUEL in Ar-purged 0.1 mol L$^{-1}$ NaCl solution at pH~9.5 (red) with 0.01 mol L$^{-1}$ carbonate and (black) without carbonate.

**Figure 5.4** $R_p$ values as a function of $[\text{H}_2\text{O}_2]$ recorded on a 1.5 at % SIMFUEL in Ar-purged 0.1 mol L$^{-1}$ NaCl solution at pH~9.5 with 0.01 mol L$^{-1}$ carbonate (red) and (black) without carbonate.
not depend on either the presence of carbonate or \([\text{H}_2\text{O}_2]\). An independence of the rate of interfacial charge transfer (proportional to \(R_p^{-1}\)) on \([\text{H}_2\text{O}_2]\) would be consistent with a condition of redox buffering by \(\text{H}_2\text{O}_2\) decomposition, since the two half reactions involved,

\[
\begin{align*}
\text{H}_2\text{O}_2 + 2\text{e}^- & \rightarrow 2\text{OH}^- \\
\text{H}_2\text{O}_2 & \rightarrow \text{O}_2 + 2\text{H}^+ + 2\text{e}^-
\end{align*}
\]  

(5.2)

(5.3)

have equal but opposite equilibrium potential dependencies on \([\text{H}_2\text{O}_2]\) [39]. However, it is not consistent with the claim that the rate of this decomposition reaction is controlled by the rate of release of \(\text{U}^{\text{VI}}\) species from the electrode surface as previously claimed [39]. This release reaction would be expected to be accelerated by the presence of carbonate, a strong complexant for \(\text{U}^{\text{VI}}\) species (as \(\text{UO}_2^{2+}\)),

\[
\text{UO}_2^{2+} + x\text{CO}_3^{2-} \rightarrow \text{UO}_2(\text{CO}_3)_x^{(2-x)+}
\]

(5.4)

leading to an increased rate of \(\text{H}_2\text{O}_2\) decomposition by the coupling of reactions 5.2 and 5.3. The similarity in \(R_p\) values measured in solutions with and without \(\text{HCO}_3^-/\text{CO}_3^{2-}\) shows this is not the case. Previous studies on the anodic dissolution of \(\text{UO}_2\) (1.5at\% SIMFUEL) in carbonate-containing solutions [10] shows a negligible dependence of the anodic dissolution current on \([\text{H}_2\text{O}_2]\) at an applied potential equal to the \(E_{\text{CORR}}\) observed in these experiments (~ 0.1 V). These electrochemical results suggest that the corrosion rate of \(\text{UO}_2\) at an \(E_{\text{CORR}} = 0.1\) V is controlled by the rate of production of \(\text{U}^{\text{VI}}\) species not
their rate of release to solution. This rate would be expected to be independent of the presence of $\text{HCO}_3^-/\text{CO}_3^{2-}$.

Figure 5.5 shows SEM micrographs of the electrode surface recorded before and after the experiments performed in the anaerobic chamber (Fig. 5.2). No significant changes in surface morphology are apparent demonstrating that only minor corrosion occurred irrespective of whether $\text{HCO}_3^-/\text{CO}_3^{2-}$ was present or not.

Figure 5.6 shows the response of $E_{\text{CORR}}$ to $\text{H}_2\text{O}_2$ additions in solutions purged with 5% $\text{H}_2/\text{Ar}$. In this case, in the absence of $\text{HCO}_3^-/\text{CO}_3^{2-}$, Fig. 5.6 (a) $E_{\text{CORR}}$ immediately increases for $[\text{H}_2\text{O}_2] \leq 10^{-7}$ mol L$^{-1}$, but then begins to decrease again. Previous experiments at higher temperature (60°C) [26] indicate that this decrease in $E_{\text{CORR}}$ can be attributed to the consumption of $\text{H}_2\text{O}_2$ by reaction with dissolved $\text{H}_2$ primarily by radical reactions catalyzed on the surface of the noble metal ($\epsilon$) particles in the SIMFUEL [26]. At 60°C it was demonstrated that a concentration ratio, $[\text{H}_2]/[\text{H}_2\text{O}_2]$ of $\geq 10^6$ M was required to completely inhibit oxidation of the $\text{UO}_2$ surface by $\text{H}_2\text{O}_2$. In these experiments $E_{\text{CORR}}$ was not followed for a sufficient period of time at these low $[\text{H}_2\text{O}_2]$ to determine whether the value measured prior to $\text{H}_2\text{O}_2$ addition would eventually be re-established; i.e., whether a dissolved $[\text{H}_2] \sim 10^{-4}$ mol L$^{-1}$ was sufficient to inhibit surface oxidation for $[\text{H}_2\text{O}_2] \leq 10^{-7}$ mol L$^{-1}$.

Further increases in $[\text{H}_2\text{O}_2]$ in the absence of $\text{HCO}_3^-/\text{CO}_3^{2-}$ lead to increased $E_{\text{CORR}}$ values which are maintained for substantially longer periods, although even at $[\text{H}_2\text{O}_2] \sim 10^6$ mol L$^{-1}$ there is some indication that $E_{\text{CORR}}$ is slowly decreasing indicating the catalyzed consumption of $\text{H}_2\text{O}_2$ by reaction with $\text{H}_2$ and a decrease in extent of oxidation of the $\text{UO}_2$ surface. Even at $[\text{H}_2\text{O}_2]$ in the range $10^{-6}$ to $10^{-5}$ mol L$^{-1}$ the
**Figure 5.5** SEM micrographs obtained on completion of the $E_{\text{CORR}}$ measurements (shown in Fig. 5.2) (a) freshly polished surface; (b) after the experiment without carbonate; (c) after the experiment with carbonate

The response of $E_{\text{CORR}}$ to the presence or absence of convection indicates that the $[\text{H}_2\text{O}_2]$ is locally depleted at the electrode surface in the absence of convection; i.e., when the
Figure 5.6 $E_{\text{CORR}}$ as a function of time for different [H$_2$O$_2$] obtained on a 1.5 at. % SIMFUEL electrode in 5% H$_2$/95% Ar-purged 0.1 mol L$^{-1}$ NaCl (pH ~ 9) (a) without and (b) with 0.05 mol L$^{-1}$ HCO$_3^-$ /CO$_3^{2-}$
stirring is turned off. This sensitivity to the local \([\text{H}_2\text{O}_2]\) was observed previously in thin-layer experiments in which the local concentration of \(\text{H}_2\text{O}_2\) was generated by \(\alpha\)-radiolysis [40]. Since these referenced experiments were conducted on \(\text{UO}_2\) not SIMFUEL this sensitivity to local \([\text{H}_2\text{O}_2]\) can be considered a feature of the \(\text{UO}_2\) surface and not dependent on the presence of noble metal particles.

When \(\text{HCO}_3^-/\text{CO}_3^{2-}\) is present in the solution, \(E_{\text{CORR}}\) does not increase significantly up to a concentration of \([\text{H}_2\text{O}_2] \leq 10^{-6} \text{ mol L}^{-1}\), Fig. 5.6 (b). At higher \([\text{H}_2\text{O}_2]\), \(E_{\text{CORR}}\) begins to increase, indicating irreversible oxidation of the \(\text{UO}_2\) surface. However, the time-dependent behaviour at \([\text{H}_2\text{O}_2] = 10^{-5} \text{ mol L}^{-1}\) can be contrasted to that observed in Ar-purged solution at approximately the same \([\text{H}_2\text{O}_2]\) \((8.6 \times 10^{-6} \text{ mol L}^{-1})\), Fig. 5.1(b). In the Ar-purged solution, \(E_{\text{CORR}}\) rises steadily to a steady-state value > 0V, indicating irreversible oxidation of the \(\text{UO}_2\) surface. By contrast, in \(\text{H}_2/\text{Ar}\)-purged solution, \(E_{\text{CORR}}\) initially increases before eventually decreasing towards a much lower steady-state value (< - 0.1V). This transient behaviour suggests that while the added \(\text{H}_2\text{O}_2\) may initially oxidize the surface, its consumption by reaction with \(\text{H}_2\) eventually leads to a decrease in extent of oxidation of the surface. Such transient behaviour was much more marked at 60°C even at considerably lower \([\text{H}_2\text{O}_2]\) [26]. Similar transient behaviour was observed at 60°C on a SIMFUEL not containing noble metal \((\varepsilon)\) particles, consistent with the \(\alpha\)-radiolysis experiments [40], and suggesting a similar reversible oxidation of the \(\text{UO}_2\) is possible on the \(\text{UO}_2\) surface itself and does not require catalysis by noble metal particles. This was attributed to the ability of dissolved \(\text{H}_2\), when present in sufficient concentration, to scavenge the \(\text{OH}^*\) radicals produced during \(\text{H}_2\text{O}_2\) oxidation of the \(\text{UO}_2\) surface [41].
Figure 5.7 summarizes the final steady-state $E_{\text{CORR}}$ values as a function of $[\text{H}_2\text{O}_2]$ for the experimental results plotted in Figs. 5.1 and 5.6. The open and closed data points represent the values in solutions with and without carbonate, respectively. The full and dashed lines show the $E_{\text{CORR}}$ values recorded in the individual experiments prior to the addition of $\text{H}_2\text{O}_2$.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.7}
\caption{Steady state $E_{\text{CORR}}$ values for various $[\text{H}_2\text{O}_2]$ obtained on a 1.5 at\% SIMFUEL electrode (from Figs. 5.1 and 5.6) in either Ar or 5\% $\text{H}_2$/95\% Ar-purged solutions with (open data points) and without carbonate (closed data points).}
\end{figure}
Figure 5.8 shows CSV’s recorded once $E_{\text{CORR}}$ achieved the final steady-state value after the full sequence of H$_2$O$_2$ additions. In Ar-purged solutions there is a significant difference in the cathodic currents recorded prior to water reduction ($E \leq -1.0\text{V}$). In the absence of HCO$_3^-$/CO$_3^{2-}$ a substantial current for the reduction of a surface layer of corrosion product (UO$_{2+x}$/UO$_3$yH$_2$O) is observed. When no HCO$_3^{2-}$/CO$_3^{2-}$ is present only a very shallow reduction process attributable to the reduction of $U^V$ present in the SIMFUEL as a consequence of the RE$^{\text{III}}$ doping of the UO$_2$ matrix is observed [26]. This indicates no significant accumulation of corrosion product occurs on the UO$_2$ surface. However, after H$_2$O$_2$ addition to the H$_2$/Ar-purged solution no current attributable to the reduction of corrosion product is observed, confirming that significant H$_2$O$_2$ oxidation of the surface was avoided in the presence of dissolved H$_2$, only reduction of the matrix $U^V$ being observed.

A further series of experiments was performed for all four conditions in which $E_{\text{CORR}}$ was measured before and after a single addition of H$_2$O$_2$. As in the previous experiments (described above) $E_{\text{CORR}}$ was allowed to achieve a steady-state prior to the addition of H$_2$O$_2$. On completion of the experiment the electrode was removed and analyzed by XPS. A series of these experiments was performed for each of the solutions used (above) for different [H$_2$O$_2$], Figs. 5.9 ((a) to (d)). In these figures the time of addition of the H$_2$O$_2$ is indicated by the arrow. The final $E_{\text{CORR}}$ values achieved are compared to those recorded in the experiments preceding the CSV measurements in Fig. 5.10, showing that while the time-dependent responses may vary, the final $E_{\text{CORR}}$ values are generally similar. The generally small differences observed may partially reflect uncertainties in [H$_2$O$_2$] in dilute solutions. Figure 5.11 shows a comparison of the
final steady-state $E_{\text{CORR}}$ values for the four experiments compared in Fig. 5.9, confirming that the trends in the four sets of conditions are similar to those in the experiments followed by CSVs.

**Figure 5.8** CSVs recorded on a 1.5 atom % SIMFUEL electrode after the final $E_{\text{CORR}}$ measurement in the experiments shown in Fig 5.1 and 5.6 (a) Ar-purged solution with/without carbonate (b) 5% H$_2$/95% Ar-purged solution with/without carbonate
Figure 5.9 $E_{\text{CORR}}$ recorded on a 1.5 atom % SIMFUEL electrode before and after $\text{H}_2\text{O}_2$ addition and prior to XPS analyses in (a, b) Ar and (c, d) 5% $\text{H}_2$/95% Ar-purged solution. The time at which $\text{H}_2\text{O}_2$ was added in individual experiments is indicated by the arrows.
Figure 5.10 Comparison of steady-state $E_{\text{CORR}}$ values measured on a 1.5 at% SIMFUEL electrode at various $[\text{H}_2\text{O}_2]$ from Figs. 5.1 and 5.6: (a) Ar or (b) 5% H$_2$/95% Ar-purged with (triangular data points) and without carbonate (squared data points) in solution.
Figure 5.11 Comparison of final steady-state $E_{\text{CORR}}$ values recorded on a 1.5 at% SIMFUEL electrode at various $[\text{H}_2\text{O}_2]$ prior to XPS analyses.

Figure 5.12 compares the atomic fractions of oxidized states (i.e., $(U^V + U^{VI})/U_{\text{total}}$) as a function of $[\text{H}_2\text{O}_2]$ for all four conditions. In the Ar-purged solutions, the fractions measured when $\text{HCO}_3^-/\text{CO}_3^{2-}$ is present are considerably lower than those measured when no carbonate is present. This suppression corresponds to the $E_{\text{CORR}}$ range $\sim$-0.3V to 0V (Fig. 5.11) and confirms that the extent of surface oxidation was considerably lower in the presence of carbonate. This is consistent with the absence of any current for corrosion product reduction in the CSV (Fig. 5.8 (a)). When H$_2$ is present, the extent of surface oxidation, Fig. 5.12, is further suppressed especially if carbonate is present, when significant oxidation of the surface is only observed for $[\text{H}_2\text{O}_2] \geq 10^{-5}$ mol L$^{-1}$.
The suppression of surface oxidation in the presence of $\text{HCO}_3^-$/$\text{CO}_3^{2-}$ could be attributed to an ability of these anions to block the sites used in $\text{H}_2\text{O}_2$ reduction in the $E_{\text{CORR}}$ range -0.3V to 0V, thereby inhibiting both UO$_2$ corrosion and H$_2$O$_2$ decomposition. However, if this was the case the rate of electron transfer reactions ($R_p^{-1}$) would decrease, whereas it increases. This indicates that the primary function of $\text{HCO}_3^-$/$\text{CO}_3^{2-}$ is to accelerate corrosion by maintaining a surface free of corrosion products.
Whether or not this also leads to an increase in $\text{H}_2\text{O}_2$ decomposition cannot be determined in these experiments. When dissolved $\text{H}_2$ is present the suppression of surface oxidation can be attributed to the ability of $\text{H}_2$ to act as a reductant as previously demonstrated [25, 26]. This can be primarily attributed to the activation of $\text{H}_2$ (by dissociation to form surface absorbed $\text{H}$ atoms) catalyzed by the noble metal particles present in the SIMFUEL.

For a sufficiently high $[\text{H}_2\text{O}_2] (\geq 10^{-5} \text{ mol L}^{-1})$ the ability of $\text{H}_2$ to influence the oxidation of the surface is lost. At these concentrations the $E_{\text{CORR}}$ is in the region 0 to 0.1V and the value of $R_P$ decreases substantially and becomes independent of the present/absence of $\text{HCO}_3^-/\text{CO}_3^{2-}$. The XPS analyses confirm the surface is extensively oxidized and it is not presently clear why electron transfer reactions are not faster when $\text{HCO}_3^-/\text{CO}_3^{2-}$ is present when $\text{U}^{VI}$ would be expected to be more rapidly dissolved.

5.4 Summary

The combined effects of dissolved $\text{H}_2$ and $\text{H}_2\text{O}_2$ on the surface oxidation of 1.5 at% SIMFUEL electrodes was studied with and without $\text{HCO}_3^-/\text{CO}_3^{2-}$ present in the solution. Suppression of $E_{\text{CORR}}$ at small $[\text{H}_2\text{O}_2]$ shows that $\text{H}_2$ is catalytically active under ambient conditions and in the presence of carbonate. However, this activity depends on the $[\text{H}_2\text{O}_2]$. Compared to previous experiments conducted at higher temperatures the ability of $\text{H}_2$ to suppress oxidation by $\text{H}_2\text{O}_2$ is less marked.

The presence of $\text{HCO}_3^-/\text{CO}_3^{2-}$ keeps the electrode surface unoxidized by either increasing the rate of dissolution of $\text{UO}_2$, as $\text{UO}_2(\text{CO}_3)^{(2-x)+}$, by adsorption on active sites
used for H_2O_2 reduction. Polarization resistance measurements indicate the primary influence is on the anodic dissolution reaction.

In the presence of HCO_3^−/CO_3^{2−} and H_2 oxidation of the surface by H_2O_2 appears to be reversible. On H_2O_2 addition at a sufficient concentration oxidation occurs rapidly but then reverses. This can be attributed to either H_2 oxidation (H_2 ↔ H^+) on noble metal particles or acceleration of U^{VI} dissolution in carbonate solution. The absence of oxidation is confirmed by XPS analyses. For [H_2O_2] > 10^{-5} mol.L^{-1} the surface becomes irreversibly oxidized even in the presence of both HCO_3^−/CO_3^{2−} and H_2.
5.5 References


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Chapter 6

Surface and Electrochemical Characterization of Rare-Earth Oxide
(Y$_2$O$_3$)/Metal Particle (Pd) Doped Uranium Dioxide

6.1 Introduction

A major issue in the nuclear industry is how to minimize the potential impact of hazardous radioactive spent-fuel on the environment. The solutions proposed by different countries vary; some planning to re-process the used nuclear fuel whereas others, including Canada, plan direct disposal in a deep geologic repository. This repository will be constructed 500 to 1000 m deep in a stable geologic location and would employ a multi-barrier approach to contain radionuclides, comprising the waste form itself, a metal container, a clay buffer compacted around the container, repository sealing materials, and the geosphere [1-3].

The spent-fuel has a very low solubility in the reducing groundwater expected to prevail at a repository depth of $\geq$ 500 m. However, radioactive decay processes within the fuel will cause water radiolysis to produce reactive species (H$_2$O$_2$, H$_2$, HO’ etc) [1]. Since the molecular H$_2$ produced should have a low reactivity, oxidizing conditions at the UO$_2$ surface are expected. Consequently, H$_2$O$_2$, expected to be the most stable radiolytic oxidant, could promote corrosion of the UO$_2$ [4], especially when the UO$_2^{2+}$ complexing agent HCO$_3^-$/CO$_3^{2-}$ is present in the groundwater [5-8].
While the establishment of oxidizing conditions provides the primary driving force, the corrosion performance of the fuel is strongly influenced by the fission products produced in the fuel matrix during in-reactor burnup. The composition of fission products is determined by the initial enrichment of the fuel and its irradiation history. The typical burn-up range for CANDU fuel is 120 to 320 MWh/kgU [3] but is significantly higher for LWR/PWR fuel [9, 10]. Consequently, used nuclear fuel will consist of ~95% UO₂, with the remaining 5% being radioactive fission products and transuranium elements present in various chemical states. Depending on in-reactor history these fission products redistribute within the fuel. Volatile species (Xe, Kr, I) can diffuse out of the fuel matrix to the fuel cladding gap while other elements precipitate in metallic (Mo, Ru, Pd, Ru) and oxide form (Rb, Cs, Ba, Zr) or remain in solid solution (transuranium and rare earth elements (REE)) in the UO₂ matrix [9]. These fission products can cause significant changes in fuel properties and oxidation/dissolution rates.

While the dominant radiolytic oxidant is expected to be H₂O₂ from α-radiolysis, redox conditions within a failed waste container will be strongly influenced by the H₂ produced by anaerobic corrosion of the steel container vessel. Since steel corrodes readily in water significant H₂ pressures are expected to develop [14, 15],

\[
\begin{align*}
Fe + 2H₂O & \rightarrow Fe^{2+} + 2OH^- + H_2 \\
3Fe + 4H₂O & \rightarrow Fe₃O₄ + 4H₂
\end{align*}
\]
Due to the compacted condition of the clay surrounding the container, steel corrosion will produce dissolved H$_2$ at a higher rate than its diffusive mass transport away from the canister leading to pressures of ~ 5MPa and dissolved H$_2$ concentrations in the range of 10$^{-2}$ to 10$^{-1}$ mol.L$^{-1}$ [16]. Though H$_2$ is kinetically hindered at low temperatures and should be inert, many studies have shown that dissolved H$_2$ suppresses the corrosion of UO$_2$ [8, 17-23] even when present at submillimolar concentrations [8]. Autoclave tests on spent fuel have shown there are many contributing factors to this effect [12, 24-27] and, based on modeling studies, it has been suggested that fuel corrosion could be inhibited completely by H$_2$ [28].

Since this influence of H$_2$ has the potential to completely suppress fuel corrosion, and hence radionuclide release, considerable effort has been expended in trying to determine the mechanism involved. Nilsson and Jonsson showed that H$_2$ can scavenge the radiolytic oxidant (H$_2$O$_2$) in the presence of UO$_2$ containing Pd [29], and also suggested that Pd could catalyze the slow reduction of U$^{VI}$ to U$^{IV}$ by reaction with H$_2$ in the aqueous phase [30, 31]. These results are in agreement with electrochemical investigations [17, 20, 22, 32, 33] in which H$_2$ was shown to significantly lower the corrosion potential ($E_{CORR}$) on solid UO$_2$ doped with noble metal particles. Measurements on SIMFUEL specimens doped to various levels to simulate in-reactor burnup (1.5 at% to 6.0 at%) showed the $E_{CORR}$ decreased as the number density of noble metal particles increased in the presence of H$_2$ [33]. These observations are consistent with leaching experiments on spent nuclear fuel and Pd-doped UO$_2$ which show lower U(VI) dissolution rates in the presence of H$_2$ [12, 13, 21, 27, 30, 31, 34].
The reaction has been shown to proceed as a surface heterogeneous process involving the noble metal particles. In the absence of H$_2$ these particles can catalyze the reduction of the molecular radiolytic oxidant, H$_2$O$_2$ which should enhance UO$_2$ corrosion when the OH$^\cdot$ radicals formed,

$$H_2O_2 + e^- \rightarrow OH^\cdot + OH^- \quad (6.3)$$

are consumed in the oxidation/dissolution of the UO$_2$ [6, 21, 22, 30, 35]. However, these radicals can be scavenged on the noble metal particle surface by electrochemical reaction with dissolved H$_2$,

$$H_2 + OH^\cdot \rightarrow H_2O + H^+ + e^- \quad (6.4)$$

Depending on the concentration of dissolved H$_2$, the rate of reaction 6.4 can be significantly larger than the rate of OH$^\cdot$ production (reaction 6.3) leading to the total inhibition of UO$_2$ oxidation.

While these results confirm the role of noble metal particles in activating H$_2$ and inhibiting the corrosion of galvanically-coupled rare-earth doped UO$_2$, the question of whether a similar process can occur on the UO$_2$ surface itself remains unresolved. A number of possible mechanisms by which H$_2$ activation on a UO$_2$ surface could occur have been demonstrated or proposed [36]. Studies on $\alpha$-doped UO$_2$ pellets devoid of noble metal particles show H$_2$ can be activated leading to the suppression of corrosion [13, 37, 38]. Based on the reaction scheme for water radiolysis [39], the reaction of H$_2$ with radiolytically-produced OH$^\cdot$ radicals could reduce the concentration of H$_2$O$_2$, 

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and suppress corrosion. However, the efficiency of this oxidant scavenging at even very low $[H_2]$ suggests a significant role of the UO$_2$ surface in this process although no clear mechanism has been defined [36].

Nilsson and Jonsson [29] have reported that the UO$_2$ surface itself, in the absence of radiation and noble metal particles, does not catalyze the reaction between H$_2$O$_2$ and H$_2$ although other studies suggest it does [23, 40]. Studies on H$_2$O$_2$ decomposition show this reaction can be catalyzed on metal oxide surfaces [41, 42] via the reaction steps,

\[
\begin{align*}
\text{H}_2\text{O}_2 + \text{MO} &\rightarrow 2\text{HO}^\cdot + \text{MO} \quad (6.7) \\
\text{HO}^\cdot + \text{H}_2\text{O}_2 &\rightarrow \text{HO}_2^\cdot + \text{H}_2\text{O} \quad (6.8) \\
2\text{HO}_2^\cdot &\rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \quad (6.9)
\end{align*}
\]

This makes it possible that, in the presence of dissolved H$_2$, the OH$^\cdot$ on the oxide surface could be scavenged by reaction with H$_2$ to produce the reducing H$^\cdot$ radical (reaction 5). Whether or not such a sequence of reactions can occur on rare-earth doped UO$_2$ remains uninvestigated.

The influence of rare-earth dopants, which occupy lattice sites in the fuel matrix, on air oxidation of UO$_2$ has been well studied (M = Gd, Y, La [43-48]. This reaction proceeds in two stages,
\[
\text{UO}_2 \rightarrow \text{U}_3\text{O}_7/\text{U}_4\text{O}_9 \rightarrow \text{U}_3\text{O}_8
\]  
(6.10)

via a U\textsubscript{3}O\textsubscript{7} intermediate for pure UO\textsubscript{2} whereas, when the UO\textsubscript{2} is substantially doped, the intermediate is U\textsubscript{4}O\textsubscript{9}. The second step involving the recrystallization to U\textsubscript{3}O\textsubscript{8} is kinetically hindered by rare earth doping [43, 48, 49] as indicated by the increase in temperature required to force the recrystallization to occur. Based on this evidence for air oxidation, a similar influence of rare earth doping on corrosion might be anticipated since the reaction proceeds by a similar two stage sequence,

\[
\text{UO}_2 \rightarrow \text{UO}_{2+x} \rightarrow \text{UO}_2^{2+}
\]  
(6.11)

except the final product is dissolved \text{UO}_2^{2+} as opposed to a recrystallized deposit of U\textsubscript{3}O\textsubscript{8}.

Some support for this expectation is evident in electrochemical experiments on SIMFUELs in which a decrease in anodic dissolution current was observed as the extent of simulated burn up increased. This was attributed to the influence of rare earth dopants in the UO\textsubscript{2} matrix. However SIMFUELs [10,11] contain up to 11 different fission products making them chemically complex and the determination of the influence of individual radionuclides on fuel oxidation and dissolution behavior difficult. In addition they do not simulate the expected radiation conditions. This is generally achieved using \(\alpha\)-doped UO\textsubscript{2} [12, 13], but these electrodes do not contain the radionuclides that simulate the fission product inventory.
Recent studies [50] showed that the addition of small amounts of Y$_2$O$_3$ (0.3 wt%) to UO$_2$ decreased the corrosion rate (compared to UO$_2$) by a factor of 3 to 5. Since the rate of H$_2$O$_2$ consumption was very similar for UO$_2$ and UO$_2$/Y$_2$O$_3$, this decrease was attributed to a decrease in reactivity of the UO$_2$/Y$_2$O$_3$ pellet.

To determine whether or not rare earth doping influences the reactivity of UO$_2$ we have performed a series of electrochemical and corrosion experiments on UO$_2$ and UO$_2$/Y$_2$O$_3$ pellets with and without added Pd. The electrodes were characterized by scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). The redox behavior was characterized by cyclic voltammetry (CV) and the anodic reactivity by potentiostatic oxidation. Corrosion behavior was investigated in H$_2$O$_2$-containing solutions purged with Ar.

6.2 Experimental

6.2.1 Fuel specimens and electrode preparation

Four different electrodes were used in this study consisting of pure UO$_2$ and UO$_2$ doped with Y$_2$O$_3$ (0.3 wt%) and/or Pd (1 wt%) received from The Royal Institute of Technology, Stockholm, Sweden. These electrodes were fabricated using depleted UO$_2$ powder, Y$_2$O$_3$ powder (particle size ~ 5μm) and Pd powder (particle size ~ 1.0–1.5 μm) as described by Trummer et al [30, 50]. The electrodes were prepared from the pellets using a previously published methodology [51] and are designated UO$_2$, UO$_2$-Pd, UO$_2$-
Y$_2$O$_3$, and UO$_2$-Y$_2$O$_3$-Pd. Prior to electrochemical experiments and surface analyses electrodes were polished (wet) with a 1200 grit polishing paper and rinsed with deionized water.

6.2.2 Solutions

All solutions were prepared with analytical grade chemicals and distilled deionized water ($\rho =$18.2 M$\Omega$ cm) prepared using a Millipore Milli-Q-plus unit to remove organic and inorganic impurities. Experiments were performed in a 0.1 mol.L$^{-1}$ NaCl solution (Caledon, >99%) purged with Ar (Praxair). Prior to the start of any experiment solutions were purged with Ar gas for a minimum of 1 hr. When borate buffered solution was used, 0.05 mol.L$^{-1}$ borax (Merck) was added to the solution prior to the pH adjustment. The solution pH was adjusted to the desired value using NaOH and was monitored with an Orion model 720A pH meter and adjusted accordingly. Solutions containing H$_2$O$_2$ (Fisher Scientific, 3%) were prepared by dilution. The concentration of H$_2$O$_2$ was determined using a BioLogic Science Instruments MOS UV/VIS spectrophotometer [52].

6.2.3 Electrochemical measurements

All experiments were carried out in a standard three-electrode, three-compartment cell. A Luggin capillary was used to minimize the ohmic potential drop due to solution resistance between the reference and working electrodes (WE). The WE was attached to
the shaft of a Pine Instruments model AFASR analytical rotator to allow electrode rotation when required. The counter electrode was a Pt sheet (~6 cm²) spot-welded to a Pt wire. All electrochemical experiments were performed using a Solartron model 1287 potentiostat to control applied potentials and record current responses. The current interrupt method was employed to eliminate the potential (iR) drop caused by the ohmic resistance (R) primarily in the electrode. Corrware™, version 3.0, software was used to analyze the data. All the potential measurements reported are quoted on the saturated calomel electrode (SCE) scale.

6.2.4 Experimental procedure

Before all experiments the electrode was cathodically reduced at two different potentials (usually -1.5V and -1.2V) for 2 to 5 minutes, the H₂ gas bubbles produced at the more negative potential being released while still maintaining cathodic control at the less negative potential. In CV experiments the potential was scanned from the starting potential to different anodic limits and back while recording the current.

In potentiostatic experiments the potential was pulsed to +0.4V after cathodic cleaning and the current measured over a period of 30 min at an electrode rotation rate of 16.67 Hz in Ar-purged solution. In corrosion experiments the $E_{\text{CORR}}$ was followed in a 0.1 mol.L⁻¹ NaCl + 0.01 mol.L⁻¹ NaHCO₃ (pH ~ 9.0) solution purged with Ar until a steady-state value was achieved. Hydrogen peroxide was then added and the $E_{\text{CORR}}$ measurement continued. A series of linear polarization resistance (LPR) measurements was made before and after H₂O₂ addition. In LPR measurements a small potential, in the
range of ±10mV with respect to $E_{\text{CORR}}$ is applied at a scan rate of 0.0167 mV/sec and the resulting (linear) current response measured. The LPR ($R_p$) is the ratio of the applied potential to the current response and is inversely proportional to the uniform charge transfer rate at the electrode/solution interface.

6.2.5 Surface Analysis

6.2.5.1 Scanning Electron Microscopy (SEM)/ Energy Dispersive X-ray (EDX) Analyses

An Hitachi S-4500 Field emission scanning electron microscope (SEM) coupled with a Quartz XOne energy dispersive X-ray (EDX) system was used for imaging. The SEM micrographs were obtained on polished electrodes with the varied electron beam potential ranging from 10.0 kV to 15.0 kV. The SEM micrographs were obtained at various magnifications (2500-10000X) to investigate the surface morphology of the samples. EDX mapping was performed to obtain the size, distribution and elemental composition of the doping elements in the host matrix. The chemical composition of individual particles was also determined.

6.2.5.2 Raman spectroscopy

Raman spectra were acquired on all four electrodes using a Renishaw 2000 confocal Raman spectrometer (Renishaw PLC., UK). Raman active vibrations were
excited on a UO₂ sample by a HeNe laser with a wavelength of 632.8 nm which produces an ~ 1 μm diameter focused beam at the sample surface. The laser was used at 50% power to avoid laser heating effects since small changes in temperature can easily produce small changes in the frequency and width of Raman lines. The spectrometer was calibrated using a Si crystal standard at room temperature. The laser beam was focused onto the sample mounted on a Leica DMLM microscope with a 50x uncoated objective lens. Each spectrum was measured for an exposure time of ~45 sec over the wavenumber range 120 to 1400 cm⁻¹. Measurements were repeated at a number of different locations on the electrode to ensure uniformity of response. The Lorentzian peak model and a Shirley baseline correction were used to fit the Raman peaks.

6.2.5.3 X-ray photoelectron spectroscopy (XPS)

XPS analyses were performed on a Kratos Axis NOVA spectrometer. Spectra were collected using Al Kα-monochromatic radiation (15 mA, 14 kV) to bombard the surface with high energy monochromatic X-rays (hv = 1486.6 eV). The instrument work function was set to give a binding energy (BE) of 83.96 eV for the Au 4f⁷/₂ line for metallic gold and the spectrometer dispersion was adjusted to give a BE of 932.62 eV for the Cu 2p⁵/₂ line of metallic Cu. Survey spectra were recorded for the energy range 0 to 1100 eV with an analysis area of ~300 x 700 microns at a pass energy of 160 eV. High resolution spectra for the U 4f, O 1s, C 1s and the U 5f valence band regions were collected with a pass energy of 20 eV. The instrument charge neutralizer was used on all specimens. The carbon 1s line at 285 eV was used as a standard, when necessary, to
correct for surface charging. Spectra were analysed using CasaXPS software (version 2.3.14). The 4f spectrum on each electrode was deconvoluted into contributions from U$^{IV}$, U$^{V}$ and U$^{VI}$ by fitting both the two spin-orbit split peaks and the associated satellite structures following the procedure described elsewhere [52].

6.3 Results

6.3.1 Voltammetric Behavior

Figures 6.1 (a to d) shows a series of IR-compensated CVs recorded on the four electrodes to different anodic potential limits. Several stages of oxidation and reduction are observed and the profiles for UO$_2$ and UO$_2$-Y$_2$O$_3$ ((a) and (b)) are effectively identical. On the two electrodes which contain Pd (UO$_2$-Pd and UO$_2$-Y$_2$O$_3$-Pd; ((c) and (d)) the same stages of oxidation and reduction appear to be present but are swamped by the very large currents observed at the positive and negative potential limits of the scan.

According to previous electrochemical and XPS studies performed on UO$_2$ and SIMFUEL (1.5 at% simulated burn-up; i.e., only lightly doped) oxidation of a stoichiometric surface should not be observed until the applied potential is $> -0.4$V [1, 51]. However, on the electrodes used in this study, a shallow oxidation is observed over the potential range -0.8V to -0.4V, leading to an equally shallow reduction process over the potential range -0.6V to -1.2V. A current at such low potentials was previously attributed to the oxidation of hyperstoichiometric UO$_{2+x}$ locations on the UO$_2$ surface [1].
Figure 6.1 CV’s to various anodic limiting potentials recorded on the (a) UO$_2$, (b) UO$_2$-Y$_2$O$_3$, (c) UO$_2$-Y$_2$O$_3$-Pd, (d) UO$_2$-Pd electrodes in Ar-purged 0.1M NaCl solution buffered with sodium borate (0.05 mol.L$^{-1}$) at pH~9.2. The scan rate=5 mV s$^{-1}$.
More recently, this “sub-thermodynamic” oxidation was shown to be a feature of non-stoichiometric \( \text{UO}_2^{2+} \) [53].

Over the potential range -0.4V to -0.1V a distinct anodic oxidation peak is observed leading to a distinct cathodic reduction peak at ~ -1.2V. A similar oxidation-reduction couple was observed previously on a uranium dioxide specimen with an average stoichiometry of \( \text{UO}_{2.011} \) and known to possess distinct regions with various stoichiometries [54]. As noted previously, anodic oxidation at sub-thermodynamic potentials leading to a reduction process requiring such a negative potential is indicative of a kinetically facile oxidation to produce a very stable oxidized state. The nature of this state is presently obscure although it is clearly associated with the oxidation of already non-stoichiometric locations.

When the anodic limit is extended to potentials ≥ -0.2V the oxidation current is sustained and leads to the development of a cathodic reduction peak at ~ -0.7V. Oxidation and reduction in these potential ranges has been convincingly attributed to the oxidation of stoichiometric \( \text{UO}_2 \) and the subsequent reduction of the \( \text{UO}_2^{2+}/\text{UO}_3 \cdot y\text{H}_2\text{O} \) formed [1, 53, 55]. For potentials positive to ~ 0.2V the current increases further leading to an increase in the reduction peaks at both -1.2V and -0.7V consistent with the more extensive oxidation of both non-stoichiometric and stoichiometric locations on the \( \text{UO}_2 \) surface. In addition, a new reduction peak develops in the potential range -0.9 to -1.0V. A similar oxidation peak was observed previously [54] and tentatively attributed to the anodic oxidation of deeper locations in an already oxidized surface layer. The potential required to reduce this oxidized state is considerably more negative (~ -0.9V) than that required to reduce the film formed on stoichiometric \( \text{UO}_2 \) (-0.7V) consistent with the
claim by He [54] that the reduction of deeply oxidized states is involved. Previously, the reduction peaks at -0.9V and -1.2V have only been seen after the anodic oxidation of a non-stoichiometric UO$_{2.011}$ electrode [54] clearly indicating that the UO$_2$ and UO$_2$-Y$_2$O$_3$ electrodes are non-stoichiometric or a mixture of non-stoichiometric and stoichiometric regions.

The same general features are observed on the UO$_2$-Pd and UO$_2$-Y$_2$O$_3$-Pd electrodes but are more difficult to see due to the large positive and negative currents, most likely due to water oxidation (to O$_2$) and reduction (to H$_2$) on the Pd particles in the electrodes. These features are clearly shown in Fig. 6.2 which shows the anodic currents recorded in Ar-purged 0.1 mol L$^{-1}$ NaCl solution buffered with sodium borate (0.05 mol L$^{-1}$) at pH ~9.2.

![Figure 6.2](image-url)

**Figure 6.2** Anodic currents taken from the CV’s (Fig. 6.1) recorded on all four electrodes in Ar-purged 0.1 mol L$^{-1}$ NaCl solution buffered with sodium borate (0.05 mol L$^{-1}$) at pH ~9.2
on all four electrodes as a function of potential. These results demonstrate, (i) the influence of the Pd content on the anodic current and (ii) the marginal influence of the Y-content on the anodic behaviour of the UO$_{2+x}$.

While voltammetry may provide an overall indication of the stages of anodic oxidation and cathodic reduction it does not provide a reliable measure of the overall anodic reactivity of the UO$_2$ matrix. This is more reliably achieved by measuring the current in an experiment in which a constant potential is applied to the electrode and the eventual steady-state current is measured. Fig. 6.3 shows a series of such experiments

![Graph of potentiostatic current-time curves](image)

**Figure 6.3** Potentiostatic current-time curves recorded on a 1.5 at% SIMFUEL, and the four electrodes at +0.4 V for 30 min in Ar purged 0.1mol.L$^{-1}$ NaCl buffered with sodium borate (0.025 mol.L$^{-1}$) at pH~ 9.2
conducted at a potential of 0.4V for 30 minutes at an electrode rotation rate of 16.7 Hz with the current density (I) plotted logarithmically as a function of the log of time. An experiment on 1.5 at% SIMFUEL is included for comparison since this electrode has been well studied previously [51, 55].

As shown, the SIMFUEL behavior is very different to that observed on the other four electrodes. The current at short times is considerably lower and the decrease in current at longer times consistent with previous electrochemical and XPS experiments which showed anodic oxidation proceeded through the sequence

\[
\text{UO}_2 \rightarrow \text{UO}_{2+x} \rightarrow \text{UO}_3.y\text{H}_2\text{O} \quad (6.12)
\]

with the formation of the U\text{VI} oxide layer leading to a general passivation of the surface [56]. The other four electrodes all exhibited considerably higher currents at short times and especially at longer times. The increased currents at short times indicate a significant increase in overall reactivity of the electrodes compared to the stoichiometric, but rare earth doped SIMFUEL. Also, at short times, the currents observed on the two Pd-containing electrodes are slightly higher than on the other two electrodes as observed at this potential under voltammetric conditions (Fig. 6.1). However, this difference is temporary and disappears for times ≥ 30s. As noted when discussing the CV behavior it is likely that this enhanced current can be attributed to H\text{2}O oxidation on Pd particles (see below). At longer times all four electrodes exhibit indistinguishable behavior and approach steady-state with no tendency to passivate. Such behavior has only previously
been observed on non-stoichiometric electrodes which have been shown to exhibit enhanced anodic reactivity [54].

6.3.2 Surface Characterization

6.3.2.1 SEM/EDX Analysis

Figure 6.4 shows SEM images of the surfaces of the four electrodes. At the higher magnification the surfaces appear rough and finely particulate. Figures 6.5 to 6.7 show SEM images and EDX maps recorded on the three doped electrodes and show that both the Y and Pd are unevenly distributed in the host matrix and present as individual particles of different sizes and shapes. This is expected for Pd which has a very low solubility in the UO$_2$ matrix. The Pd particles formed are significantly larger than the particle size of the Pd powder (1-1.5 µm), used in their fabrication, Fig. 6.7, which has been attributed to the compaction technique used when forming the pellets [50].
**Figure 6.4** SEM micrographs at magnifications of 2500X and 10000X on (a) UO₂, (b) UO₂-Y₂O₃, (c) UO₂-Y₂O₃-Pd and (d) UO₂-Pd electrodes
Figure 6.5 SEM micrographs recorded on a UO$_2$-Y$_2$O$_3$ electrode at a magnification of 500X and the corresponding EDX maps for U, Y and O. An EDX spectrum recorded on the particle is also shown.
Figure 6.6 SEM micrographs recorded on the UO$_2$-Y$_2$O$_3$-Pd electrode at a magnification of 500X and the corresponding EDX maps for U, Y, Pd and O
**Figure 6.7** SEM micrograph on a UO$_2$-Pd at a magnification of 500X and corresponding EDX maps after polishing on a 1200 grit SiC paper

EDX maps, Figs. 6.5 and 6.6, show that the majority, perhaps all, of the Y is present in particulate form as a separate phase and not incorporated in solid solution in the UO$_{2+x}$ matrix. This is consistent with the voltammetric data, Figs. 6.1 and 6.2, which show no significant influence of Y on the electrochemical behavior of the pellets.
6.3.2.2 Raman analysis

Figure 6.8 shows the Raman spectra recorded on all four electrodes. Raman scattering for stoichiometric UO$_2$ should generate a fundamental vibrational stretch at ~450 cm$^{-1}$ and a second band at ~1150 cm$^{-1}$ [57-59]. The 450 cm$^{-1}$ ($T_{2g}$) stretch is ascribed to the symmetric (g) stretching mode due to O breathing vibrations around U$^{IV}$ in the fluorite structure of UO$_2$, whereas the ~1150 cm$^{-1}$ band has been attributed to electron scattering explained by a crystal field transition ($\Gamma_5 \rightarrow \Gamma_3$) (for the quasi-perfect fluorite structure) [58]. More recently, this last band has been reassigned as an overtone of the first order LO phonon at 575 cm$^{-1}$. Irrespective of its assignment, this peak has been shown to be highly sensitive to the extent of non-stoichiometry of the UO$_2$ [60].

Inspection of the spectra showed the $T_{2g}$ band is broad and shifted to higher frequency (445 to 455 cm$^{-1}$). Deconvolution of this band yields peaks at 445 and 470 cm$^{-1}$, Fig. 6.9, the 470 cm$^{-1}$ indicating a distortion of the cubic symmetry induced by the influence of the increasing concentration of O excess defects [60]. A similar Raman shift to higher frequency and the development of asymmetry was reported as a consequence of the rare-earth (Sm$^{III}$) doping in TiO$_2$ samples [61], and Desgranges et al. [62] attributed this $T_{2g}$ Raman shift from 445 to 455 cm$^{-1}$ in UO$_2$ to the local disorder involved in U$_4$O$_9$ formation. U$_4$O$_9$ is a UO$_2$ based lattice containing clusters of interstitial oxygen atoms (cuboctahedra) and U in higher oxidation states. Other authors reported a peak at ~480 cm$^{-1}$ and attributed it to the Raman active $E_g$ (U-O) stretching mode, a characteristic of the tri-uranium octaoxide ($\alpha$-U$_3$O$_8$) [58, 63, 64]. As shown in Fig. 6.9, the peak at 455
cm$^{-1}$ is observed on all four electrodes and can be deconvoluted into peaks at 445 cm$^{-1}$ and $\sim$ 475 cm$^{-1}$. The relative intensities are effectively the same for all four specimens.

In addition to this shift in the T$_{2g}$ band, all four spectra exhibit a broad band between 500 and 700 cm$^{-1}$ commonly attributed to O sublattice damage [56, 57, 62, 65], Fig. 6.8. The intensity of this band is significantly greater than that of the T$_{2g}$ band, a feature previously shown to be associated with a high degree of non-stoichiometry ($0.25 \leq x \leq 0.33$) [60]. As shown in Fig. 6.9 this broad band can be deconvoluted into peaks at 585 cm$^{-1}$ and 630 cm$^{-1}$. The peak at 585 cm$^{-1}$ is not generally associated with stoichiometric UO$_2$ and has been attributed to the presence of bulk defects [66]. It is also possible it is associated with the peak commonly observed at 575 cm$^{-1}$, a forbidden first order LO
Raman scattering mode allowed due to the breakdown in selection rules due to disorder induced by the presence of defects. Such a breakdown would be expected from a loss of translational symmetry at vacancy sites due to O defect clustering and the change in cation radius when $U^{IV}$ is converted to $U^{V}$ with increasing non-stoichiometry.

![Raman Spectra](image)

**Figure 6.9** Fitted and deconvoluted Raman bands for the wavenumber range 350 cm$^{-1}$ to 850 cm$^{-1}$ for the four electrodes
The strong peak at 630 cm\(^{-1}\) (an A\(_{1g}\) stretch) has been frequently observed on hyperstoichiometric UO\(_{2+x}\) and on rare earth doped SIMFUELs [60, 62, 67, 68]. Original suggestions that this band could be attributed to distortion of the anion sublattice due to the O ion displacements required to accommodate excess O ions were recently confirmed by Desgranges et al. [62] who demonstrated this peak was a signature of the cuboctahedral cluster associated with the presence of U\(_4\)O\(_9\). The small peak at 155 to 160 cm\(^{-1}\) is similarly associated with U\(_4\)O\(_9\) [62] and attributed to the distortion of the cation sublattice associated with the formation of a tetragonal structure. A similar band has been reported for tetragonal zirconia (ZrO\(_2\)) [69].

6.3.2.3 XPS analysis

Figure 6.10 (a) shows the deconvoluted high resolution XPS spectra recorded on the freshly polished electrodes to characterize the influence of doping on surface composition. The location of the satellite peak at a binding energy of \(~7\) eV higher than the U 4f\(_{5/2}\) peak confirms that U\(^{IV}\) is the dominant oxidation state present in the electrode surface. There is also a measurable U\(^V\) content indicated by the presence of the satellite peak at a binding energy \(\sim 8\) eV above the U 4f\(_{5/2}\) peak. The relative amounts of U\(^{IV}\) and
$^{4}f_{7/2}$ Data
Fit envelop $^IV$ $^V$ $^VI$

$^4f_{5/2}$

$UO_2$ $Y_2O_3$

$UO_2-Pd$

$UO_2-Y_2O_3-Pd$

$UO_2-Y_2O_3$

~6.9 eV

~8.0 eV

Intensity (arbitrary counts)

Binding energy (eV)

402 396 390 384 378
Figure 6.10 (a) Fitted and deconvoluted XPS spectra for the U-4f region recorded on the four electrodes; (b) Relative fractions of all three oxidation states obtained from the XPS curve fitting.

$U^V$ are only marginally influenced by the presence of Y and Pd, Fig. 6.10 (b). This is especially true for $U^V$. Noticeable amounts of $U^{VI}$ were also detected, possibly due to air-oxidation while transferring the specimens from the polishing area to the vacuum chamber of the XPS spectrometer. These observations, and the very high $U^V$ content, confirm the specimens are non-stoichiometric in agreement with the Raman and electrochemical results. It is worth noting that XPS analyses on SIMFUELs showed the $U^V$ content increased from ~17% to ~26% as the extent of simulated burnup (and hence
the rare earth doping level of the UO\(_2\) matrix) increased from 1.5 at\% to 6.0 at\%. This can be compared to the 36 to 37% measured on these four electrodes.

6.3.3 Corrosion potential (\(E_{\text{CORR}}\)) and Linear Polarization Resistance (\(R_p\))

Measurements in \(H_2O_2\) Solutions

Corrosion experiments were conducted on rotating electrodes (16.7 Hz) in an Ar-purged \(2 \times 10^{-3}\) mol.L\(^{-1}\) NaCl solution containing \(10^{-2}\) mol.L\(^{-1}\) NaHCO\(_3\) (pH ~ 9.0). The corrosion potential, \(E_{\text{CORR}}\), was monitored on each electrode until steady-state was achieved and then \(2 \times 10^{-3}\) mol.L\(^{-1}\) \(H_2O_2\) was added to the cell and the \(E_{\text{CORR}}\) measurement continued, Fig. 6.11. Series of LPR measurements were conducted and the \(R_p\) values are plotted in Fig. 6.12. The first two data points are the \(R_p\) values after four and two hours prior to \(H_2O_2\) addition and the subsequent five data points show the values recorded with \(H_2O_2\) present. Once the \(H_2O_2\) was added the solution composition was identical to that used by Trummer et al. [50, 70] in experiments on these electrodes in which \(H_2O_2\) consumption and U dissolution rates were measured.

Prior to \(H_2O_2\) addition, \(E_{\text{CORR}}\) reaches a steady-state value almost immediately on the SIMFUEL electrode but this required a few hours on the other four electrodes. Eventually, \(E_{\text{CORR}}\) for the SIMFUEL achieves a value ~ 70 mV more negative than the other four electrodes. For these electrodes no significant influence of electrode composition on \(E_{\text{CORR}}\) is observed. This difference in \(E_{\text{CORR}}\) leads to differences in \(R_p\), the value for SIMFUEL being over an order of magnitude greater than the values on the
other electrodes. The $R_p$ values on the two Pd-containing electrodes are ~30% higher than on the two Pd-free electrodes.

**Figure 6.11** $E_{\text{CORR}}$ recorded as a function of time before and after the addition of $\text{H}_2\text{O}_2$ (2mmolL$^{-1}$) to an Ar-purged 0.1molL$^{-1}$ NaCl solution containing 10 mmolL$^{-1}$ NaHCO$_3$ at pH ~9.0: the sudden increases in $E_{\text{CORR}}$ occur immediately on $\text{H}_2\text{O}_2$ addition.

After $\text{H}_2\text{O}_2$ addition, $E_{\text{CORR}}$ increases immediately to a steady-state value of 100 mV on all five electrodes. This shift is accompanied by a decrease in $R_p$ values consistent with a reactivity of $\text{H}_2\text{O}_2$ on the electrode surfaces. While the $R_p$ value on SIMFUEL remains larger than that on the other four electrodes the difference is reduced to only a factor of 2 to 4. For the four non-stoichiometric electrodes the difference in $R_p$ values remains small but the value on the UO$_2$-Pd electrode is noticeably different than on the
other three electrodes. The values are effectively constant with time on all the electrodes. Subsequent inspection of the electrodes by SEM (not shown) shows no visible change in the state of the surfaces, indicating that no significant corrosion damage occurred over the duration of the corrosion experiments.

Figure 6.12 Polarization resistance ($R_p$) values recorded at various times before and after the addition of 2mmolL$^{-1}$ of H$_2$O$_2$ to an Ar-purged 0.1molL$^{-1}$ NaCl solution containing 10mmolL$^{-1}$ NaHCO$_3$ at pH ~9.0. The $R_p$ values are normalized to ejected time which is four hours prior to H$_2$O$_2$ addition.
SEM/EDX, Raman spectroscopy and XPS have been used to characterize uranium dioxide electrodes containing Y and Pd. SEM/EDX showed the electrodes were rough and finely particulate with Y and Pd generally distributed throughout the matrix as $Y_2O_3$ and Pd particles.

All four materials (UO$_2$, UO$_2$-Y$_2$O$_3$, UO$_2$-Pd, UO$_2$-Y$_2$O$_3$-Pd) exhibited very similar Raman and XPS spectra. The dominance of the Raman peak in the wavelength number range 500 to 700 cm$^{-1}$ and the absence of the LO phonon overtone at 1150 cm$^{-1}$ indicate the oxide is non-stoichiometric. According to Manara and Renker [58], the 1150 cm$^{-1}$ peak disappears as the stoichiometry approaches UO$_{2.1}$ but more recent studies indicate that the O in non-stoichiometric UO$_{2+x}$ may not be homogeneously distributed [54]. Evidence that the latter is the case with the materials in this study comes from deconvolution of the peak in the 500 to 700 cm$^{-1}$ region which yields peaks at 585 cm$^{-1}$ and 630 cm$^{-1}$. The dominance of the latter peak confirms that the oxide contains a large number of cuboctahedral U$_4$O$_9$ clusters. In addition small bands at 470 cm$^{-1}$ and 155 cm$^{-1}$ indicate a distortion of the U sublattice consistent with the onset of the transformation to U$_3$O$_7$. These features show that, at least some areas within the oxide are highly non-stoichiometric.

The XPS results confirm that this non-stoichiometry is reflected in the surface composition. The deconvoluted U4f peaks show that all the specimens exhibited a $U^V$ content in the range 36 to 37% compared to 17 to 26% for rare earth doped SIMFUELS (over the simulated burn up range from 1.5 at% to 6.0 at%).
The electrochemical behavior is consistent with specimens containing a mixture of stoichiometric and non-stoichiometric domains. In voltammetric experiments the presence of a current at sub-thermodynamic potentials is attributed to the facile oxidation of non-stoichiometric domains. The composition of the oxidized product is unknown but the need for a very negative potential to cause its reduction confirms that it is very stable. The oxidation and reduction processes expected for stoichiometric UO$_2$ are also observed. From voltammetric experiments alone it is not possible to determine either the degree of non-stoichiometry or the distribution of stoichiometric and non-stoichiometric material.

An anodic oxidation experiment comparing the electrochemical reactivity of these specimens to that of the well characterized 1.5 at% SIMFUEL showed them to be very reactive. Unlike on SIMFUEL the anodic current did not decrease substantially with time as expected for the formation of a passivating U$^{VI}$ surface layer. Instead the four specimens behaved identically (at times $> 40$s) in establishing a long-term steady-state oxidation current. Although this anodic reactivity has not been investigated in detail the anodic product must be either a deeply oxidized, but non-passivating, surface layer or the enhanced dissolution of U$^{VI}$ (as UO$_2^{2+}$). Since the pH is borate buffered at pH $\sim$ 9.0 extensive dissolution is not anticipated.

The reciprocal of $R_p$ ($R_p^{-1}$) is directly proportional to the rate of charge transfer at the electrode/solution interface and for a corroding system would be proportional to the corrosion rate. Prior to the addition of H$_2$O$_2$ the corrosion experiments show there is a significant difference between the $R_p$ values measured on SIMFUEL and those measured on the other four electrodes. In the absence of a specific oxidant in the solution this
difference most likely reflects charge transfer processes within the surface of the UO$_{2+x}$.

For stoichiometric SIMFUEL previous studies show no discernible reactivity at potentials in the vicinity of the measured $E_{\text{CORR}}$ (~ -0.5V) at which the $R_P$ measurements were made. For the other electrodes the CVs in Fig. 6.1 show that charge transfer processes occur on non-stoichiometric locations, and this could account for the much lower $R_P$ values recorded.

After the addition of H$_2$O$_2$ two charge transfer processes are possible: (i) corrosion of the UO$_{2+x}$ (UO$_2$) leading to the formation of soluble UO$_2$$^{2+}$; while dissolution would be expected to dominate over the formation of a U$^{VI}$ deposit in the carbonate solution used, the deep oxidation of the non-stoichiometric surface is also likely [54]; (ii) H$_2$O$_2$ decomposition to O$_2$ and H$_2$O. This last reaction could occur on the UO$_2$(UO$_{2+x}$) surface, Y$_2$O$_3$ particles, and especially Pd particles.

In the absence of additional analytical information, a linear polarization measurement cannot distinguish between these two reactions and the $R_P$ value will reflect some composite value of the resistance to both processes. In comparison to the analytical results of Trummer et al. [50] and Pehrman et al. [70] the $R_P$ value will be comparable to the H$_2$O$_2$ consumption rate by both the corrosion and decomposition reactions.

The values in Fig. 6.12 show $R_P$ for the SIMFUEL is noticeably greater than the values for the other electrodes when H$_2$O$_2$ is present, and with the exception of the UO$_2$-Pd specimen the other values are effectively indistinguishable. Analytical experiments on SIMFUEL [70] show that while the rate of H$_2$O$_2$ consumption is similar to that observed on the UO$_2$ and UO$_2$-Y$_2$O$_3$ electrodes, the U dissolution rate (which is a measure of the corrosion rate) is negligible. Although the doping level (expressed as a simulated burnup)
of the SIMFUEL used is not given it will contain noble metal particles which would support the decomposition process. However, a considerable amount of electrochemical evidence exists [7, 71] showing that the H\textsubscript{2}O\textsubscript{2} is reactive on the UO\textsubscript{2} surface and that, at the E\textsubscript{CORR} achieved (~+0.1V) the system is redox buffered by the H\textsubscript{2}O\textsubscript{2} decomposition reaction. The results of Pehrman et al. [70] indicate that the rare earth doped stoichiometric UO\textsubscript{2} matrix in the fuel is very stable under these conditions.

The similarity in R\textsubscript{P} values for the UO\textsubscript{2} and UO\textsubscript{2}-Y\textsubscript{2}O\textsubscript{3} electrodes is consistent with the observations of Trummer et al. [50] who showed that the H\textsubscript{2}O\textsubscript{2} consumption and U dissolution rates were only slightly lower on the UO\textsubscript{2}-Y\textsubscript{2}O\textsubscript{3} pellet than on the UO\textsubscript{2} pellet. This small difference was attributed to the stabilizing influence of the Y on the UO\textsubscript{2} matrix. However, this conclusion cannot be justified by the present results which show both electrodes are dominated by non-stoichiometry with the majority of the Y isolated in the Y\textsubscript{2}O\textsubscript{3} particles. The lower R\textsubscript{P} values on the UO\textsubscript{2} and UO\textsubscript{2}-Y\textsubscript{2}O\textsubscript{3} electrodes compared to the SIMFUEL can be predominantly attributed to the destabilizing influence of cuboctahedral clusters in the matrix and their ability to support reactions involving H\textsubscript{2}O\textsubscript{2}. According to Trummer et al. [50] H\textsubscript{2}O\textsubscript{2} remains the dominant reaction.
6.5 References


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Chapter 7

Influence of Trivalent-Dopants on Electrochemical and Structural Property of Uranium Dioxide (UO$_2$)

7.1. Introduction

The safe disposal of spent nuclear fuel (SNF) is one of the key issues facing the modern nuclear power industry, and a major international effort is underway to develop safe management and disposal procedures. One potential management strategy in Canada is permanent disposal in a deep geologic repository [1]. The spent fuel would be sealed in metallic containers, emplaced in a repository and surrounded with compacted clay. The prospects for long term containment using copper containers are very good and corrosion models predict only minimal corrosion damage should be sustained [2, 3]. However, if failure were to occur, contact of the fuel wasteform (uranium dioxide (UO$_2$)) with groundwater would become possible. Although the solubility of UO$_2$ is very low under the anticipated anoxic conditions, radiolysis of the groundwater, due to the inherent radioactivity of the spent fuel, could lead to fuel corrosion, the U(IV) in the fuel being oxidized to the significantly more soluble U(VI) state [4]. This would make radionuclide release to the groundwater possible.

Spent fuel is mainly UO$_2$ (> 95%), the remainder being the radioactive fission products and actinides produced during the in-reactor process. The inventory of radionuclides within the fuel depends on in-reactor burn-up and the linear power rating of
the fuel [5]. Formation of these products leads to many physical and chemical changes within the fuel [5], and post irradiation inspection of the fuel shows the presence of both volatile and non-volatile fission products. While volatile products may escape to the fuel-cladding gap, the non volatile products remain fixed within the fuel matrix in three distinct phases: the lanthanides in the fcc-fluorite lattice; the noble metals in metallic precipitates; and radionuclides unstable in the fluorite matrix in mixed metal oxides (perovskites) [6].

The key changes likely to influence the chemical reactivity of the UO$_2$ matrix are the rare earth (RE) doping of the matrix and the development of non-stoichiometry [7]. Micro Raman spectroscopic studies show that non-stoichiometry leads to very significant changes in fuel structure as x (in UO$_{2+x}$) increases [8]. Close to stoichiometry there is an increase in randomly distributed O interstitial defects as x increases. As the degree of non-stoichiometry increases further these defects associate into clusters, and for a sufficiently high degree of non-stoichiometry cuboctahedrals clusters are formed [8, 9]. Studies using atomic force microscopy (AFM), current sensing AFM and scanning electrochemical microscopy clearly demonstrate that the fuel reactivity increases as the extent of defect clustering increases [7]. While the exact anodic oxidation mechanism remains to be resolved, the extent of oxidation on a surface close to stoichiometric appears to be limited by the low O interstitial (O$_I$) mobility within the matrix. At higher degrees of non-stoichiometry the formation of defect clusters enhances O$_I$ mobility in the matrix facilitating a deeper and more extensive surface oxidation.

Considerable experimental evidence exists to show that fission product and actinide-lanthanide doping have a significant effect on the kinetics of air oxidation of the
fuel [10-13] and preliminary electrochemical experiments on SIMFUEL suggest a similar influence in aqueous environments [6]. Since there has been a continuous trend towards higher in-reactor fuel burn-up [14-16], the extent of doping and its influence on reactivity are becoming more important. Both the mechanism and the rate of oxidation are influenced by the presence of dopants. The reaction proceeds in two stages

\[
\text{UO}_2 \rightarrow \text{U}_4\text{O}_9/\text{U}_3\text{O}_7 \rightarrow \text{U}_3\text{O}_8
\] (7.1)

The first step involves the diffusion of O through the growing surface oxidized layer of either U$_4$O$_9$ (O:U = 2.25 to 2.4) or tetragonal U$_3$O$_7$ (O:U = 2.33), while the second step involves a recrystallization via a nucleation and growth mechanism to the orthorhombic U$_3$O$_8$ [10].

A key feature of this oxidation process is that the nature of the intermediate phase changes as the doping level is increased. For pure, or lightly doped, UO$_2$ oxidation occurs relatively rapidly to the tetragonal U$_3$O$_7$ and the subsequent conversion to orthorhombic U$_3$O$_8$ is easily completed. However, the oxidation of UO$_2$ containing large amounts of dopants (such as Gd) is kinetically slower and proceeds through U$_4$O$_9$ which retains the fluorite structure and is kinetically more difficult to transform to U$_3$O$_8$. These observations are supported by a range of studies with SIMFUELs [17, 18], LWR fuels (highly doped) [19] and CANDU fuels (lightly doped) [20].

Park and Olander [21, 22] offered an explanation for the stabilization of RE(III)-doped UO$_2$ against oxidation based on O potential calculations, this potential being an indirect indicator of oxide-defect structure. A defect model for Gd-doped UO$_2$ was
developed based on their original model for UO$_2$ which incorporated both intrinsic point defects and defect clusters. Experimental O potential data could be fitted by assuming Gd dopants existed mainly as isolated defects in the cation sublattice of the oxide. As the Gd content increased the Gd dopants were stabilized by the formation of dopant- oxygen vacancy clusters (O$_V$) clusters. This leads to a reduction in availability of the interstitial sites required for the incorporation of O$_I$ during oxidation.

In this study we have investigated the electrochemical reactivity of two RE(III)-doped electrodes and a SIMFUEL, and correlated this reactivity to their oxide structures determined by Raman spectroscopy. SIMFUELs are UO$_2$ pellets doped with non-radioactive elements including rare earths (Ba, Ce, La, Sr, Mo, Y, Zr, Rh, Pd, Ru, Nd) to replicate the chemical effects of in-reactor irradiation, and have been well studied electrochemically [23]. The Re(III)-doped electrodes employed were doped with Gd (6.0 wt%) and Dy (12.9 wt%). While all rare earth dopants are not expected to have an identical effect on UO$_2$ [22], this comparison offers a first opportunity to determine their influence on the oxidative behavior of UO$_2$ in an aqueous environment.

7.2 Experimental

7.2.1 Electrode Material and Preparation

Experiments were performed on 1.5 at% SIMFUEL, 6.0 wt% Gd$_2$O$_3$ (rare-earth) doped UO$_2$ (Gd-UO$_2$) and 12.9 wt% Dy$_2$O$_3$ (rare-earth) doped UO$_2$ (Dy-UO$_2$) electrodes. SIMFUEL and Dy-doped UO$_2$ pellets were fabricated and supplied by Atomic Energy of
Canada Limited (AECL, Chalk River, Canada) and the Gd-doped UO$_2$ by Cameco (Port Hope, Canada). All the pellets were sintered and reduced to produce high density stoichiometric ceramics. The pellets were cut into 2 mm thick slices and fabricated into electrodes using our previously published procedure [24].

7.2.2 Electrochemical Procedure

Prior to experiments, electrodes were prepared by polishing on wet 1200 grit SiC paper and rinsed with distilled deionized water. Subsequently, the electrodes were electrochemically reduced at -1.5 V and -1.2 V for 5 min each (vs. SCE) to remove any air-formed oxides or organic contaminants present on the surface. Cyclic voltammetric experiments were performed by scanning the potential from -1.5 V to an anodic limit of $\leq$ 0.4 V and back at a scan rate of 5 mV.s$^{-1}$.

7.2.3 Solution Preparation

Solutions were prepared using distilled deionized water (resistivity ($\rho$) =18.2 M$\Omega$ cm) purified using a Millipore Milli-Q plus unit which removes organic and inorganic impurities. Experiments were performed in 0.1 mol.L$^{-1}$ NaCl (Caledon) solution purged with Ar gas (Praxair). The solution pH was monitored with an Orion model 720A pH meter and adjusted to 9.5 using 0.1 mol.L$^{-1}$ NaOH.
7.2.4 Electrochemical Cell and Equipment

A standard three-electrode, three-compartment cell was employed for all the experiments. The three compartments were separated by glass frits to avoid contamination of the working electrode. A Luggin capillary was used to minimize the ohmic potential drop due to solution resistance between the reference and working electrode. A Pt sheet (~ 6 cm²) spot-welded to a Pt wire was used as the counter electrode. A Solartron model 1287 potentiostat was used to control applied potentials and to record current responses. Corrware™, version 3.0, software was used to analyze the data. The current interrupt method was employed to compensate for voltage drop due to ohmic resistance in the electrodes. All potential measurements were recorded against a saturated calomel reference electrode (SCE).

7.2.5 SEM/EDX Measurements

A Hitachi S-4500 Field emission scanning electron microscope (SEM) equipped with an energy dispersive X-ray (EDX) analyzer was used to collect images and determine elemental compositions. SEM micrographs were obtained on polished electrodes with the electron beam potential ranging from 10.0 kV to 15.0 kV according to requirements. The working distance was set at 10mm during image collection. EDX mapping was used to determine the distribution of the dopants in the host UO₂ matrix. A number of randomly located areas of the surface were examined to determine whether the elemental composition was uniform.
7.2.6 Raman Analysis

All the Raman spectra were acquired using a Renishaw 2000 confocal Raman spectrometer (Renishaw PLC., UK). Raman active vibrations were excited on a UO₂ sample by a HeNe laser with a wavelength of 632.8 nm which produces a focused beam of about 2 µm diameter at the sample surface. The laser was used at 50% power to avoid any specimen heating effects since small changes in temperature can easily produce small changes in the frequency and width of Raman lines. The Raman spectrometer was calibrated using a Si crystal standard at room temperature. The laser beam was focused onto the sample using a Leica DMLM microscope with a 50x uncoated objective lens. Each spectrum was measured for an exposure time of ~45 sec over the wavenumber range 120 to 1400 cm⁻¹. Repeated measurements were conducted at different locations on the electrode to ensure that bands do not show any shifts in vibrational frequency. After the measurement, the Lorentzian peak model and a Shirley baseline correction were used to fit the Raman peaks.

7.3 Results

7.3.1 SEM/EDX Analysis

Figure 7.1 shows the surface morphology of the Gd-UO₂, Dy-UO₂ and 1.5 at% SIMFUEL electrodes at two magnifications. The Dy-UO₂ is characterized by large grains
with closed and interconnected porosity on grain boundaries and at triple points (Fig. 7.1 (b)).

**Figure 7.1** SEM micrographs recorded on (a) Dy-doped UO₂ (b) Gd-doped UO₂ and (c) 1.5 at% SIMFUEL electrode at 1000 and 5000X
SEM images collected on the Gd-doped UO$_2$ shows some porosity in the structure, Fig. 7.1 (a), which is commonly observed on undoped UO$_2$. SIMFUEL micrographs showed a similar porosity. EDX measurements were performed on a number of locations on the Gd-UO$_2$ and Dy-UO$_2$ electrodes, and representative patterns are shown in Figs. 7.2 and 7.3. As expected, EDX maps show a homogeneous distribution of the doping elements. No accumulation of Gd (as Gd$_2$O$_3$) or Dy (as Dy$_2$O$_3$) was observed. Also, analyses of randomly chosen locations confirmed that the Gd and Dy were both uniformly distributed as dopants in the UO$_2$ matrices.

Figure 7.2 EDX maps recorded on a Dy-doped UO$_2$ at a magnification of 2000X
Figure 7.3 EDX maps recorded on a Gd-doped UO$_2$ at a magnification of 2000X

7.3.2 Surface Electrochemistry

Cyclic voltammetric (CV) experiments were conducted on each electrode to determine their electrochemical reactivity, especially their susceptibility to anodic oxidation.

Figure 7.4 shows IR-compensated CVs recorded on the three electrodes. The current-potential profiles, Fig. 7.4 (a), are similar on all three electrodes but the current densities recorded differ considerably especially at the anodic and cathodic limits of the scan. The expanded sections in Fig. 7.4 (b) show that the distinct stages of oxidation/reduction observed differ in current density on the three electrodes. At the cathodic limit of the scan
the currents can be attributed to $\text{H}_2\text{O}$ reduction to $\text{H}_2$. The very high current for this reaction on the SIMFUEL electrode has been shown to be due to the catalysis of this reaction on the noble metal particles present in this material. While considerably lower than on SIMFUEL, the heavily-doped Dy-UO$_2$ electrode supports a measurably higher current for this reaction than the Gd-UO$_2$ electrode.

In the potential range $-0.8\text{V} \leq E \leq -0.4\text{V}$ (region I, Fig. 7.4 (b)) no significant oxidation current was observed on any electrode. Current in this potential range has been attributed to the oxidation of hyperstoichiometric ($\text{UO}_{2+x}$) surface sites [24, 25], as discussed in chapter 6.
**Figure 7.4** CVs recorded on Dy-doped UO$_2$, Gd-doped UO$_2$ and 1.5 at% SIMFUEL electrodes in an Ar-purged 0.1M NaCl solution (pH=9.5): (a) scans are offset by 1 mA cm$^{-2}$ and (b) individual scans. The scan rate=5 mV/s
Over the potential range \(-0.4V \leq E \leq 0.0V\) (region II), a shallow increase in anodic current is observed on the SIMFUEL electrode and, to a lesser degree, the Dy-UO\(_2\) electrode. No significant current increase is observed on the Gd-UO\(_2\) electrode. The current increase commences for \(E \geq -0.4V\). Anodic oxidation in this region has been studied extensively on 1.5 at\% SIMFUEL and surface oxidation clearly demonstrated by X-ray photoelectron spectroscopy [24]. Oxidation involves the incorporation of \(O^{2-}\) ions into interstitial sites in the stoichiometric UO\(_2\) lattice (i.e., the creation of O interstitial ions, O\(_I\)) accompanied by the conversion of U\(^{IV}\) to U\(^V\). Oxidation at these locations yields a surface layer of \(U^{IV}_{1-2x}U^{V}_{2x}O_{2+x}\) with a thickness limited by diffusion of O to sub-surface locations. Although difficult to demonstrate, it has been claimed that the limiting composition of the UO\(_{2+x}\) surface is UO\(_{2.33}\) [25]. On hyperstoichiometric surfaces oxidation in this region, which commences in region I, can be extensive (Chapter 6) since \(O^{2-}\) diffusion to sub-surface locations is facilitated [26].

The very low currents observed, even on the most reactive SIMFUEL, are consistent with these electrodes being close to stoichiometric. This can be appreciated by comparing the anodic currents in this region to those observed on the non-stoichiometric UO\(_2\)-Y\(_2\)O\(_3\) electrodes discussed in chapter 6. For the three electrodes investigated, the currents in this region are in the order

\[
\text{SIMFUEL} > \text{Dy-UO}_2 > \text{Gd-UO}_2
\]  

(7.2)

For the potential range \(0.0V \leq E \leq 0.4V\) (region III) the anodic current increases markedly on the SIMFUEL and Dy-UO\(_2\) but only slightly on Gd-UO\(_2\). This increase has been shown to be due to the onset of U\(^{VI}\) formation and dissolution as UO\(_2^{2+}\) [25]. In the neutral to slightly alkaline solutions employed in these experiments, the U\(^{VI}\) accumulates.
on the electrode surface as UO$_3$.yH$_2$O, although dissolution can be maintained by a
decrease in pH as a consequence of U$^{VI}$ hydrolysis as the current increases at potentials >
+0.3V [27].

The order of reactivity in this potential range is the same as at the lower
potentials. This is not surprising since the formation of UO$_{2+x}$ is a precursor to the
formation of U$^{VI}$

\[ \text{UO}_2 \rightarrow \text{UO}_{2+x} \rightarrow \text{UO}_3$.yH$_2$O/UO$_2^{2+} \]

(7.3)

In this regard electrochemical oxidation in an aqueous environment follows a
similar sequential process to that observed in air oxidation. Figure 7.5 compares the
currents recorded at 0V and 0.3V for all three electrodes.

Figure 7.5 Anodic currents recorded at 0 and 0.3 V on three UO$_2$ electrodes in Ar-purged
0.1M NaCl solution (pH=9.5).
On the reverse scan the extent of oxidation of the electrodes can be gauged by the size of the reduction peak in region IV. This peak has been shown to be due to the cathodic reduction of the UO$_{2+x}$/UO$_3$.yH$_2$O surface oxidation products. On SIMFUEL and Dy-UO$_2$ the extent of surface oxidation, indicated by the charge required for its reduction, is approximately the same, although the reduction process is partially obscured on the SIMFUEL by the H$_2$O reduction current. By comparison, the extent of oxidation of the Gd-UO$_2$ electrode is minor, as expected considering the very small anodic oxidation currents measured on this electrode.

Considering the large difference in anodic currents observed at E > 0.1V, the similarity in the extent of oxidation of SIMFUEL and Dy-UO$_2$ is surprising. A possibility is that both electrodes experience a similar degree of oxidation to the UO$_{2+x}$ stage, but the subsequent oxidation to U$^{VI}$ is inhibited on the Dy-UO$_2$ electrode leading to a lower anodic dissolution current but a similar degree of surface oxidation compared to SIMFUEL. In the absence of surface analytical evidence this claim is unproven.

Based on these results, the anodic reactivity is in the order noted in sequence 2. Since all three electrodes are RE(III)-doped the small extent of anodic oxidation on all electrodes is consistent with the expectation from air oxidation results that the reactivity will be limited. However, the expectation that the extent of oxidation will be proportional to the total RE(III) content is not borne out, since the more heavily doped Dy-UO$_2$ electrode is more extensively oxidized than the Gd-UO$_2$ electrode.
7.3.3 Raman Analyses

Raman spectroscopy has been commonly used to investigate the structure of the U-O system [6, 8, 9]. Uranium dioxide has a cubic fluorite structure and belongs to the space group $O_h$ ($Fm\overline{3}m$) [28] and should exhibit two vibrational modes; i.e., a Raman-active phonon ($T_{2g}$) and an infrared-active phonon ($T_{1u}$) [29]. This structure possesses six optical-phonon branches which show three zone-center frequencies i.e 278 cm$^{-1}$, 445 cm$^{-1}$ and 578 cm$^{-1}$ corresponding to the doubly degenerate IR active ($T_{1u}$) TO mode, the triply degenerate Raman active ($T_{2g}$) mode, and the nondegenerate IR active ($T_{1u}$) LO mode. Therefore, Raman scattering for pure UO$_2$ should generate a fundamental vibrational stretch at $\sim$ 445 cm$^{-1}$ and a second band at $\sim$ 1150 cm$^{-1}$. The 445 cm$^{-1}$ stretch is ascribed to the symmetric stretching mode which arises due to oxygen breathing vibrations around U$^{IV}$ in the fluorite structure of UO$_2$. The second band at $\sim$ 1150 cm$^{-1}$ was initially reported by Graves [29] on single crystal UO$_2$ and by Schoenes and Manara [30, 31] on polycrystalline UO$_2$ using a similar source (514 nm laser) and attributed to a crystal field transition ($\Gamma_5 \rightarrow \Gamma_3$) (for the quasi-perfect fluorite structure). More recently this band has been reassigned as an overtone (2L-O) of the first order L-O phonon (575 cm$^{-1}$) [32]. Manara et al. [31] claimed this band can be taken as a fingerprint for the quasi-perfect fluorite structure and showed that its intensity decreased considerably as the defect structure due to increasing non-stoichiometry developed. This feature was recently confirmed by He et al. [8].
Raman spectra recorded on the three electrodes are shown in Fig. 7.6. While all three exhibit similar structure, the relative peak intensities differ considerably. A number of general features can be noted:

(i) For the RE$^{III}$-doped electrodes, no peaks indicating the presence of Gd$_2$O$_3$ or Dy$_2$O$_3$ are observed. For the cubic Gd$_2$O$_3$ peaks at 375 cm$^{-1}$ and 480 cm$^{-1}$, due to the basic vibrational modes would have been expected. The absence of such peaks confirms the RE$^{III}$ cations are in solid solution within the UO$_2$ matrix.

(ii) The two bands associated with the fluorite lattice at 445 cm$^{-1}$ and 1150 cm$^{-1}$ decrease in intensity in the order SIMFUEL > Gd-UO$_2$ > Dy-UO$_2$; i.e., as the overall extent of RE$^{III}$-doping increases.
(iii) The peak at 445 cm\(^{-1}\) shifts to a higher wavelength and appears to develop asymmetry on the high wavenumber side;

(iv) The broad band in the region 500 to 700 cm\(^{-1}\) becomes dominant as the doping level increases and its structure changes considerably.

(v) The intensity of the small peak at ~ 155 cm\(^{-1}\) decreases with increasing doping level.

### 7.3.3.1 SIMFUEL

Raman and XRD analyses on a range of SIMFUELs (1.5 at%, 3.0 at% and 6.0 at%) have been reported [6]. The XRD diffraction patterns indicated a decrease in UO\(_2\) lattice constant with an increase in simulated burn-up consistent with published literature. However, whether or not this can be attributed to rare earth doping alone is dubious since the influence of dopants on the UO\(_2\) lattice parameter has been shown to vary with the identity of the dopant. Kapoor et al [33] observed a decrease in lattice constant when the dopant was Gd, whereas Tsuji [34] reported an increase with Th and La. In addition, the presence of Zr in these SIMFUELs would be expected to have an over-riding influence on the lattice constant [6]. The Raman spectrum for SIMFUEL shown in Fig. 7.6 is consistent with the literature [6] and exhibits the peaks at 450 and 1150 cm\(^{-1}\) expected for stoichiometric UO\(_2\) [9]. The band at 1150 cm\(^{-1}\) was comparatively weak compared to that at 450 cm\(^{-1}\) consistent with a distortion of the cubic fluorite lattice.

The Raman spectrum for undoped UO\(_2\) [9, 28] does not exhibit the broad band between 500-700 cm\(^{-1}\) observed here on the 1.5 at% SIMFUEL (Fig. 7.7 (a)).
Figure 7.7 Raman spectra recorded on three UO$_2$ electrodes deconvoluted into contributions from bands at ~450, 540, 570 and 640 cm$^{-1}$
occurrence of this band has been attributed to UO$_2$ lattice damage, in the present case due to the formation of defects due to doping. A broad band centered at 585 cm$^{-1}$ is observed on single crystal UO$_2$ which can be deconvoluted into bands at 578 and 640 cm$^{-1}$ [28]. The band at 578 cm$^{-1}$ has been attributed to the longitudinal optical (LO) component of the T$_{2g}$ mode which arises due to the crystal lattice disorder whereas the band at 640 cm$^{-1}$ (observed at 630 cm$^{-1}$ [9]) has been attributed to distortion of the anion sublattice [8] and more recently attributed to a vibrational mode involving atoms in clusters of interstitial O atoms [9].

Based on these considerations, this broad band for 1.5 at% SIMFUEL was deconvoluted into three peaks at ~ 540, 570 and 640 cm$^{-1}$, Fig. 7.7 (a). The peak at 570 cm$^{-1}$ was shown to be independent of doping level in the series of SIMFUELs investigated previously [6] and is associated with the close-to-perfect fluorite structure [8]. While previously observed in the series of SIMFUELs the peak at 540 cm$^{-1}$ was unassigned although it was tentatively suggested it could be attributed to the formation of a phase with a perovskite (ABO$_3$) structure [6]. While this may have been a possibility in SIMFUELs containing dopants such as Ba and Sr (able to occupy A sites) and Zr (B sites), it is highly unlikely in a matrix containing only RE$^{III}$ cations. The prominent peak at 640 cm$^{-1}$ has been associated with the cuboctahedra constituting the U$_4$O$_9$ phase [8, 9] and would not be expected in stoichiometric SIMFUEL.
7.3.3.2 Gd-UO$_2$

For the Gd-UO$_2$ specimen the intensity of the peak at 445 cm$^{-1}$ is considerably lower than observed on the SIMFUEL and the band at 1150 cm$^{-1}$ is very weak confirming the degradation of the fluorite structure due to doping, Fig. 7.6. Relative to these two peaks, the broad band in the 500 to 700 cm$^{-1}$ wavelength region becomes more intense than observed for SIMFUEL.

Deconvolution of this region shows that the peak at 540 cm$^{-1}$ dominates over those at 570 cm$^{-1}$ and 640 cm$^{-1}$, Fig. 7.7 (b). As noted above, the peak at 540 cm$^{-1}$ is not observed in undoped UO$_2$. However, a peak at ~ 560 cm$^{-1}$, observed on RE$^{III}$-doped (Gd, La, Pr, Nd, Eu) CeO$_2$ (which also has a similar fluorite lattice) has been attributed to the creation of oxygen vacancies (O$_V$) [35]. The presence of such vacancies in UO$_2$ would be consistent with the calculations of Park and Olander [21, 22]. The dominance of this peak in Gd-UO$_2$ confirms that the primary influence of RE$^{III}$-doping is the creation of O$_V$ due to the need for charge compensation. Only a very small peak is observed at 640 cm$^{-1}$ confirming the absence of any clustering of O$_I$ associated with excess O in the oxide.

7.3.3.3 Dy-UO$_2$

For the Dy-UO$_2$ electrode the peak at 1150 cm$^{-1}$ is effectively absent and the broad band between 500 cm$^{-1}$ and 700 cm$^{-1}$ becomes even more dominant over the T$_{2g}$ band, Fig. 7.6. Inspection of the T$_{2g}$ band shows a shift to higher frequencies (445 cm$^{-1}$ to 455 cm$^{-1}$) and a Fano-type, rather than Lorentzian, line shape. Such a shift has been variously interpreted. For the RE$^{III}$-doped CeO$_2$ this shift was attributed to the increasing presence of O$_V$ [36], whereas for non-stoichiometric UO$_2$ a similar shift was attributed to
the clustering of O due to cuboctahedral formation as UO converted to UO [9]. For high degrees of non-stoichiometry this broadened peak could be deconvoluted into peaks at 445 cm\(^{-1}\) and a second peak at 470 cm\(^{-1}\) [8], which was shown to be a characteristic feature of the distortion to a tetragonal phase.

Deconvolution of the broad band between 500 cm\(^{-1}\) and 700 cm\(^{-1}\) yields the same three peaks observed for Gd-UO with the peak at 540 cm\(^{-1}\) dominant, Fig. 7.7 (c). The ratio of the intensities of the 540 cm\(^{-1}\) and 570 cm\(^{-1}\) peaks is approximately the same as for Gd-UO, and the peak at 640 cm\(^{-1}\) is effectively negligible.

### 7.3.3.4 General Raman features

Figure 7.8 shows the ratio between the areas of the T\(_{2g}\) peak (445 cm\(^{-1}\)) and the peak at 540 cm\(^{-1}\). Since the T\(_{2g}\) peak is characteristic of the undisturbed fluorite lattice and the 540 cm\(^{-1}\) peak is attributed to the creation of O associated with the RE\(_{III}\) dopant, the ratio of these two peaks is commonly taken as a measure of the number of such vacancies [37, 38]. The ratio changes in the sequence.

\[
\text{SIMFUEL} > \text{Gd-UO} > \text{Dy-UO} \quad (7.4)
\]

demonstrating an increase in the number of O as the level of RE\(_{III}\) doping increases.

A second feature worth noting is that the decrease in intensity of the minor broad peak around 155 cm\(^{-1}\) follows this same sequence. This peak has been related to the
Figure 7.8 The area ratio of the Raman peaks recorded ~ 445 cm$^{-1}$ and 540 cm$^{-1}$ ($A_{445}/A_{540}$: Fig. 7.7) as a function of doping level.

change in unit cell size in U$_4$O$_9$ [9] and, by comparison to ZrO$_2$ spectra, to a distortion of the U sublattice associated with the transition to tetragonal U$_3$O$_7$ [8]. Some XRD evidence was offered in support of this claim. Although a peak in this wavelength range cannot be attributed to the presence of the significant amounts of O$_1$ that would be required to form U$_4$O$_9$/U$_3$O$_7$, the loss of intensity suggests a decreasing tendency to form the distorted structures associated with the clustering of O$_1$ ions.

7.4 Discussion

The plots in Fig. 7.4 show the influence of the changes in electrode composition on the anodic oxidation reaction. At a potential of 0V, the electrode would be expected
to be oxidized to $\text{UO}_{2+x}$ [24] and the current to reflect, approximately, the rate and extent of the first step in reaction 7.3 ($\text{UO}_2 \rightarrow \text{UO}_2^{2+}$). At 0.3V, the currents would be representative of the rate of the second step ($\text{UO}_{2+x} \rightarrow \text{UO}_3.y\text{H}_2\text{O}/\text{UO}_2^{2+}$). While this separation is somewhat arbitrary, it clearly illustrates the influence of doping on both stages of the surface oxidation / conversion / dissolution reaction. In this regard electrochemical oxidation in an aqueous environment follows a similar two step reaction sequence to that observed for air oxidation. Additionally, the influence on the second step is greater than that on the first step, consistent with observations for air oxidation.

The observation that the two RE$^{\text{III}}$-doped electrodes are significantly less reactive than the SIMFUEL can be related to their tendency to form RE$^{\text{III}}$-O$_V$ clusters as indicated by the Raman spectra. Both electrodes show a strong Raman peak at 540 cm$^{-1}$ which, by comparison to the spectra observed for RE$^{\text{III}}$-doped CeO$_2$, can be attributed to the formation of O vacancies in response to the need for charge compensation. This leads to the formation of RE$^{\text{III}}$-O$_V$ clusters which limits the number of available O$_V$ sites and any incorporated O$_1$, which possess a double negative charge, will be repelled from the RE$^{\text{III}}$ dopant site. According to Park and Olander [22] the formation of Gd$^{\text{III}}$-O$_V$ clusters does not increase the number of extrinsic vacancies but diminishes already existing ones.

This effect is compounded by the influence of doping on the fluorite lattice parameter. For CeO$_2$, the cation radii for RE dopants (e.g., La$^{\text{III}}$, Eu$^{\text{III}}$, Gd$^{\text{III}}$) are generally greater than that of the matrix cation (Ce$^{\text{IV}}$) [39]. This leads to an increase in lattice parameter which expands the fluorite lattice and facilitates the incorporation of O$^{2-}$ and increases its mobility within the lattice. This enhances the catalytic capability of the
oxide and improves its ability to act as a high temperature oxygen anion conductor in solid oxide fuel cells [40].

By contrast the ionic radius of U^{IV} is approximately the same as that of Gd^{III}, and a similar influence of doping on lattice parameter would not necessarily be expected. However, there is considerable XRD evidence to show that, due to RE^{III}-O_{V} clustering, Gd doping causes a lattice contraction in UO_{2} [13, 33], which would lead to a decreased mobility of O^{2-} ions within the doped UO_{2} matrix. Since the initial step in the anodic oxidation reaction (UO_{2} \rightarrow UO_{2+x}) involves the incorporation of O^{2-} ions into O vacancies in the fluorite lattice these effects would be expected to limit the anodic rate as indicated by the small amount of cathodic charge required to reduce it, Figs. 7.4 and 7.5.

The more heavily doped Dy-UO_{2} would be expected to be even less reactive than the Gd-UO_{2} if anodic reactivity was controlled solely by the influence of RE^{III}-O_{V} clustering. However, the electrochemical behavior (Figs. 7.4 and 7.5) does not support this, the Dy-UO_{2} being more reactive for both stages of anodic oxidation, reaction 7.3. The ionic radius of Dy is slightly less than that of Gd making it more incompatible with the UO_{2} matrix. The low intensity of the 455 cm\(^{-1}\) peak and the total absence of the 1150 cm\(^{-1}\) peak confirm the greater extent of disorder in the Dy-UO_{2} electrode compared to the other two electrodes but provide no detailed explanation for this decreased reactivity.

Andersson et al [41] studied the influence of different trivalent dopants on the ionic conductivity of O ions in CeO_{2} and predicted that the optimum dopant combinations to improve conductivity, and hence catalytic activity, would be Nd/Sm and Pr/Gd. While this is the opposite influence to the decreased ionic conductivity required to suppress UO_{2} oxidation, similar calculations and/or experimental data would be
required if the difference in susceptibility to anodic oxidation due to \( \text{RE}^{\text{III}} \)-doping is to be more clearly understood.

While the number of dopant-vacancy clusters in SIMFUEL, as indicated by the ratio \( A_{455}/A_{540} \) (Fig. 7.8), is consistent with the higher anodic reactivity of this electrode, Figs. 7.4 and 7.5, a number of ambiguities exist, in particular the origin of the Raman peak at 640 cm\(^{-1} \). As noted above, a peak around this wavelength has been assigned to the presence of the cuboctahedral clusters associated with the presence of \( \text{U}_4\text{O}_9 \).

However, the presence of such clusters is associated with a much higher anodic reactivity than observed on the 1.5at\% SIMFUEL used in this study [42, 43].

The previous study with SIMFUELs showed that this peak at 640 cm\(^{-1} \) increased in relative intensity while that for the peak at 540 cm\(^{-1} \) decreased [6] as the degree of simulated burn-up (increase in doping level) was increased. This decrease in relative intensity of the 540 cm\(^{-1} \) peak suggests the number, or at least the relative importance, of \( \text{RE}^{\text{III}}-\text{O}_\text{V} \) clusters is decreasing despite the increase in \( \text{RE}^{\text{III}} \) content. However, this decrease is accompanied by the decrease in lattice parameter expected as \( \text{RE}^{\text{III}} \) doping increases. The SIMFUEL contains primarily \( \text{La}^{\text{III}}, \text{Nd}^{\text{III}} \) and \( \text{Y}^{\text{III}} \). While \( \text{Y}^{\text{III}} \) has an ionic radius close to that of \( \text{U}^{\text{IV}} \) the two \( \text{RE}^{\text{III}} \) cations have considerable larger radii than that of \( \text{Gd}^{\text{III}} \). Consequently, it is possible they might not be as effective as \( \text{Gd}^{\text{III}} \) in forming \( \text{RE}^{\text{III}}-\text{O}_\text{V} \) clusters.

Irrespective of this influence, this does not explain the greater importance of the peak at 640 cm\(^{-1} \) as the doping content increases. As noted above, the SIMFUEL also contains \( \text{Zr}^{\text{IV}} \), the content of which also increases as the degree of simulated burn-up increases. The cation, \( \text{Zr}^{\text{IV}} \), has an ionic radius significantly less than that of \( \text{U}^{\text{IV}} \) and
because of this size differential exerts a large, effectively controlling, influence on the lattice dimensions of irradiated nuclear fuel [[6] and references therein]. It is likely, therefore, that the decrease in lattice parameter observed in the sequence of SIMFUELs [6] can be attributed primarily to the presence of Zr$^{IV}$ rather than that of the RE$^{III}$ dopants.

If this is the case, then it suggests a different assignment of the peak at 640 cm$^{-1}$ in the Raman spectrum. In CeO$_2$, the presence of Zr$^{IV}$ leads to the formation of defects with O$_h$ symmetry in which the Zr$^{IV}$ cation is in 8-fold coordination with O$^{2-}$ (a Zr-O$_8$-type complex). This complex forms as a consequence of the difference in ionic radii between Zr$^{IV}$ and the host matrix Ce$^{IV}$ cation and contains a very limited concentration of O$_V$ [35, 44]. In CeO$_2$ doped only with Zr$^{IV}$ this leads to a Raman peak around 600 to 620 cm$^{-1}$ [35]. However, in CeO$_2$ doped with both Zr$^{IV}$ and RE$^{III}$ cations, peaks at 560 cm$^{-1}$, attributed to the formation of O$_V$ due to the RE$^{III}$-doping, and this peak at 600-620 cm$^{-1}$ are both observed. A similar influence of Zr$^{IV}$ in UO$_2$ could account for the Raman peak at 640 cm$^{-1}$ and its increase in relative importance as the doping level of the SIMFUELs is increased [6]. Since Zr$^{IV}$ doping also leads to a decrease in lattice parameter it would be expected to stabilize the UO$_2$ lattice against anodic oxidation and, by analogy air oxidation.

7.5 Conclusions

Two RE$^{III}$-doped UO$_2$ electrodes and a lightly doped SIMFUEL (1.5at%) have been characterized by Raman spectroscopy and cyclic voltammetry. The reactivity decreased in the order SIMFUEL > Dy-UO$_2$ > Gd-UO$_2$. While this sequence shows a
decrease in reactivity with RE$^\text{III}$ doping, the reactivity is not directly related to the RE$^\text{III}$ content suggesting an influence of the nature of the dopant.

Voltammetry shows that doping suppresses both stages of anodic oxidation; matrix oxidation ($\text{UO}_2 \rightarrow \text{UO}_{2+x}$) and its further oxidation to soluble U$^\text{VI}$ (as $\text{UO}_2^{2+}$). The second step appears to be more influenced than the first. This is consistent with the influence of RE$^\text{III}$ doping on the kinetics of air oxidation which also proceeds in two stages ($\text{UO}_2 \rightarrow \text{U}_3\text{O}_7/\text{U}_4\text{O}_9 \rightarrow \text{U}_3\text{O}_8$).

Raman spectroscopy shows the structure becomes increasingly dominated by the presence of RE$^\text{III}$-O$_V$ clusters as the doping level increases. This decreases the number of O$_V$ available to accommodate the injection of the O$_1$ required for oxidation to occur.

The Raman spectra recorded on the SIMFUEL suggests the behavior of this matrix is strongly influenced by the lattice contraction caused by the formation of Zr-O$_8$ clusters. The influence of these clusters on the reactivity of the UO$_2$ matrix remains to be characterized.
7.6 References

35. L. Li, F. Chen, J. Q Lu and M. F. Luo, Study of Defect Sites in Ce$_{1-x}$M$_x$O$_{2.5}$ ($x = 0.2$) Solid Solutions Using Raman Spectroscopy, *The Journal of Physical Chemistry A*, 2011 115 p. 7972-7977


Chapter 8

Influence of Carbonate on the Electrochemical Reactivity of 6.0 wt% Gd-doped UO₂

8.1 Introduction

The direct disposal of spent nuclear fuel in geologic repositories has been under consideration internationally for over 30 years. In the Canadian concept, spent CANDU (CANada Deuterium Uranium) fuel bundles would be sealed in corrosion-resistant copper containers with an inner steel vessel and placed in an engineered repository constructed 500m to 1000m deep in a stable geologic location [1]. The concept is based on a multiple barrier system involving spent fuel bundles, the corrosion resistant container, and a clay buffer which seals around the container in a deep geologic environment [2]. Container failure is not expected, since model calculations predict a loss of wall thickness by general corrosion of only a few microns [3]. However, it is judicious to assume some containers will fail allowing groundwater to contact the fuel causing radionuclide release [4]. Since the majority of the radionuclides in used fuel (UO₂) are located within the oxide matrix, their release rate to the groundwater will be controlled by the fuel corrosion/dissolution rate.

Of key importance in determining fuel corrosion and, hence, radionuclide release rates, is the reactivity of the UO₂ matrix and how it is modified by in-reactor irradiation. The key changes expected to influence the reactivity of the fuel are; (i) the presence of
non-stoichiometry, possibly associated with grain boundaries; (ii) the formation of noble metal particles which can act as microanodes or cathodes; and (iii) the rare earth (RE$^{III}$) doping of UO$_2$ which will change the conductivity and structural properties of the matrix [5]. We have been systematically studying all these influences. In this paper, the influence of rare earth doping (Gd$^{III}$ in this case) has been investigated.

The influence of fission products, including RE$^{III}$, on the air oxidation of UO$_2$ has been well studied and reviewed [5-15]. These studies show that the oxidation of UO$_2$ (or UO$_2$ doped with low concentrations of impurities) proceeds through U$_3$O$_7$ to the final product U$_3$O$_8$. By contrast UO$_2$ substantially doped ($\geq$ 4 to 10%) with rare earths or other fission products proceeds via U$_4$O$_{9+y}$ with this phase accommodating excess O beyond the nominal stoichiometry of UO$_{2.25}$. The further conversion of U$_4$O$_{9+y}$ to U$_3$O$_8$ is also kinetically inhibited.

For Gd-doped UO$_2$, the oxidized intermediate achieved the composition (U,Gd)O$_{2.4}$ which is more O-rich than U$_3$O$_7$ (UO$_{2.33}$). Similarly, spent LWR fuel with burn-ups in the range 190 to 960 MWh/kgU also yield U$_4$O$_{9+y}$ with a stoichiometry of $\sim$ 2.4 when oxidized at low temperature. By contrast, oxidation of spent CANDU fuel, which has a considerably lower burn up (120 to 320 MWh/kgU) and hence lower RE$^{III}$ doping, proceeded via a U$_3$O$_7$ intermediate [6, 8, 15-17].

In chapter 7 it was shown that doping with Gd to 6 wt% significantly reduced the reactivity of the UO$_2$ matrix, suggesting that the aqueous oxidation/dissolution (corrosion) of UO$_2$ would also be considerably slower than for undoped UO$_2$. However, these studies were conducted in solutions with a pH close to neutral when reactivity would be expected to be low. In this chapter a more extensive electrochemical study of
Gd-doped UO₂ (Gd-UO₂) is described in which experiments were conducted in chloride solutions containing various concentrations of bicarbonate/carbonate (pH ~9), since the groundwater contacting the fuel could contain significant levels of these anions which are well known to complex UO₂²⁺ [18] and to accelerate UO₂ corrosion [5]. The anodic dissolution kinetics of UO₂ in carbonate solution have been previously studied [19].

8.2 Experimental

8.2.1 Electrode Material and Preparation

All experiments were performed on chemically doped 6 wt% Gd-doped UO₂ (Gd-UO₂) received from Cameco Corporation, Port Hope, Canada. Pellets were cut into discs (thickness ~ 3mm) and electrodes were fabricated using a previously published methodology [20]. Before each experiment, the electrode was polished with wet silicon carbide paper (1200 grit) and rinsed with Millipore water (ρ =18.2MΩcm). Subsequently the electrode was cleaned in an ultrasonic deionized water bath to remove any polishing residue. The electrode resistance, measured using electrochemical impedance spectroscopy, was ~50 Ω cm, which is very close to the value (~55 Ω cm) measured previously on 1.5 at% SIMFUEL electrodes [20, 21].
8.2.2 Electrochemical Cell and Equipment

Experiments were performed in a standard three-electrode, three-compartment cell. Compartments were separated by sintered glass frits to avoid the contamination of the working electrode chamber. A commercial saturated calomel reference electrode (SCE) (+0.242 V, 25°C vs. SHE) was used, and a Pt wire with a spot-welded Pt mesh (surface area ~ 6 cm²) was employed as the counter electrode. All potentials are quoted on the SCE scale.

All electrochemical experiments were carried out using a Solartron model 1287 potentiostat to control applied potentials and record current responses. The current interrupt (IR) method was employed to compensate for the electrode resistance. Corrware™, version 3.0, software (Scribner Associates) was used to analyze the data.

8.2.3 Solutions

Solutions were prepared with deionized water (ρ =18.2 MΩ cm) purified using a Millipore milli-Q plus unit to remove organic and inorganic impurities. In order to study the effect of carbonate Na₂CO₃ and NaHCO₃ (Caledon, > 99%), salts were added in a 0.1 mol L⁻¹ NaCl (Caledon > 99%) solution maintaining a total carbonate concentration [HCO₃⁻/CO₃²⁻] = 5x10⁻² mol L⁻¹. The pH was adjusted to the desired value of ~ 9.0 using either HCl or NaOH and was monitored with an Orion model 720A pH meter. All chemicals used to prepare solutions were of reagent grade. Prior to an experiment the
solution in the electrochemical cell was purged with Ar-gas (Praxair) for an hour and purging was maintained throughout the experiment.

8.2.4 Electrochemical Techniques

In Cyclic Voltammetry (CV) experiments the potential was scanned from -1.5 V (depending on the experiment) to different anodic limits (up to +0.4V) and back while recording the current. In potentiostatic experiments a constant potential was applied to the electrode for an hour. Current-time profiles were recorded at potentials in the range from -0.5 to 0.4V.

8.2.5 Surface Characterization

8.2.5.1 Scanning Electron Microscopy and (SEM)/Energy Dispersive X-ray (EDX) Analysis

The surface morphology of the electrodes was determined using a field emission scanning electron microscope (Hitachi S-4500) equipped with a Quartz XOne energy dispersive X-ray (EDX) analyzer. An electron beam with an accelerating voltage of 15kV and a working distance of 10 mm was used to collect high resolution SEM micrographs at various magnifications (100-5000X).
8.2.5.2 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) was used to investigate the changes in stoichiometry of the electrode surface after electrochemical treatment at various applied potentials. A Kratos Axis Ultra spectrometer was used to record all the XPS spectra. An Al K$_\alpha$ (15mA, 14 kV) high energy monochromatic X-ray radiation source ($\nu = 1486.6$ eV) was used to bombard the fuel surface. The spectrometer work function was set to give a binding energy (BE) value of 83.96 eV for the metallic Au (4f$_{7/2}$) line. Instrument dispersion was adjusted to give a BE of 932.62 eV for the metallic Cu 2p3/2 line. Survey spectra were collected over the energy range from 0 to 1100 eV with an X-ray spot size $\approx 300 \times 700$ microns at a pass energy of 160 eV. High resolution spectra for all major species, i.e. U 4f, O 1s, C 1s were recorded at a pass energy of 20 eV with a step size of 0.05 eV. Charge neutralization was used on all specimens. The C 1s peak at 285.0 eV was used as a standard, when required, to correct for surface charging. All spectra were analyzed using CasaXPS software (version 2.3.14). The spectra were fitted using a 50% Gaussian/50% Lorentzian routine with a Shirley background correction [20].

Quantification of uranium oxidation states (U$^{IV}$, U$^{V}$ and U$^{VI}$) was achieved by curve-fitting the whole spectrum using the binding energies, as discussed elsewhere [22]. The resolved components in both spin-orbit split peaks and the associated satellite structures were used to calculate the total proportion of each oxidation state. The position and shape of the satellite structure were used to confirm the validity of the deconvolution of the U4f peaks, since this structure is dependent on their intensity, position and structure.
8.2.5.3 Raman Spectroscopy

Raman spectra were obtained with a Renishaw 1000 confocal Raman spectrometer (Renishaw PLC., UK) equipped with a Leica DMLM microscope. Spectra were excited using a He-Ne laser with a wavelength of 632.8 nm. The laser beam was focused to ~ 1 μm diameter with a 50x uncoated objective lens on an electrode mounted on carbon tape attached to a glass slide. The power of the laser beam at the sample surface was kept at 50% to avoid laser heating effects. The calibration of the spectrometer was verified by acquiring Raman spectra of a standard Si wafer which has only one intense Raman band (520 cm\(^{-1}\)). Spectra were measured for an exposure time of ~45 sec over the wavenumber range 120 to 1400 cm\(^{-1}\). Repeated measurements were carried out at different locations (plane area and pits/depressions) on the electrode to ensure that bands do not show any shifts in vibrational frequencies or relative change in peak intensities. A mixed Gaussian and Lorentzian peak model with a Shirley baseline correction was used to fit the Raman peaks, as discussed elsewhere [20].

8.3 Results and Discussions

8.3.1 Surface Characterization

Figure 8.1 (a) shows the typical surface morphology of the polished sintered Gd-UO\(_2\) pellet at various magnifications revealing a plane surface with a small number of shallow voids but no other well defined features. EDX analysis (Fig. 8.1 (b)) shows the
Gd is evenly distributed within the UO$_2$ matrix with no indication of a segregated Gd oxide. Such an even distribution is readily achieved since the ionic radii of Gd$^{III}$ (~0.107 nm) and U$^{IV}$ (~0.100 nm) are similar leading to a high solid solubility of Gd$^{III}$ in the U$^{IV}$O$_2$ matrix.

Figure 8.1 (a) SEM micrographs at various magnifications (100-5000X) and (b) EDX maps recorded on a Gd-UO$_2$ electrode at 1000X

Figure 8.2 (a) shows an optical image of the Gd-UO$_2$ electrode, and Fig. 8.2 (b) the Raman spectra collected at the two numbered locations. Both spectra exhibited a band at 450 cm$^{-1}$ which is assigned to the symmetric (O-U) stretching mode of the fluorite.
lattice of UO$_2$ [23]. The broad, low intensity peak around 1150 cm$^{-1}$ is commonly taken as diagnostic for the stoichiometric fluorite structure [24].

Figure 8.2 (a) An optical image of a polished Gd-UO$_2$ surface and, (b) the corresponding Raman spectra recorded at the two different locations.
The Raman spectrum obtained for Gd-UO$_2$ has been discussed in detail elsewhere (Chapter 7). Deconvolution of the 500 to 700 cm$^{-1}$ region shows the dominant peak is at 540 cm$^{-1}$, which has been attributed to the presence of Gd$^{III}$-O$_V$ clusters. The very shallow peak at 640 cm$^{-1}$ provides supporting evidence that the lattice is effectively stoichiometric, this band having been attributed to the presence of cuboctahedral clusters associated with the presence of U$_4$O$_9$ [25].

The influence of Gd doping on the surface composition of UO$_2$ was determined using XPS (Fig. 8.3). The fitted spectrum, which includes the U4f$_{5/2}$, U4f$_{7/2}$ and satellite peaks, clearly shows the presence of three U oxidation states (IV, V and VI). As indicated on Fig. 8.3, U$^{IV}$ is the dominant oxidation state present in the electrode surface as

![Figure 8.3](image.png)

**Figure 8.3** A fitted and background-corrected high resolution U4f XPS spectrum recorded on a polished Gd-UO$_2$ electrode
demonstrated by the sharpness of the spin-orbit peaks and from the location of the satellite peak at a binding energy ~7 eV higher than the U 4f_{5/2} peak. Identification of the satellite peaks is difficult since those associated with the U4f_{7/2} peak are generally obscured by the intense U4f_{5/2} peak or appear only as a shoulder. Besides, U^{IV}, a significant U^{V} content is observed. The presence of low amounts of U^{VI} may be due to air oxidation while transferring the electrode from the polishing area to the spectrometer.

8.3.2 Voltammetry

Figure 8.4 (a) shows a series of voltammograms recorded in solutions containing various carbonate concentrations (0 to 5 x 10^{-2} mol L^{-1}). The vertical dashed line shows that anodic oxidation becomes detectable in the forward scan for E ≥ -0.2V with and without carbonate in solution. As discussed in Chapter 7, and elsewhere for SIMFUEL [20], this can be attributed to the oxidation of a thin surface layer to a mixed U^{IV}/U^{V} oxide (U^{IV}_{1-2x}U^{V}_{2x}O_{2+x}). Over the carbonate concentration range from 0 to 5 x 10^{-4} mol L^{-1}, a current plateau is observed around 0 to 0.2 V, while at more positive potentials the current increases substantially but is independent of carbonate concentration. For carbonate concentrations in the range 10^{-3} to 10^{-2} mol L^{-1}, the current in this plateau region increases markedly, but the current at the anodic limit of 0.4 V is suppressed. A further increase in carbonate concentration leads to almost no current increase up to ~ -0.2 V, the disappearance of the plateau, and a marked increase in current at the anodic limit.
Figure 8.4 CVs recorded on a freshly polished Gd-UO₂ electrode in an Ar-purged 0.1 mol L⁻¹ NaCl, pH 9 solution: (a) [CO₃²⁻] = 0 to 5x10⁻² mol L⁻¹ (b) Repeated scans in a solution containing [CO₃²⁻] = 5x10⁻² mol L⁻¹ and on a rotating disk electrode at 16.67 Hz
In the reverse scan, a broad cathodic reduction peak occurs with a maximum at ~ - 0.75V. The size and breadth of this peak is independent of carbonate concentration. This reduction peak is generally associated with the reduction of a U^{IV}_{1-x}U^{V}_{2x}O_{2+x} /UO_2.yH_2O surface layer in the absence of carbonate and on 1.5 at % SIMFUEL is considerably reduced in size when carbonate is present. The disappearance of this reduction peak on SIMFUEL was attributed to the enhanced dissolution of U^{VI} (as UO_2(CO_3)_{x}(2-2x)^+) on the forward scan. The presence of this reduction peak in Fig. 8.4 (a) indicates that an oxidized surface layer is maintained on the Gd-UO_2 surface despite the presence of carbonate. Although only shallow, and difficult to see on the scale of this figure, a second shallow reduction peak (more visible in Fig. 8.4 (b)) is observed in the potential range +0.1V to -0.2V. This peak is only observed at high carbonate concentration suggesting it could be due to the presence of a thin layer of readily reducible U^{VI}O_2CO_3.

Figure 8.4 (b) shows there is a significant difference in the anodic current observed on the first scan compared to subsequent scans (recorded without repolishing the electrode). This may reflect the slightly enhanced anodic oxidation of the electrode surface due to the polishing procedure. Once this effect of polishing damage is removed the subsequent scans show very reproducible behavior including a measurable anodic reactivity between -0.9 V and -0.2 V. Previously, oxidation in this potential region has been associated with the presence of readily oxidizable non-stoichiometric UO_{2+x} locations on the electrode surface, possibly associated with grain boundaries [4]. The lack of any influence of electrode rotation on both the anodic and cathodic currents
demonstrates that the anodic and cathodic processes involved are activation or chemically controlled and not influenced by solution diffusion processes.

8.3.3 Potentiostatic Oxidation

Figure 8.5 shows a series of current density (log i) vs. time (log t) plots recorded at individual potentials in the range -0.5 to 0.5 V in 0.1 mol L^{-1} NaCl with (Fig. 8.5 (a)) and without (Fig. 8.5 (b)) carbonate (5x10^{-2} mol L^{-1}) present.

For the carbonate solution, at the lowest potential employed, -0.5V, the current rapidly became cathodic (Fig. 8.5 (b) black solid line) and eventually established a value in the range 1-3 µA. A similar switch was not observed at this potential in the non-carbonate containing solution. Although not shown in Fig 8.5 (a, b) (since the currents become extremely noisy) for all potentials ≤ 0V the final current recorded is negative. The absence of a similar shift to negative currents in the absence of carbonate suggests this cathodic current may be attributable to reduction of protons provided by bicarbonate dissociation. Over the potential range -0.4 to -0.1V (Fig. 8.5 (a, b)), the anodic current decreased with time with only a slight dependence on potential, consistent with a loss in surface reactivity. The current stabilizes in the long term beyond 1000 s in solutions both with and without carbonate. Although the log i-log t plots have the same slopes at each potential in the respective solutions, the current densities in carbonate solutions are higher.

Over the potential range 0 to 0.3V (Fig. 8.5 (c, d)), three distinct regions (A, B, C) are visible in which the log i-log t plots change slope. These regions are observed with
Figure 8.5 Potentiostatic current-time curves recorded for 1 h in Ar-purged 0.1 mol L^{-1} NaCl, pH 9, in the range -0.5 to 0.5 V without (a, c, e) and with (b, d, f) carbonate ([CO_3^{2-}] = 5x10^{-2} mol L^{-1}). Curve recorded at -0.5V in carbonate solution (b) switched from anodic to cathodic current after 100 s. The final currents established at all potentials ≤ 0 V were also negative but this is not shown for clarity. Regions A, B and C are discussed in the text.

and without carbonate but are more distinct when carbonate (Fig. 8.5 (d)) is present.

Similar behavior has been observed and discussed previously [20]. At short times (region A), the log i- log t plots, in the absence of carbonate (Fig. 8.5 (c)), are linear indicating a loss of surface reactivity. As observed in the CVs the current is only slightly dependent on potential until the potential exceeds ~ 0.2V. For oxidation times greater than ~ 100 sec (region B), the change in slope, which increases, indicates the formation of an insulating U^{VI} layer (UO_3.yH_2O) as previously discussed for SIMFUEL [20]. Finally, in region C, the current tends towards a steady-state value, and for potentials > 0.2V increases markedly, eventually eliminating region B. This increase in current at longer times was shown to be due to local acidification within surface asperities due to the hydrolysis of dissolved UO_2^{2+}

\[
UO_2^{2+} + yH_2O \rightarrow (UO_2)_n(OH)_{(2n-y)}^{(2n-y)^+} + yH^+ \tag{8.1}
\]

leading to an accelerated anodic dissolution rate at these locations.
In carbonate-containing solutions similar behavior is observed in region A indicating a similar deactivating film formation process. Except at the most positive potentials (≥ 0.4V; (Fig. 8.5 (f))) the current in this region is higher than in the absence of carbonate suggesting the deactivation of the surface is more extensive possibly due to an anodic dissolution process.

The major difference in behavior when carbonate is present occurs in regions B and C for potentials ≥ 0V. Over the range 0V to 0.35V (Fig. 8.5 (e, f)) the current in carbonate containing solutions is considerably higher suggesting, as expected, an enhanced anodic dissolution (as $\text{UO}_2(\text{CO}_3)_{x}^{(2-2x)^+}$). At the highest potentials the current is lower than in the absence of carbonate (Fig. 8.5 (f)). This can be attributed to the buffering of the local surface pH and the avoidance of the acceleration of dissolution as a consequence of local acidification.

Figure 8.6 shows the final steady state anodic current ($i_{ss}$) values recorded after 1 hour of polarization plotted against E in the Tafel format ($\log i_{ss}$ vs E). A similar set of data previously obtained for 1.5 at% SIMFUEL in the presence of carbonate is included [26]. In the presence of carbonate, the anodic currents for Gd-UO$_2$ are considerably lower than those recorded on SIMFUEL. The Tafel slopes at lower potentials (≤ 0.3V) are in the range 120 to 150mV indicating the mechanism of anodic oxidation/dissolution does not change, only the overall reactivity of the matrix. At higher potentials the currents tend to a plateau value although this occurs at lower potentials on the Gd-UO$_2$ electrode than on the SIMFUEL. The observation of a potential-independent current on SIMFUEL was previously attributed to control of the overall anodic dissolution process by the chemical dissolution of a UO$_2$CO$_3$ surface layer.
\[
\text{UO}_2\text{CO}_3 + \text{HCO}_3^- \rightarrow \text{UO}_2(\text{CO}_3)_2^{2-} + \text{H}^+
\]  

(8.2)

In the absence of carbonate, the Tafel slope at low potentials (100-300 mV) is very low (412 mV) indicating the formation of an almost passivating surface layer. The influence of local acidification leading to a higher current at more positive potentials is clear.

**Figure 8.6** Tafel plots for the anodic oxidation/dissolution of a Gd-doped \( \text{UO}_2 \) electrode in an Ar-purged 0.1 mol L\(^{-1} \) NaCl solution, pH 9, with ([\( \text{CO}_3^{2-} \]) = 5 \times 10^{-2} \text{ mol L}^{-1} \) and without carbonate. Data recorded on a 1.5 at% SIMFUEL in the carbonate solution is also included [26].
8.3.4 XPS Analysis

A detailed investigation of the oxidation state of U in the surface of the oxidized Gd-UO₂ electrode was carried out using XPS. Figures 8.7 and 8.8 show representative deconvoluted spectra for the U (4f₅/₂) and U (4f₇/₂) regions and their associated satellite structures recorded after a 1 hr of potentiostatic polarization at -0.5, -0.1, 0.2 and 0.5V in solutions without and with carbonate, respectively. The vertical dashed lines indicate the positions of the satellite peaks expected for U⁴⁺ (-0.5 and -0.1V), U⁵⁺ (-0.1, 0.2 and 0.5 V), and (hidden) for U⁶⁺ (0.2 and 0.5V) used to confirm the deconvolution of the main peaks. However, it is not straightforward to assign these satellites to specific oxidation states since they evolve due to multi-electronic effects. The percentages of U⁴⁺, U⁵⁺ and U⁶⁺ in the electrode surface are shown as a function of applied potential in Fig. 8.9.

In the potential range -0.5 to -0.25 V, changes in the composition of the surface are undetectable indicating that a potential of ~ -0.25 V is the lower limit for surface oxidation. The traces of U⁵⁺ and U⁶⁺ detected in this range may be due to a slight degree of surface oxidation on transfer of the electrode from the electrochemical cell to the vacuum chamber of the spectrometer. The measurable fraction of U⁵⁺ is likely due to the RE³⁺ doping of the electrode. This leaves unexplained the small degree of anodic oxidation observed electrochemically in this potential range (Fig. 8.4, Figs. 8.5 (a, b)), which leads to a loss of reactivity of the surface, Figs. 8.5 (a) to 8.5 (d).

Over the potential range -0.2 to 0.1V, anodic oxidation is clearly observed, the amounts of U⁴⁺ and U⁵⁺ continuously decreasing and increasing, respectively, with potential. In carbonate-free solutions, the U⁶⁺ content of the surface also increases with
increasing anodic potential. By contrast, in the carbonate solution, the U\textsuperscript{VI} content of the surface does not increase, consistent with the expectation that U\textsuperscript{VI} (as UO\textsubscript{2}\textsuperscript{2+}) will dissolve from the surface by complexation with carbonate (as UO\textsubscript{2}(CO\textsubscript{3})\textsubscript{x}\textsuperscript{(2-2x)+}).

**Figure 8.7** Representative U 4f XPS spectra resolved into contributions from U\textsuperscript{IV}, U\textsuperscript{V} and U\textsuperscript{VI} recorded on a Gd-doped UO\textsubscript{2} electrode in an Ar-purged 0.1 mol L\textsuperscript{-1} NaCl solution, pH 9, at a series of applied potentials -0.5, -0.1, 0 and 0.2V
Figure 8.8 Representative U 4f XPS spectra resolved into contributions from U^{IV}, U^{V} and U^{VI} recorded on a Gd-doped UO_{2} electrode in an Ar-purged 0.1 mol L^{-1} NaCl solution, pH 9, containing [CO_{3}^{2-}] = 5 \times 10^{-2} mol L^{-1} at a series of applied potentials -0.5, -0.1, 0 and 0.2 V.
**Figure 8.9** Relative fractions of all three U oxidation states as a function of applied potential (for 1 hour) in an Ar-purged 0.1 mol L\(^{-1}\) NaCl solution, pH 9, (a) without (from Fig. 8.7) and (b) with (from Fig. 8.8) carbonate ([CO\(_3^{2-}\)] = 5x10\(^{-2}\) mol L\(^{-1}\)) in solution.
For the Gd-UO₂ electrode, for potentials ≥ 0.2V in the presence of carbonate, the surface composition (U⁴⁺/U⁵⁺ ratio) becomes independent of potential which coincides with the range (0.2V to 0.4V) over which the steady-state currents become potential-independent, Fig. 8.6. This indicates that the surface U⁴⁺_{1-2x}U⁵⁺_{2x}O_{2+x} layer has achieved compositional steady-state in the presence of carbonate. The absence of U⁶⁺ on the electrode surface over the full potential range indicates that any UO₂^{2+} species formed are chemically dissolved into solution as soon as they are electrochemically formed. In addition, the presence of a strong U⁵⁺ signal is consistent with the voltammetric data (Fig. 8.4) which shows that the extent of oxidation of the surface, as illustrated by the constant height of the cathodic reduction peak, remains constant as the carbonate concentration is increased.

In the absence of carbonate, the U⁵⁺ content of the surface also becomes effectively constant at high potentials, the changes in fractional composition occurring mainly between U⁴⁺ and U⁶⁺. The retention of U⁶⁺ as a partially insulating surface layer would account for the lower anodic currents observed, Fig. 8.6. The slight loss of U⁶⁺ at the most positive potentials (0.45V and 0.5V) is consistent with the enhanced anodic dissolution currents, Fig. 8.6, attributable to local acidification at some locations on the electrode surface.

Figure 8.10 compares the influence of potential on the U⁵⁺ content of the surface for Gd-UO₂ in both carbonate and non-carbonate containing solutions to that of SIMFUEL in the absence of carbonate. The higher U⁵⁺ content on SIMFUEL in the potential range < - 0.25 V may reflect our improved procedure in avoiding air oxidation when the anodically oxidized electrode is transferred from the electrochemical cell to the
spectrometer. Despite this apparent artifact it is clear that extensive oxidation of the surface, via the incorporation of $O^{2-}$ interstitial ions and the creation of $U^{V}$ states, begins in all cases around $\sim -0.25$ V consistent with the current increases observed in CVs, Fig. 8.4. This observation confirms that the surface oxidation to $U_{1.2x}^{IV}U_{2x}^{V}O_{2+x}$ is not noticeably delayed on the potential scale by RE$^{III}$-doping at least up to the 6 wt% Gd used in the present studies.

**Figure 8.10** Fraction in the surface of Gd-UO$_2$ and SIMFUEL as a function of applied potential after potentiostatic treatment (for 1 hour) in an Ar-purged 0.1 mol L$^{-1}$ NaCl solution, pH 9, with and without carbonate.

The anodic currents measured in this potential range are small and only marginally dependent on carbonate concentration, Figs. 8.4 and 8.5, indicating only
marginal dissolution as U^{VI} is occurring. However, as shown previously in voltammetric experiments (Chapter 7) the extent of oxidation on Gd-UO_{2} is considerably lower than on SIMFUEL. This is confirmed by the larger U^{V} content, and its more rapid increase with potential, on the surface of the SIMFUEL compared to that of Gd-UO_{2} (in the absence of carbonate).

In chapter 7, the ability of RE^{III} doping to suppress anodic oxidation of the UO_{2} matrix (to U^{IV}_{1-2x}U^{V}_{2x}O_{2+x}) was attributed to the formation of RE^{III}-O_{V} clusters which limits the availability of the O_{V} required for the incorporation of O^{II} ions as oxidation proceeds. In addition, Gd-doping leads to a lattice contraction and a decreased mobility of O^{II} to deeper locations within the UO_{2} surface. This combination of unavailable O_{V} and limited O^{II} mobility in the UO_{2} matrix would account for the lower U^{V} surface content and its slower increase with potential on Gd-UO_{2} compared to SIMFUEL.

At more positive potentials, when the conversion of U^{V} to U^{VI} becomes important there is a considerable difference in the U^{V} contents. The very high content on the Gd-UO_{2} surface when carbonate is present reflects the absence of U^{VI} rapidly dissolved into solution as UO_{2}(CO_{3})_{x}^{(2-2x)^{+}}. Unfortunately, a similar set of XPS experiments on SIMFUEL in the presence of carbonate are presently unavailable. In the absence of carbonate, the U^{V} content begins to decrease at a much lower potential and decreases to considerably lower values at high potentials on SIMFUEL than on Gd-UO_{2}. This is attributable to the oxidation step

\[ U^{IV}_{1-2x}U^{V}_{2x}O_{2+x} \rightarrow UO_{3}.yH_{2}O \]  

(8.3)
and is consistent with the higher U\text{VI} content on the SIMFUEL surface compared to the Gd-UO\textsubscript{2} surface, Fig. 8.9 (a). These results show that Gd-doping (to 6 wt\%) inhibits both the kinetics of the matrix surface oxidation (to U\textsuperscript{IV\textsubscript{1-2x}}U\textsuperscript{V\textsubscript{2x}}O\textsubscript{2+x}) and its further oxidation (to UO\textsubscript{3,yH\textsubscript{2}O}).

**Figure 8.11** Representative O (1s) XPS spectra resolved into contributions from O\textsuperscript{2-}, OH\textsuperscript{-}, and H\textsubsuperscript{2}O recorded on a Gd-doped UO\textsubscript{2} electrode after potentiostatic treatment (for 1 hour) in an Ar-purged 0.1 mol L\textsuperscript{-1} NaCl solution, pH 9, at various constant potentials.
High resolution spectra for the O1s region, deconvoluted into contributions from O\(^2^-\), OH\(^-\) and H\(_2\)O are shown for the Gd-UO\(_2\) electrode in Figs. 8.11 (without carbonate) and 8.12 (with carbonate). The most intense peak (529.5 – 530.1 eV) can be assigned to the lattice O (O\(^2^-\)) and the peak in the region 530.2 to 531.5eV to hydroxyl (OH\(^-\)) species.

**Figure 8.12** Representative O (1s) XPS spectra resolved into contributions from O\(^2^-\), OH\(^-\), and H\(_2\)O recorded on a Gd-doped UO\(_2\) electrode after potentiostatic treatment (for 1 hour) in Ar-purged 0.1 mol L\(^{-1}\) NaCl solution, pH 9, with [CO\(_3^{2-}\)] = 5x10\(^{-2}\) mol L\(^{-1}\) at various applied potentials
The observed binding energies of these peaks are consistent with previous observations [18]. The shoulder at the highest binding energy (532.0 to 532.7 eV) indicates a significant presence of H₂O on the electrode surface. The binding energy for this peak is shifted compared to that previously observed on SIMFUEL [18]. This could be due to the fact that Gd oxides are hygroscopic when exposed to atmospheric conditions. In both carbonate and non-carbonate containing solutions the contribution from the lattice O is dominant at all potentials, consistent with the presence of only low surface contents of U⁶⁺ solids (expected to be present as U⁶⁺O₃,yH₂O). This is in contrast to previous observations on SIMFUEL when the surface becomes dominated by OH⁻/H₂O, an indication of the more facile conversion of U⁴⁺1−x,U⁵⁺xO₂+x to UO₃,yH₂O on SIMFUEL than on Gd-UO₂.

8.3.5 Cathodic Stripping Voltammetry (CSV)

Figure 8.13 shows a series of cathodic stripping voltammograms (CSV) recorded after potentiostatic polarization for 1 hour at individual potentials in the range -0.5V to 0.4V. Figure 8.13(a) shows the results recorded in a solution containing no carbonate and Fig. 8.13(b) the results recorded in a solution containing 5x10⁻² mol L⁻¹ of carbonate. The main reduction peak, centred in the potential range -0.6V to -0.9V has been previously observed on undoped UO₂ [4] and SIMFUEL [18], and attributed to the reduction of the anodically formed surface films.
Figure 8.13 Cathodic stripping voltammograms (CSVs) recorded on a Gd-doped UO$_2$ electrode after potentiostatic treatments (for 1 hour) at various potentials in an Ar-purged 0.1 mol L$^{-1}$ NaCl solution, pH 9, (a) without and (b) with carbonate ([CO$_3^{2-}$] = 5x10$^{-2}$ mol L$^{-1}$) at electrode rotation rate of 16.67 Hz
In the absence of carbonate, Fig. 8.13(a), there appear to be two reduction peaks in this region, possibly reflecting the dual phase nature of the surface film \( \text{U}^{\text{IV}}_{1.2} \text{U}^{\text{V}}_{2x} \text{O}_{2+2x} / \text{U}^{\text{VI}}_{2x} \text{O}_{3+y} \text{H}_{2} \text{O} \). In the presence of carbonate, Fig. 8.13 (b), the reduction peak at more negative potentials is not present. Since XPS shows no \( \text{U}^{\text{VI}} \) accumulates on the electrode surface when carbonate is present, Fig. 8.9 (b), it is possible this reduction process at more negative potentials can be attributed to the reduction of \( \text{UO}_{3+y} \text{H}_{2} \text{O} \) present on the electrode surface when carbonate is absent. This would then indicate the reduction at less negative potentials, observed irrespective of whether carbonate is present, can be attributed to the reduction of the oxidized matrix \( \text{U}^{\text{IV}}_{1-2x} \text{U}^{\text{V}}_{2x} \text{O}_{2+2x} \).

Figure 8.14 shows the total charge due to film reduction as a function of the applied potential, calculated by integrating the CSVs in Fig. 8.13 between the potential limits -1.2 V and 0.4 V. Two distinct regions of behavior are observed. Up to 0.1 V the charge is independent of whether carbonate is present or not, confirming that the matrix oxidation reaction does not involve carbonate. At more positive potentials the reduction charge increases in the absence of carbonate, consistent with the accumulation of \( \text{U}^{\text{VI}} \) (as \( \text{U}^{\text{VI}}_{2x} \text{O}_{3+y} \text{H}_{2} \text{O} \)) on the electrode surface (Fig. 8.9 (a)) and the presence of a dual reduction peak in the CSV, Fig. 8.13 (a).

When carbonate is present the charge due to film reduction reaches a peak value around 0.1 V; i.e., the potential at which the composition reaches a plateau value (Fig. 8.9 (b)). At more positive potentials the charge decreases slightly to a potential independent value. Since EDX analyses, Fig. 8.1 (b) show the Gd is uniformly distributed within the \( \text{UO}_{2} \) matrix it is reasonable to assume that matrix oxidation is also uniform, and the charge can be taken as a measure of the thickness of the oxidized surface layer. Thus,
when carbonate is present the $U^{IV}_{1-2x}U^V_{2x}O_{2+x}$ surface layer achieves both a constant thickness and a constant composition. This combination and the absence of $U^{VI}$ on the electrode surface indicates that the overall rate determining step in the anodic reaction is the creation of $U^{VI}$ by oxidation of the $U^{IV}_{1-2x}U^V_{2x}O_{2+x}$ surface layer.

**Figure 8.14** Total cathodic charge obtained by integration of the reduction peaks in the CSVs in Fig. 8.13

This provides strong evidence that the dominant influence of Gd doping is the inhibition of reaction 8.3; i.e., the second stage of the oxidation/dissolution step. In this regard the influence of $RE^{III}$ doping on the two stages of anodic oxidation/dissolution is very similar to its influence on the two stages of air oxidation [8, 10, 13, 27].
8.4 Summary and Conclusions

The effect of Gd doping (to 6 wt%) on the electrochemical behavior of UO₂ has been investigated in neutral to slightly alkaline solutions with and without carbonate, and the results compared to similar experiments performed previously on 1.5 at% SIMFUEL.

The anodic oxidation/dissolution mechanism on Gd-UO₂ is similar to that observed on SIMFUEL although the overall reactivity of Gd-UO₂ is much lower.

Gd-doping inhibits the anodic oxidation of UO₂. This can be attributed to the presence of Gd³⁺-Oᵥ clusters which reduces the availability of the Oᵥ required to accommodate excess Oᴵᴵ ions when oxidation occurs. Doping also leads to a lattice contraction which reduces the Oᴵᴵ mobility in the UO₂ matrix and limits oxidation to a thin surface layer of $\text{U}^{IV}_{1-2x}\text{U}^{V}_{2x}\text{O}_{2+x}$.

Gd-doping also hinders further oxidation of this thin layer to produce soluble UO₂²⁺. In carbonate solutions any UO₂²⁺ formed is rapidly dissolved (as $\text{UO}_2(\text{CO}_3)_{x}^{(2-2x)+}$) and the rate determining step in the overall anodic matrix oxidation/dissolution process is the oxidation of the $\text{U}^{IV}_{1-2x}\text{U}^{V}_{2x}\text{O}_{2+x}$ to produce UO₂²⁺.
8.5 References


18. I. Grenthe, J. Fuger, R. J. Konings, R. J. Lemire, A. B. Muller, C. Nguyen-Trung,
Chapter 9

Summary and Future Work

9.1 Project Summary

The overall research objective of this thesis was to develop a more detailed understanding of UO₂ (nuclear fuel) corrosion in acidic pH conditions and to investigate the influence of rare earth doping on the fuel corrosion process. Research has been concentrated on the following areas: (i) a determination of the reduction mechanism for H₂O₂ in low pH solutions; (ii) a study of the combined influence of H₂O₂ and H₂ on UO₂ corrosion in carbonate solutions; (iii) a determination of the influence of rare-earth doping on UO₂ electrochemistry; (iv) the characterization of different levels of rare-earth doping on the structural properties and anodic reactivity of UO₂; and (v) the influence of carbonate on the anodic reactivity of rare-earth doped UO₂. A combination of electrochemical and surface analytical techniques have been applied to identify the solid state structure of UO₂ and its surface composition as a function of potential, pH and dissolved oxidant (H₂O₂) concentration. The findings are important in understanding and assessing the behavior of spent nuclear fuel under permanent disposal conditions.

9.1.1 Mechanism of H₂O₂ Reduction in an Acidic Environment

Chapter 4 describes a study of H₂O₂ reduction on UO₂ (SIMFUEL) in a narrow pH range (1 to 4) to determine how the reduction mechanism changes with pH and how
this dictates, or is influenced by, the composition of the UO\textsubscript{2} surface. It was shown that the reduction mechanism depends on the locally established surface composition which is controlled by the bulk pH and H\textsubscript{2}O\textsubscript{2} concentration and the interfacial diffusive transport conditions. If the surface concentration ratio for [H\textsubscript{2}O\textsubscript{2}]/[H\textsuperscript{+}] is $\geq$ 1, H\textsubscript{2}O\textsubscript{2} reduction proceeds through the chemical formation of a U\textsuperscript{IV}\textsubscript{1-2x}U\textsuperscript{V}\textsubscript{2x}O\textsubscript{2+x} surface layer formed by O\textsuperscript{2-} injection into the readily-available interstitial sites in the UO\textsubscript{2} fluorite lattice. This mixed oxide surface is relatively stable in the neutral to alkaline conditions, and the current approaches the diffusion-controlled limit at the potentials required for H\textsubscript{2}O\textsubscript{2} reduction.

However, if the above ratio is $< 1$, the stabilization of a U\textsuperscript{IV}\textsubscript{1-2x}U\textsuperscript{V}\textsubscript{2x}O\textsubscript{2+x} layer is not feasible and H\textsubscript{2}O\textsubscript{2} reduction is catalyzed by the chemical formation of a (U\textsuperscript{V}O\textsubscript{2}OH)\textsubscript{ads} surface intermediate followed by its electrochemical reduction. This (U\textsuperscript{V}O\textsubscript{2}OH)\textsubscript{ads} layer can also be further chemically oxidized and dissolved. The instability of this adsorbed intermediate towards both electrochemical reduction and chemical oxidation prevents the H\textsubscript{2}O\textsubscript{2} reduction current from achieving the diffusion-controlled limit.

9.1.2 The Combined Influence of Dissolved H\textsubscript{2}O\textsubscript{2} and H\textsubscript{2} on the Electrochemistry of UO\textsubscript{2} in Carbonate Solution

In Chapter 5, the corrosion behavior of UO\textsubscript{2} in the presence of H\textsubscript{2}O\textsubscript{2} and H\textsubscript{2}O\textsubscript{2}/H\textsubscript{2} in both carbonate-free and carbonate-containing solutions is described. In carbonate-free solution, the steady state corrosion potential was found to depend on the nature of the purging gas (Ar or H\textsubscript{2}/Ar) and [H\textsubscript{2}O\textsubscript{2}]. In the absence of carbonate, H\textsubscript{2}O\textsubscript{2} caused an
increasing level of oxidation depending on [H₂O₂]. When carbonate was present oxidation was prevented at low [H₂O₂] any oxidized states being complexed and transferred to solution. At higher [H₂O₂] the UO₂ surface becomes irreversibly oxidized irrespective of whether carbonate was present.

Corrosion experiments in the presence of dissolved H₂ show it catalytically consumes H₂O₂ in the presence of carbonate, but the extent of this reaction depends on [H₂O₂]. In the presence of carbonate and H₂ oxidation of the surface by H₂O₂ appears to be reversible. On H₂O₂ addition at a sufficient concentration oxidation occurs rapidly but then reverses. This can be attributed to either H₂ oxidation on noble metal particles or to U°VI dissolution. The absence of oxidation is confirmed by XPS analyses.

9.1.3 Influence of Rare-Earth Doping on Structural and Redox Behavior of UO₂

Chapter 6 discusses the structure of UO₂ and UO₂/Y₂O₃ pellets with and without added Pd. All these materials exhibited very similar Raman and XPS spectra. The dominance of the Raman peak in the wavelength number range 500 to 700 cm⁻¹ and the absence of the LO phonon overtone at 1150 cm⁻¹ indicated that oxide matrix is non-stoichiometric. Deconvolution of the broad band in the 500 to 700 cm⁻¹ region yielded peaks at 585 cm⁻¹ and 630 cm⁻¹. The dominance of the latter peak confirmed that the oxide contains a large number of cuboctahedral U₄O₉ clusters.

XPS results supported the Raman evidence that these electrodes are non-stoichiometric, the deconvoluted U4f peaks showing a U°VI content in the range 36 to 37% compared to 17 to 26% for rare earth doped, but stoichiometric, SIMFUELs (over the simulated burn up range from 1.5 at% to 6.0 at%).
The electrochemical behavior is also consistent with specimens containing a mixture of stoichiometric and non-stoichiometric domains, voltammetric experiments exhibiting a current at $E \leq -0.4$ V which can be attributed to the more facile oxidation of non-stoichiometric domains. The overall electrochemical reactivity of these specimens was shown to be much higher than that of the well characterized 1.5 at% SIMFUEL.

The reactivity of these electrodes was also studied in solutions containing $\text{H}_2\text{O}_2$. Prior to $\text{H}_2\text{O}_2$ addition, linear polarization resistance ($R_p$) values (which indicate the rate of charge transfer on the $\text{UO}_2^{2+}$) were significantly different on SIMFUEL compared to the four doped electrodes. However, after $\text{H}_2\text{O}_2$ addition lower $R_p$ values were recorded on the $\text{UO}_2$ and $\text{UO}_2$-$\text{Y}_2\text{O}_3$ electrodes than on the SIMFUEL. These values are representative of the sum of the resistances for the two charge transfer processes: (i) the corrosion of the $\text{UO}_2^{2+}$ ($\text{UO}_2$) leading to the formation of soluble $\text{UO}_2^{2+}$; and (ii) the decomposition of $\text{H}_2\text{O}_2$ to $\text{O}_2$ and $\text{H}_2\text{O}$. The lower $R_p$ values measured on the $\text{UO}_2$ and $\text{UO}_2$-$\text{Y}_2\text{O}_3$ electrodes, compared to the SIMFUEL, can be predominantly attributed to the reactivity of the cuboctahedral clusters in the matrix and their ability to support reactions involving $\text{H}_2\text{O}_2$.

9.1.4 The Influence of Rare-Earth Doping on the Defect Structure and Anodic Reactivity of $\text{UO}_2$

In Chapter 7, the characterization of two $\text{RE}^{III}$-doped $\text{UO}_2$ electrodes (6 wt% Gd and 12.9 wt% Dy) and a lightly doped SIMFUEL (1.5 at%) by Raman spectroscopy is described. The increased level of rare-earth dopants was found to promote the formation of rare earth-oxygen vacancy ($\text{RE}^{III}$-$\text{O}_V$) clusters (characterized by a strong Raman peak
at 540 cm\(^{-1}\)). This leads to a decrease in the number of O\(_v\) and lowers the number of interstitial locations available to accommodate the extra oxygen anion (O\(_I\)) required for oxidation to occur.

Voltammetry experiments showed that the reactivity of these materials decreased in the order, SIMFUEL > Dy-UO\(_2\) > Gd-UO\(_2\). While the electrochemical reactivity decreased with a rise in RE\(^{III}\) doping level, the relationship is not direct indicating that the nature of the dopant may also be important. The results also show that doping suppresses both stages of the anodic oxidation process; the matrix oxidation (UO\(_2\) \(\rightarrow\) UO\(_2+x\)) and its further oxidation to soluble U\(^{VI}\) (as UO\(_2^{2+}\)).

### 9.1.5 Influence of CO\(_3^{2-}\) ions on the Composition of Gd-doped UO\(_2\) in Neutral Solutions

Chapter 8 describes an electrochemical study performed on a Gd-doped UO\(_2\) (Gd-UO\(_2\)) in carbonate solutions and shows that carbonate has a significant effect on the oxidative dissolution of the electrode. Voltammetric profiles recorded in solutions with various carbonate concentrations reveal that the surface layer (UO\(_2+x\)) formed at low potentials remains stable even at high positive applied potentials.

Constant potential experiments, with and without carbonate, at potentials in the range, -0.5 to 0.5V, showed that the oxidation/dissolution currents are higher in the presence of carbonate due to its complexation with UO\(_2^{2+}\). However, this behavior changes for E > 0.4V; when currents are relatively higher in carbonate-free solutions.
This can be attributed to the generation of local acidity due to the hydrolysis of UO$_2^{2+}$, which leads to an increase in anodic dissolution rate.

XPS analyses show that the onset potential for surface oxidation of Gd-UO$_2$ is similar to that for 1.5 at% SIMFUEL. However, at potentials higher than this threshold the rate of oxidation and dissolution of the Gd-UO$_2$ is suppressed compared to that of SIMFUEL. This is attributed to the presence of Gd$^{III}$-O$_V$ clusters, as discussed in Chapter 7. The absence of U$^{VI}$ species on the electrode surface at very positive potentials shows that the suppression of anodic dissolution is due to the stabilization of the UO$_2$ lattice against anodic dissolution.

9.2 Future Work

- The experiments conducted in this project were confined to room temperature. However, this is not within the temperature range expected under disposal conditions. Both electrochemical and corrosion experiments on doped UO$_2$ need to be conducted at higher temperatures (60-70 °C).

- The mechanism for H$_2$O$_2$ reduction, Chapter 4, was determined without considering the effects of the presence of H$_2$. Since H$_2$ is the most important reducing species anticipated in a repository, the influence of H$_2$ on the mechanism of H$_2$O$_2$ reduction should be determined.
• In Chapter 7 the influence of rare earth doping was determined for only two rare
earths at a single, but different, doping level for each. In order to determine
whether fuel burn up will have a significant influence on fuel reactivity, an
extended range of doping levels (e.g., 2 to 15 wt% Gd) needs to be investigated.

• The kinetics of $\text{H}_2\text{O}_2$ reduction on $\text{UO}_2 \text{RE}^{\text{III}}$ doped to different levels needs to be
investigated, if models to predict fuel performance are to be developed.

• In this thesis the electrochemical oxidation of doped $\text{UO}_2$ was studied. These
studies need to be extended to the study of corrosion in the presence of $\text{H}_2\text{O}_2$ and
$\text{H}_2$.

• A key unknown in spent fuel behavior is the reactivity of grain boundaries, which
are sites expected to accommodate a substantial inventory of fission products.
Electron backscatter diffraction (EBSD), which is capable of detecting two-
dimensional (2D) defects (grain boundaries) could be used to determine grain
boundary character (i.e., grain size and misorientation). By combining these
evaluations with etching experiments designed to determine the relative reactivity
of grain boundaries, it might be possible to determine whether or not the long
term performance of these locations will be important.

Since, compared to metals, little work has been done to characterize their
atomic structure in fluorite structured materials. So, attempting to examine GB
distribution and characterizing that how much difference in their atomic details
can influence fuel properties would give a more understanding about fuel microstructure dependent kinetic processes.
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**CONFERENCE PRESENTATIONS**

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- **M. Razdan** and D. W. Shoesmith, 32nd *Annual Canadian Nuclear Society Conference*, Niagara Falls, ON, Canada (2011) (Poster).


