Studies of the Charge Storage Properties of Poly(bithiophene) and Amorphous Carbon Nitride

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A thesis submitted in partial fulfillment of the requirements for the degree in Master of Science

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STUDIES OF THE CHARGE STORAGE PROPERTIES OF POLY(BITHIOPHENE) AND AMORPHOUS CARBON NITRIDE

(Thesis format: Monograph)

by

Timothy Adam Forristal

Department of Chemistry

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science

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Abstract

The charge storage properties of several potential materials for battery applications have been investigated. Poly(bithiophene) films were prepared by potentiostatic and potentiodynamic electropolymerization methods. These films were then subject to galvanic cycles at varying rates and to various potential limits in order to explore their use as electrodes in a battery. Potentiodynamically deposited films retain their charge better over multiple cycles. By comparing to data collected by atomic force microscopy, we conclude that these films are less crystalline than films deposited potentiostatically and are better suited for the volume changes that occur when being charged and discharged.

Amorphous carbon nitride films of various nitrogen contents were deposited on to aluminum substrates and subjected to galvanic cycles at varying currents in a solution containing lithium hexafluorophosphate. It is demonstrated that amorphous carbon nitride could potentially be a candidate to replace graphite used as an anode in traditional lithium-ion batteries.

Keywords

Electronically Conducting Polymers (ECPs); Polybithiophene; Electropolymerization; Lithium Ion; Carbon Nitride; Battery; Charge Storage
Co-Authorship Statement

All of the experimental work was carried out by Adam Forristal under the direction and supervision of Dr. Oleg Semenikhin except where noted below.

AFM (Atomic Force Microscopy) imaging and sample preparation for AFM was performed by Dr. Kevin O’Neil.

Deposition of Carbon Nitride thin films was done by Michael Nieradko.
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1 Introduction

1.1 Motivation for this work

1.1.1 Charge Storage Applications

The problem of energy storage is very important, and as of yet unsolved. There are many popular applications that currently require reliable methods of storing energy for long periods of time, including electric vehicles and renewable energy sources. For electric cars in particular, the few suitable storage methods currently available to store the required energy are prohibitively expensive and inefficient.\(^1\)

Many forms of renewable energy can also benefit from better energy storage materials. Because many types of renewable energy are intermittent, including solar and wind power, it is critical that good storage solutions be available for times when the weather required for their production is not available. Even the traditional power grid can benefit from improved storage. A significant amount of energy is generated during low-use hours, such as overnight. It would be much more efficient if this could be kept for longer periods of time for consumption during times of intensive power usage. A more specific case can be made for energy storage in rural areas, which in Canada have been seen to go for days without power while waiting for repairs to the grid during periods of maintenance or following a natural disaster.\(^2\)

The lithium-ion battery is currently the most common option for energy storage, and can be found in a wide variety of devices from home electronics to electric vehicles and aircraft. Their ability to store large amounts of power in a relatively small and light space makes them useful as a key tool in many charge storage applications. However, there are many ways to improve upon this technology.

One of the main bottlenecks in lithium-ion battery technology is the performance of the anode. Currently, the most common anode used in these batteries is graphite, which has been shown to have relatively low specific capacity and poor mechanical properties.
Therefore, it is worth investigating the chemistry of the batteries in order to find new materials to use as lithium-ion anodes.

Additionally, lithium-ion batteries typically do not perform well in extreme temperatures or environments. For example, there were recently problems discovered in the lithium-ion battery systems of Boeing’s 787 Dreamliner planes leading to electrical failures and fires mid-flight. This has resulted in every model 787 Dreamliner around the world being permanently grounded. While improvements have been made to try to prevent issues like Boeing’s with future battery systems\(^3\), it is also worth investigating other battery technologies to find a solution. One of these charge storage solutions, at least for some applications, may be electronically conducting polymers.

### 1.1.2 Electronically Conducting Polymers

Electronically conducting organic polymers are of significant interest for use as a material in charge storage devices. They are lightweight, flexible and non-toxic, and can be used as both cathodes and anodes in a battery cell. However, they contain their own set of issues. Specifically, the problem of degradation and stability of organic conducting polymers has been detailed repeatedly in the literature since 1980s, first with respect to overoxidation of such materials in solution\(^4-11\), and in solid-state electronic and photovoltaic devices\(^12-16\). These degradation processes are greatly accelerated by the addition of nucleophiles, such as water. Overoxidized materials rapidly lose the reversibility of their doping-undoping and in most cases their electronic conductivity; therefore preventing overoxidation and oxidative degradation of electroactive polymer materials is an important and yet to be fully solved problem of the science and technology of conducting polymers.

While the problem of chemical changes involved in oxidative degradation and deactivation has been addressed to an extent, the role of the polymer morphology and the morphological changes in general in the course of repeated doping-undoping have attracted insufficient attention of researchers beyond the well-known swelling of the polymer films due to uptake of solvent\(^17-21\). In some instances, the changes in the morphology upon cycling were noted in the literature\(^22\), such as transformation of
globular structures for freshly prepared polymers to chain-like or cauliflower structures, but no detailed analysis of these changes or the relationship between the morphology and nanoscale properties of the fresh and cycled films were performed.

Additionally, there has been no major work done that looked at the changes in the redox responses of the polymer films over the course of repeated doping-undoping cycles, especially related to the changes in the polymer morphology and nanostructure. In most cases, the analysis concerned the changes due to overoxidation\textsuperscript{23}.

1.1.3 Carbon Nitride

One of the most common materials used as an anode in lithium ion batteries is graphite. The batteries themselves rely on the intercalation of ions into the electrodes followed by an extraction step when the battery’s current reverses (i.e. when the battery stops charging and is discharged, or vice versa). During the battery’s discharge, positive lithium ions are extracted from the graphite anode and inserted into the cathode, which is generally some lithium-containing compound (common examples include lithium cobalt oxide, lithium iron phosphate or lithium manganese oxide).

Various nitrogen containing carbon materials such as carbon nanotubes have been speculated to have a higher charge storage density than graphite\textsuperscript{24}, but are still largely untested. If amorphous carbon nitride can be shown to perform better than graphite it could represents a leap forward for future charge storage devices. For a variety of reasons, especially including the availability of amorphous carbon nitride and the difficulty involved in studying its mechanical properties (due to different carbon nitride films potentially having significantly different properties), no work has actually been done in exploring this particular aspect of carbon nitride.
1.2 Scope of Thesis

Chapter 2 outlines a brief overview of the key essentials responsible for understanding organic polymers and their study. It also includes descriptions of the electrochemical deposition techniques used to polymerize the materials used, as well as the used to characterize the deposited polymers including electrochemistry and AFM. The method of preparation for carbon nitride using magnetron sputtering is also detailed.

Chapter 3 is an examination of the experimental setup used, as well as detailed descriptions of specific parameters involved in polymer and carbon nitride deposition, and the characterization parameters used in the experiments performed in chapters 4 and 5.

Chapter 4 of this thesis focused on demonstrating the role of microscopic structural factors involved in the degradation and reversibility of electron-conducting polymer materials. The role of deposition technique and its relation to the polymer morphology and nanostructure will be also considered.

Using polymer films prepared by two different electrochemical electropolymerization techniques, it was shown that otherwise identical polymer films demonstrated very different cyclability and charge storage capacity. The electrochemical data were related to structural factors such as crystallinity and degree of disorder. This was determined using atomic force microscopy (AFM) and AFM phase imaging (PI-AFM). The results show that the low cyclability may be related to mechanical and structural factors, rather than simple overoxidation of the polymer material.

Chapter 5 outlines the results regarding the prospects of the use of carbon nitride as a positive electrode for Li-ion batteries. We studied the intercalation of Li ions into CN_x using cyclic voltammetry and galvanic cycles, simulating the charging-discharging process in a functional battery. The results demonstrate that CN_x may be promising for the use in Li-ion batteries, although additional work still needs to be done in exploring this property of carbon nitride further.
2 Background

2.1 Electronically Conducting Polymers

The term electronically conducting polymer, or intrinsically conducting polymer refers to organic polymers with the capability to conduct electricity, either with full conductivity similar to that of metals or as semiconductors. The properties of these materials enable them to behave as suitable substitutes for traditional materials in a variety of common applications, including batteries, solar cells and light-emitting diodes. The key scientific interests surrounding these polymers has been in analyzing and optimizing specific properties of various polymers, or else optimizing a single polymer for use in a particular application.

Electronically conducting polymer can refer to any hydrocarbon or hetereoaromatic polymer with an extended delocalized pi-electron conjugated system, with the simplest example being polyacetylene. The energy levels in the conjugated system lead to the development of an energy band similar to the valence band in metals. In their neutral state, the valence bands of these materials is filled, with no free sites to allow for electron movement. This results in typical polymer behaviour as either insulating or semiconducting materials. In order to become conducting, the polymers must be doped through either oxidation or reduction. Becoming doped in this way creates either vacancies in the valence band (oxidation) or forces electrons to the conduction band (reduction). During this process a certain amount of solvent and electrolyte enters the polymer, resulting in swelling that reverses as the solvent leaves during any undoping step. Repeated doping and undoping of the polymers results in mechanical stress from this swelling, which leads to diminishing electroactive performance. Figure 2-1 illustrates the doping/undoping for the conducting polymer polybithiophene (PBT). It shows a cyclic voltammogram (CV) of PBT performed in a solution of supporting electrolyte without thiophene monomer.
In these conditions, we are able to observe the redox behavior of the polymer. On the forward scan, from 0 V to +1.25 V, the doping (oxidation) of the polymer occurs. In this form the polymer is conducting. During the reverse scan back to 0 V, the undoping/reduction of the polymer occurs, resulting in a return to the neutral aromatic form (or undoped, semiconducting state) of the polymer. The reduction curve is much wider and less pronounced than the doping curve due to the heterogeneity of the polymer resulting in the undoping process occurring more randomly and slowly than the oxidation of the polymer film.

### 2.2 Electrochemical Methods

Conducting polymers can be synthesized in a variety of different ways. For the purposes of this work, polymers were deposited electrochemically because it allowed for control of the polymer film thicknesses and properties. The following mechanism is a general representation of the electropolymerization process.

In this work, the polymer films were electrochemically prepared using galvanostatic, potentiostatic, or potentiodynamic deposition methods. The benefits to using these specific methods of polymerization are that they allow for easy control of the deposition
conditions of the polymer, ie. thicknesses, which is helpful in determining the possible origin of inhomogeneity of these materials.

\[ \text{Polymerization of polybithiophene} \]

2.3 Potentiostatic Deposition

This basic polymer deposition technique involves holding the working electrode at a particular potential while measuring current vs. time. For the type of films used in this thesis, the potentials used were typically under two volts. In this method, the radical-radical coupling mechanism described above is observed, and the film is produced in a charged/doped state. Discharging of the film is performed to reduce the polymer to its semiconducting state before it can be studied. Potentiostatic deposition has the benefit of generally yielding polymers with the most consistent morphology. While it is expected that potentiostatic depositions performed under identical conditions (i.e. monomer concentration in solution, working electrode size and material, deposition potential) will yield virtually identical films, changes in thickness can be difficult to predict when changing parameters. Figure 2-3 shows a typical potentiostatic deposition curve. The deposition process starts immediately,
2-3 A typical potentiostatic deposition. A polymer film has been deposited at the bottom of the deposition curve (2s). The remaining deposition time increases the thickness of the film. From reference 25.
2.3.1 Potentiodynamic Deposition

Potentiodynamic polymer deposition is the repeated cycling of the working electrode from well below a monomer’s oxidation potential to a point a few hundred mV beyond it. Over the course of repeated cycles, layers of polymer become deposited on the working electrode. It is an extremely common method of polymer deposition that creates films which are very similar, but not identical, to potentiostatically deposited films. The resulting scans, or cycles, are combined to form a cyclic voltammogram (CV) of the polymerization process (figure 2-4).

![Cyclic voltammogram](image)

2-4 A typical cyclic voltammogram illustrating the potentiodynamic synthesis of polybithiophene. Every subsequent scan results in the deposition of more polymer onto the surface of the electrode (red arrows). From reference 26.

On the forward scan (0 V to +1.5 V) of the CV, two peaks can be observed. The first peak is attributed to the oxidation of the polymer already deposited on the electrode surface. It is important to note that on the very first scan of the CV, this peak is not present. This is because there is no polymer phase present during the initial scan. The second peak located at more positive potential is due to the oxidation of the monomer in the solution. On the reverse scan (+1.5 V to 0 V), the peak located at negative current
values is due to the reduction of the polymer on the electrode surface. Every subsequent scan results in the deposition of more polymer onto the surface of the electrode (the red arrows in figure 2-4). As a result, the oxidation and reduction currents can be seen to increase with each cycle (thick arrows) as more and more polymer phase is present. In this particular method of polymerization, the film thickness can be directly controlled through the adjustment of the number of scans performed; the greater the number of scans, the greater the thickness of the polymer film. However, this can also be a drawback. While film thickness is directly related to the number of cycles performed, it can be difficult to maintain a particular thickness even when the same number of sweeps are performed. This becomes especially true when creating multiple polymers from the same solution as the concentration of monomer available in solution starts to diminish.

2.4 Carbon Nitride

2.4.1 Carbon Nitride Thin Film Deposition

Nitrogen can be incorporated into highly sp$^3$ hybridized diamond as well as sp$^2$ hybridized amorphous carbon to create nitrogen doped tetrahedral amorphous carbon and carbon nitride thin films respectively. $^{27}$ This thesis focuses exclusively on the use of sp$^2$ hybridized carbon nitride thin films.

Addition of nitrogen strongly alters the electronic properties of the native carbon materials. Highly sp$^2$ hybridized amorphous carbon has optical and electronic properties similar to graphite; being a black film with semi-metallic or semi-conducting properties depending on the nitrogen content. The main difference is that the material does not exhibit the same long range order as graphite due to the smaller and more disordered cluster sizes. The addition of a small amount of nitrogen into this material can further increase the electronic conductivity. For higher nitrogen containing films, these materials are converted from a highly conductive semi-metal to a semiconductor material. $^{28}$

Radio-frequency magnetron sputtering is a well-developed technique for the deposition of carbon nitride thin film materials. Magnetron sputtering is also an industrially practical deposition technique that can be used to deposit conductors, semiconductors, and
insulators made from elemental and compound materials. In view of high-throughput manufacturing of photovoltaic devices, this makes magnetron sputtering of carbon nitride thin films a very valuable deposition process.

Magnetron sputtering is a physical vapour deposition technique that relies on the momentum transfer of positively charged ions to eject matter from a target material towards a substrate where deposition occurs. A custom built RF magnetron sputter deposition system was used to prepare carbon nitride thin films. Figure 2-5 illustrates the sputter deposition of a graphite target using an Ar gas source. The target material to be sputtered is held at a negative bias (typically hundreds of volts) relative to the substrate and deposition chamber, which are grounded. An inert gas source such as argon is introduced into the deposition chamber which causes the pressure to increase. Some argon atoms can become ionized, which in the presence of a strong electric field between the target and substrate leads to the formation of a plasma. The plasma is a quasi-neutral gas that consists of equal numbers of positive and negative charges along with neutral atoms and/or molecules. Due to the large negative bias that is applied to the target, the positively charged ions are accelerated towards the target, collide with it, and eject some of the material by ion bombardment. The target material is ejected upward by momentum transfer towards the substrate where it is deposited to create a thin film. Magnetron sputtering utilizes magnets placed behind the target to confine the charged plasma near the surface of the target material which increases ion bombardment and sputter deposition rate. It is also possible to use a gas which is not inert and will react with the target material. Nitrogen is used to react with the carbon target material to generate carbon nitride thin films. The use of a reactive gas during the sputter deposition process is referred to as reactive magnetron sputtering.
2.4.2 Intercalation of Lithium Ions and Lithium-Ion Batteries

In order to understand how carbon nitride fits into a study of lithium intercalation, it is worth mentioning how a lithium ion battery stores energy.

Lithium ion batteries are constructed from three important segments – an anode, a cathode and an electrolyte. The anode of a lithium-ion battery is generally made of some form of carbon, while the cathode is comprised of some other metal or metal oxide. The electrolyte consists of a lithium salt dissolved in a solvent. The anode, most popularly graphite, is kept away from the cathode, a lithium-containing compound with convenient redox chemistry, by a separating material that allows the lithium ions to pass through without letting the two electrodes to be in electrical contact with one another.

Both electrodes are capable of having lithium ions insert into them through intercalation. In order to charge the battery, the positive lithium ions move from cathode to anode. When discharging, the ions move in reverse. The electrolyte serves as a reservoir of Li
ions for intercalation. Figure 2-6 demonstrates the structure of a typical lithium-ion battery cell.

![Diagram of a lithium-ion battery cell]

2-6 - visual representation of the basic structure of a lithium-ion battery cell. From reference 46.

A variety of factors control the effectiveness of lithium-ion batteries. One of the most important is the charge storage capability of the anode. While graphite is a convenient material to use, it has quite low specific charge capacity by virtue of requiring 6 carbons to contain a single lithium ion. For this reason, other materials with higher per-gram charge capacities are constantly being investigated for use in lithium ion batteries.

2.5 Atomic Force Microscopy

Atomic Force Microscopy (AFM) is a versatile technique that allows the visual characterization of surface structure and the measurement of numerous crucial sample properties on the nanoscale.
AFM is rather different from other microscope techniques in the way that it does not form an image by focusing light or electrons onto a surface like an optical or electron microscope. The AFM physically touches a sample’s surface by creating a grid over a specified area with a sharp probe, effectively building a map of the height of the sample. A laser is deflected off of an AFM cantilever attached to the probe, and into a photodetector which records the deviations in height as the probe scans over the surface. This is then translated by the computer into physical data points to form a corresponding image. While there are a few different typical AFM methods, the only one used for this thesis is referred to as Tapping Mode AFM.

One other important advantage of AFM lies with the availability of related auxiliary techniques, or extensions of AFM, which allow determination of a number of important additional parameters simultaneously with the topography scanning and at specific well defined points at the sample surface. The only relevant extension to this thesis is Phase Imaging AFM.

### 2.5.1 Phase Imaging AFM

Phase imaging is an extension of a regular tapping–mode AFM that allows simultaneous measurements of the topography and the local mechanical properties, such as adhesion, viscoelasticity, hardness, etc., of conducting or semiconducting samples with nanometer resolution. Tapping mode refers to a method in which the microscope’s cantilever is resonated across the surface of a sample in such a way that contact is established intermittently (the tip “taps” the surface). The phase imaging itself is based on assessing the phase shift of an AFM cantilever as it is brought into contact with the surface of a material against the vibration of the cantilever when it retracted from the surface (a freely vibrating cantilever). When the AFM probe is brought close to a surface, at some point there will be a dampening of the cantilever vibration amplitude. At the same time, the phase of the cantilever vibrations is also shifted depending on whether the probe-sample contact is elastic or inelastic.

For an elastic response, the probe moves back more readily upon contact with the sample and the phase shift of the cantilever vibrations stays near zero or becomes more positive
in the case of a strong repulsive interaction with the sample (known as hard tapping). Likewise, for an inelastic response, the probe is delayed, or “sticks” to the surface, when it comes into contact and the phase shift of the cantilever is negative. Overall, the magnitude of the phase shift is dependent upon the type of interaction (elastic/inelastic) or in short, it is based on assessing the dissipation of energy of the vibrating cantilever transmitted to the sample through the probe-sample contact. These processes are also influenced by the elastic modulus and other mechanical properties of the sample, which are related the crystallinity of the material\textsuperscript{30}. Since the crystallinity can be evaluated simultaneously with the regular topography information, phase imaging AFM is an excellent technique that can be used to study the distribution of crystalline and amorphous phases in a conducting polymer, or related materials.
3 Experimental

3.1 PBT Samples and Substrates

Two types of PBT samples were used for the work presented in chapter 4. The first type were electrochemically deposited poly[2,2'′-bithiophene] films on a 2 mm diameter platinum disk as a substrate for electrochemical measurements. The second type was electrochemically deposited PBT films on highly oriented pyrolytic graphite (HOPG) (NTMDT, ZYB quality). These samples were used for AFM measurements used as supporting data. Electrochemical measurements performed on samples deposited on Pt were performed in monomer-free solutions. CV characterization was performed on some PBT films deposited on HOPG in order to ensure that films grown on HOPG had similar properties to those grown on Pt; however, only freshly prepared samples were used for AFM imaging.

All PBT films were produced from a 0.005 M solution of 2,2′-bithiophene (Aldrich) in acetonitrile containing 0.1 M of tetrabutylammonium hexafluorophosphate (TBAPF$_6$) (Aldrich) as a supporting electrolyte. The monomer was purified by sublimation at a reduced pressure; the salt was used as received. Acetonitrile was purified using an SPS-400-5 solvent purification system (Innovative Technology) using columns packed with activated alumina and copper catalysts. The water content was less than 10 ppm. A Princeton Applied Research (PAR) model 263A potentiostat/galvanostat controlled using version 2.8 CorrWare/Corrview software (Scribner) was used. The monomer and supporting electrolyte were stored at room temperature in a vacuum desiccator over silica gel to prevent from moisture accumulation.

Silver pseudo-reference electrode (E = +0.05 V vs. SCE) and platinum counter electrodes were used in all cells. The potential of the pseudo-reference electrode was periodically calibrated vs. a ferrocene-ferricinium redox couple. To improve stability and consistency, between measurements the reference electrode was stored in a solution of supporting electrolyte of the same concentration as during measurements. All potentials were measured and are presented with respect to this reference electrode.
3.1.1 Deposition of Polymer Films

Electropolymerization of the samples was performed in specially designed three-electrode Pyrex glass cells without separation of anodic and cathodic compartments. The working electrode was a 2 mm diameter platinum disc embedded in a teflon holder. Prior to deposition, the platinum working electrode was cleaned on a polishing cloth with 95% ethanol, rinsed with MilliQ water, and dried under a heat gun.

Two types of PBT films on Pt were prepared using either potentiostatic or potentiodynamic deposition techniques. For potentiostatic deposition, the Pt working electrode was held at a potential of 1.25, 1.3, or 1.35 V until the desired electropolymerization charge was reached. A post-deposition cyclic voltammogram (CV) was measured in identical conditions in monomer-free electrolyte solution in order to ensure that the thicknesses were consistent for all films created. The second type of PBT films were prepared by potentiodynamic deposition with the electrode potential scanned to a maximum potential of 1.3 or 1.4 V for a given number of cycles until a selected film thickness was reached. The potential scan rate was 100 mV s\(^{-1}\). Again, a post-deposition CV was measured to confirm consistent thickness across all films and specifically between the films prepared using potentiostatic and potentiodynamic deposition. After deposition, all films were discharged in the synthesis solution at a potential of 0 V for 100 s. All the solutions were deaerated with argon gas before and after measurements, but not during deposition.

The samples made for CV characterization in a monomer-free solution had two thicknesses of 30 nm and 150 nm for both potentiostatically and potentiodynamically prepared films. The samples made for galvanostatic cycling had thicknesses of 150 nm only. The thicknesses were estimated from the comparison of their redox charges with those for PBT films deposited onto HOPG, for which the thicknesses were determined directly using AFM.

3.1.2 Polymer Deposition on HOPG

For completion, it is worth mentioning that HOPG samples used for AFM were prepared in a similar way to the platinum samples, but in a slightly different electrochemical cell.
Specifically, electropolymerization of the samples prepared on HOPG was performed using a specially designed three-electrode teflon cell positioned on top of HOPG acting as the working electrode. The exposed surface area of the electrode to the solution was 0.28 cm$^2$. After the deposition, all samples were reduced in the synthesis solution at a potential of 0.0 V for 100 s to convert them to a neutral/undoped state. They were then rinsed with pure acetonitrile and dried in a vacuum at room temperature for at least 3 days.

### 3.1.3 Electrochemical Measurements

After polymer deposition, the electrode was rinsed with pure acetonitrile and transferred into a separate cell containing 0.1 M of TBAPF$_6$ without the monomer. In this cell, both potentiostatically and potentiodynamically deposited films were subjected to 25 galvanostatic charging-discharging cycles to the potentials limits of 1.3 V, 1.4 V and 1.45 V, with the exception of potentiodynamic films that were also cycled up to a maximum potential of 1.5 V. Potentiostatically synthesized films were not cycled to 1.5 V due to significant and fast degradation already apparent in films cycled to 1.45 V. The charging-discharging current density in these experiments was 0.634 mA•cm$^{-2}$. In addition, separate polymer films of the same types were also cycled 25 times at a current densities that varied from 0.634 mA•cm$^{-2}$ to 2.536 mA•cm$^{-2}$. The potential limit for these experiments was 1.3 V. It should be mentioned that the data for the first charging-discharging cycle after the film preparation were discarded for all experiments to avoid the contributions of the trapped charges and memory effects.

As with deposition, solutions were deaerated with argon gas before and after, but not during, all measurements.

### 3.1.4 AFM Measurements

Supporting AFM data was obtained under ambient conditions using a Multi-mode atomic force microscope (Veeco Metrology) equipped with a Nanoscope IV controller (Veeco). The phase imaging measurements were performed in the tapping mode using Pointprobe n-doped Si probes (NCHR, Nanoworld, force constant 20 N/m, resonant frequency 300 kHz). The topography images presented were subjected to manual first-order plane fit to
correct for the sample tilt; the phase images were offset. The thicknesses of deposited films were determined directly using AFM by selectively removing a portion of the film with a contact AFM probe (DDESP, Nanoworld, force constant 40 N/m) by repeated scanning with high force reference over a certain area until the substrate surface is reached. The size of the areas is typically several μm² and is selected to be much greater than the size of typical polymer morphological features. The film thickness is then determined from corresponding topography cross-sections measured over areas with and without the polymer. The procedure is repeated several times at different areas of the sample and an average value is calculated.

3.2 Preparation of Carbon Nitride Samples

3.2.1 Substrate preparation

Aluminum (99.99%, McMaster-Carr) and copper (99.999%, oxygen free, McMaster-Carr) metals were cut into 0.6 cm x 2.0 cm rectangular pieces. These were then polished using MilliQ water as a lubricant under coarse and fine polishing paper. Aluminum substrates were cleaned by sonication in 1 M KOH for 15 minutes, while copper substrates were sonicated in water, 1 M HCl and finally acetone for 15 minutes each. After cleaning, substrates were dried in an oven at 90°C for 30 minutes and then placed in a nitrogen environment in a glove box where it was stored until carbon nitride deposition took place in the adjoining deposition system.

3.2.2 Deposition of CNₓ

A custom built vacuum deposition system was used for radiofrequency magnetron sputtering of carbon. The system was directly connected to a glovebox with a separate load-lock chamber for the introduction of substrates into the system. The target was biased at negative potential while the substrates were grounded. The substrate to target distance was 7 cm. A 5 cm diameter carbon target (Goodfellow, 99.997% purity) was used as a carbon source. For each CNₓ deposition, the total pressure in the vacuum chamber was approximately 3 Pa using a mixture of pure Ar gas with pure N₂ gas. The N₂ partial pressure was kept at specific intervals from 5% to 100% of the total deposition pressure to prepare films with different nitrogen contents. Specifically, the partial
pressures studied were 0%, 5%, 50%, 75% and 100% N\textsubscript{2} gas. The deposition power was 50 W for all films, and deposition was performed for 40 minutes.

The density of amorphous carbon has been established in literature as being approximately 2.0 g·cm\textsuperscript{-3}\textsuperscript{31}. This number will be used as representative of amorphous carbon nitride. Also, the thickness of the carbon nitride films used will be important in determining the charge capacity of carbon nitride per gram. Thicknesses of films were determined by depositing carbon nitride on to transparent ITO-coated glass slides and performing UV-Vis spectroscopy. Because the absorption coefficient of carbon nitride is known to be $1.19 \cdot 10^5$ cm\textsuperscript{-1} at 405 nm\textsuperscript{29}, we can determine thicknesses of films by observing the absorption of light at that wavelength. All films were prepared in our deposition system at 1 Pa working pressure, 50 W power and 40 minutes deposition time with varied nitrogen contents. Using a combination of XPS, UV-Vis and impedance spectroscopy, these conditions have been previously demonstrated to reliably and consistently make carbon nitride films of thicknesses listed in table 3.1\textsuperscript{29}. These are the thicknesses that will be used for calculations and discussion.

**Table 3.1 - List of film deposition thicknesses compared to the percent nitrogen in the plasma used to create them.**

<table>
<thead>
<tr>
<th>Percentage of Nitrogen gas in plasma (%)</th>
<th>Thickness of resultant film (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>81.7</td>
</tr>
<tr>
<td>50</td>
<td>151.6</td>
</tr>
<tr>
<td>75</td>
<td>193.6</td>
</tr>
<tr>
<td>100</td>
<td>231.1</td>
</tr>
</tbody>
</table>
3.2.3 Electrochemical Characterization

Carbon nitride samples were characterized in 0.1 M solutions of lithium hexafluorophosphate (Sigma-Aldrich, battery grade, ≥99.99% purity) dissolved in anhydrous propylene carbonate (Sigma-Aldrich, 99.7% purity), which were stored and handled inside a nitrogen-filled glovebox. CN$_x$ films deposited on metal substrates were inserted into the glass cells described above and sealed with parafilm. Silver wire pseudo-reference electrodes were used, also as above. Their potential was calibrated after each experiment via the ferrocene/ferricinium redox couple and was re-calculated vs. Li/Li$^+$ reference electrode, as is common practice in this field. Electrochemical measurements were then carried out with the same potentiostat and software as used for PBT experiments described previously. CN$_x$ films were charged to -2.2 V before being run through cyclic voltammograms, followed by galvanic cycles performed at at least three different charge/discharge current densities.
There are a variety of different techniques that can be used to prepare electrochemically deposited polymer films. The most common among these include potentiostatic and potentiodynamic polymer depositions. It is known that different methods produce films with different properties. We have been interested in studying the details of the effect of electropolymerization conditions on the properties of poly(bithiophene) thin film electrodes and, in particular, those that relate to their possible use in charge storage applications.

Further, using atomic force microscopy and AFM phase imaging we have recently found that the films prepared by potentiostatic and potentiodynamic electropolymerization techniques feature vastly different nanoscale morphologies. This is illustrated in figure 4-1, which shows high resolution 500 nm by 500 nm AFM images together with cross sections of both the topography and phase images across the same area of the polymer samples. In fig. 4-1(C) and (D), one can see that while the topographical images look quite similar for thicker films (ca. 72 nm thickness) regardless of deposition technique, there is a significant difference in the phase contrast images of thin films prepared using potentiostatic and potentiodynamic deposition. Thin films prepared by static deposition (figure 4-1(A)) seem to consist almost entirely of hard, crystalline sections, whereas films obtained through potentiodynamic deposition (fig. 4-1 (B)) show a very different, more complex structure. There is a pronounced difference in the amorphous and crystalline content of the two films, with the amount of crystalline content appearing to be lower in potentiodynamically deposited films when compared to potentiostatically deposited films. We became interested in what affect this would have on the electrochemical behavior of poly(bithiophene), specifically as it applied to its use as an electrode for charge storage.

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1The data from this chapter has been published as contributions to two articles:
Figure 4-1 Simultaneous 500 nm by 500 nm AFM images of topography (left) and phase (right) for PBT films deposited potentiodynamically on an HOPG substrate by scanning to a maximum potential of 1.45 V for (a) 1 cycle and (c) 10 cycles at a rate of 100 mV•s⁻¹. (b,d) The same images for PBT films deposited potentiostatically on an HOPG substrate at a potential of 1.45 V at a charge of (b) 0.71 mC•cm⁻² and (d) 2.9 mC•cm⁻². For images a and c, the Z scales were 40 nm (topography) and 50° (phase), and 150 nm (topography) and 50° (phase), respectively. For images b and d, the Z scales were 20 nm (topography) and 50° (phase) and 100 nm (topography) and 80° (phase), respectively. Also shown in all images are dual cross-sections indicating variations in height (top) and phase (bottom) along the same white line shown in the images. For the sake of comparison, juxtapositions of the height and phase cross-sections are also shown.
4.1 Galvanic Cycling of (Poly)bithiophene Electrodes

After seeing the structural trends of poly(bithiophene) films in AFM, we set out to determine how they would affect the polymer’s ability to behave for use in charge storage applications. For this we used galvanic cycles. Galvanic cycles are useful for testing charge storage materials because they emulate the charging and discharging of a real battery. The cycles involve a current being applied to a system while the potential is monitored. The current is applied until a particular limit of charge or potential is reached, at which point it is stopped or reversed. Figure 4-2 shows a typical galvanic cycle of a poly(bithiophene) film deposited galvanostatically on to a platinum electrode.

4-2 Typical galvanic cycle of a PBT film. This film was cycled with a current density of 1.268 mA mA\textperiodcentered cm\textsuperscript{-2} to a potential of 1.3 V.
Before a current is applied, the system sits at its open circuit potential. With the application of a current, the polymer begins to be oxidized at the working electrode. The electrode potential approaches the polymer’s redox potential, and is defined by the Nernst equation.

\[ E = E^o + \frac{0.059}{n} \log \frac{C_O}{C_R} \]

The standard potential is reached when the concentrations of the two species, that is the undoped (reduced) and oxidized polymer, are equal. When the concentration of the oxidized polymer (CO) is much less than the concentration of the reduced polymer (CR), the total value is very negative. When they are comparable, the potential approaches the standard potential and forms a plateau. The logarithmic term only changes slightly over this range. As the reduced form of the polymer is exhausted, the logarithm begins to approach infinity, and so the potential increases rapidly. Therefore, the area of the plateau shows the range of times and charges which contain both the reduced and oxidized forms of the polymer, and which can be reversibly reduced and oxidized to act as a battery electrode. From the charge required to convert all reduced polymer into all oxidized polymer (from the beginning to the end of the plateau), we can determine the maximum doping charge available under the experimental conditions. Similarly, the second plateau, which occurs on the reverse scan, is the conversion of the fully oxidized polymer to a fully reduced polymer and corresponds to the total undoping charge under the same conditions. The rate of the potential growth and decay and the size of the plateau will depend on the charging/discharging conditions such as potential limit and current density. When the current density increases, the same charge is passed over a shorter time. Because there may be kinetic limitations and competing processes at the polymer electrode, the actual doping/undoping charge, as determined from the potential plateaus, will be different. Also, the doping charge and the lengths of the plateau will change with the doping potential cutoff.
It is known that even at the highest anodic potentials, the polymer is doped only to about 30%. The reason for this is that the oxidized polymer chains are more prone to overoxidation and degradation, which starts to occur simultaneously with doping at high anodic potentials. Therefore, it was of interest to study the effect of the doping potential cutoff on the charging/discharging characteristics, as this will allow us to estimate the interplay between the doping/undoping and polymer degradation processes.

Figure 4-3 demonstrates galvanic cycles of polymer films similar to that of 4-2 charged to a variety of different potentials, and Figure 4-4 shows the same with different currents applied to the films.

Figure 4-3 Galvanic cycles of similar galvanostatically deposited PBT films run to varying maximum potentials. Cycles were performed at a current density of 0.634 mA•cm\(^{-2}\) to potentials of 1.3 V (black), 1.4 V (red), 1.45 V (blue) and 1.5 V (green).
Figure 4-4 Galvanic cycles of similar galvanostatically deposited PBT films scanned at varying current densities. Cycles were performed to a maximum potential of 1.3 V at current densities of 0.634 mA•cm$^{-2}$ (Blue), 1.268 mA•cm$^{-2}$ (Red), and 2.536 mA•cm$^{-2}$ (Black).
4.2 Polymer Film Deposition Techniques

4.2.1 Potentiostatic Deposition

Potentiostatic polymer film deposition refers to a polymer deposition in which the working electrode is held at a constant potential. A typical current-time dependence for this deposition technique is given in the chapter 2 (figure 2-3). In this technique, monomer molecules are constantly oxidized. They undergo coupling in the solution and in the vicinity of the working electrode to produce oligomers, which are themselves oxidized and undergo further coupling until they become too long to stay soluble and get deposited on the electrode to form a polymer film. Since the potential is always kept in the region of monomer oxidation, the concentration of oligomers generated in the vicinity of the electrode is quite high, and the rate of polymer deposition is high also. This technique also produces polymers of a higher molecular weight as compared to those made by other methods. The result is that, as described in literature and seen in AFM data (figure 4-1), this polymerization technique produces films that are reliably more crystalline.

Figure 4-5 shows the dependencies of the charges of charging (a) and discharging (b) and the charge recovery rate (c) on the number of charging-discharging cycles for potentiostatically deposited polymer films. In this set of experiments, each of the films was charged/doped and discharged/undoped for 25 cycles to the various maximum potentials using the same current density of 0.634 mA•cm$^{-2}$. The general trend shows that while all films tend to lose the charge storage capacity over the course of the cycling, films run to higher maximum potentials appear to lose their capacity more rapidly. In addition, the charge recovery rate determined over 25 cycles appears to show that films run to lower maximum potentials allow as much as 80% of the stored charge recovered during the discharging process, while this value drops to less than 60% in some PBT samples run to higher potentials. There was a consistent drop in the charge recovery rate with an increase in the charging potential limit, indicating that less charge of the charging scan is associated with the polymer doping and more with polymer degradation.
The effect of the charging/discharging current on the charge storage capacity was also studied. Figure 4-6 presents the charging (a) and discharging (b) charges obtained over 25 cycles for films prepared using potentiostatic deposition at varying current densities. A charging potential limit of 1.3 V was used for all films. It is apparent that all films lose their charge capacity with cycling. Furthermore, films charged and discharged at higher currents lose their capacity much faster than films cycled at lower currents. The recovery rate values (Fig. 4-6c) between charging and discharging of potentiostatically deposited films are much lower and do not exceed 80%. These facts demonstrate a poor reversibility of the charging-discharging processes for potentiostatic films, which becomes even more pronounced at high load currents.
Figure 4-5 Dependencies of (a) doping and (b) undoping charges as well as (c) the charge/discharge recovery rate for potentiostatically deposited PBT films on the number of doping-undoping cycles. The doping-undoping cycling was performed galvanostatically in solution without the monomer at a current density of 0.634 mA•cm\(^{-2}\) to the maximum potentials of (1) 1.3 V, (2) 1.4 V and (3) 1.45 V. The films were prepared at a deposition potential of 1.3V. The thicknesses of these films are ca. 150 nm.
Figure 4-6 Dependencies of (a) doping and (b) undoping charges as well as (c) the charge/discharge recovery rate for potentiostatically deposited PBT films on the number of doping-undoping cycles. The films were prepared at a deposition potential of 1.3 V and cycled galvanostatically in solution without the monomer at a current density of (1) 0.634 mA•cm⁻², (2) 1.268 mA•cm⁻², and (3) 2.536 mA•cm⁻² to the maximum potential of 1.3 V. The thicknesses of these films are ca. 150 nm.
4.2.2 Potentiodynamic Deposition

Potentiodynamic deposition refers to a deposition in which the working electrode is constantly cycled between two potentials. Unlike potentiostatically generated films, in this polymerization technique the potential is not kept constant, but rather is swept from more negative potentials, where oxidation of the monomer does not occur, to the potential region of the monomer oxidation, and then back. Therefore, in this technique the concentration of reactive oligomers generated in the vicinity of the electrode is lower, and the polymer deposition rate is slower accordingly. To compensate for this, the process is repeated several times to create a polymer film. The difference in the concentration of reactive oligomers also affects the polymerization mechanism itself. Specifically, the molecular weight of the polymer generated is lower and, as a result, the films produced this way are less crystalline. This can also be seen in the AFM data, which showed a significant difference in crystallinity, particularly between thin PBT films polymerized by different deposition methods.

Figure 4-7 represents the charging (a), discharging (b) and recovery rate (c) dependencies for polymer films deposited potentiodymanically at a deposition potential of 1.3V. As with the potentiostatically deposited films, each of the films was charged/doped and discharged/undoped over 25 cycles to the various maximum potentials using the same current density of 0.634 mA•cm$^{-2}$. A similar trend as above can be seen in these films. The charge storage capacity of films cycled to higher anodic potentials degrades more rapidly in comparison to those cycled at lower potentials. It is important to note that the drop in the charging and discharging values occurred more slowly for potentiodynamically deposited films, and the recovery ratio observed for potentiostatically deposited films (Fig. 4-5c) was significantly lower than the recovery ratio obtained for potentiodynamically deposited films (Fig. 4-7c) for all charging-discharging conditions. This indicates a higher rate of degradation of potentiostatically deposited films. These results indicate that the charge storage capacity of potentiostatic films as determined from the recovered charge was considerably lower than that for potentiodynamically deposited films.
In studying the effect of current on the charge storage capacity, the polymers deposited potentiodynamically once again maintain higher charge stability over 25 cycles for all currents applied compared to the same films deposited potentiostatically. This can be seen in comparing the charging and discharging over 25 cycles (fig 4-8a,b), and especially in the high values of the recovery rates (Fig. 4-8c) for these films approaching 100%. This indicates that very minimal degradation over 25 cycles is observed. The charge values themselves were quite stable and changed little during cycling and at different charging currents. This indicates excellent reversibility of the doping-undoping processes of potentiodynamically deposited films at various loads.

Figure 4-7 Dependencies of (a) doping and (b) undoping charges as well as (c) the charge/discharge recovery rate for potentiodynamically deposited PBT films on the number of doping-undoping cycles. The doping-undoping cycling was performed galvanostatically in solution without the monomer at a current density of 0.634 mA•cm\(^{-2}\) to the maximum potentials of (1) 1.3 V, (2) 1.4 V, (3) 1.45 V and (4) 1.5 V. The films were deposited potentiodynamically over 7 scans between 1.4 V and 0V at a rate of 100 mV•s\(^{-1}\). The thicknesses of these films are ca. 150 nm.
Figure 4-8 Dependencies of (a) doping and (b) undoping charges as well as (c) the charge/discharge recovery rate for potentiodynamically deposited PBT films on the number of doping-undoping cycles. The films were prepared as those in Figure 6.2 and cycled galvanostatically in solution without the monomer at a current density of (1) 0.634 mA\(\cdot\)cm\(^{-2}\), (2) 1.268 mA\(\cdot\)cm\(^{-2}\), and (3) 2.536 mA\(\cdot\)cm\(^{-2}\) to the maximum potential of 1.3 V. The thicknesses of these films are ca. 150 nm.
4.3 Electrochemical CV Characterization

The films prepared using different deposition methods demonstrated markedly different behavior, especially concerning their reversibility and maintaining their charge over several charge-discharge cycles. Since battery materials need to be able to demonstrate charge storage over as many cycles as possible, it was important for us to understand what changes in redox behavior were leading to the trends we noticed in the above films. Specifically, it was important to understand why potentiodynamically deposited films demonstrate significantly better charge storage and recovery over a number of cycles. To study this, we analyzed a variety of different poly(bithiophene) films using cyclic voltammetry.

Figure 4-9 shows typical voltammetric behavior of polybithiophene films. Typical polymer doping/undoping CVs all include a pronounced doping peak and subsequent plateau which corresponds to oxidation of polymer fragments with different degrees of disorder and different molecular weights. The proposed mechanistical reasons for these have already been discussed in literature. Explanations can be found in the models proposed by M. Skompska, M. Vorotyntsev and J. Heinze\textsuperscript{32-34} that relate the doping peak and the 2nd undoping peak/shoulder to redox processes occurring in more crystalline portions of the polymer films that contain stronger interacting chains. Upon charging, these chains form various aggregates that support extended electronic states delocalized across several interacting polymer chains. This charging process occurs in the vicinity of the doping peak, whereas the oxidation of more disordered polymer fragments (typically featuring shorter chain length) occurs later in the area of the doping plateau. On the reverse scan, such aggregates dissolve. This process requires extra energy and therefore occurs at less anodic potential and manifests itself as the 2nd undoping peak/shoulder. The difference in the kinetics of the doping processes occurring in crystalline and amorphous portions of polymer films has also been observed\textsuperscript{21}. 

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(1) potentiostatically at a potential of 1.3 V, (2) potentiostatically at a potential of 1.25 V and (3) potentiodynamically by scanning to a maximum potential of 1.4 V for 7 cycles at a rate of 100 mV•s⁻¹. The deposition charge for film 1 was 85 mC•cm⁻² and was selected so that the doping-undoping charge of film 1 would match that of film 2 and 3. The thicknesses of these films are ca. 150 nm. (b) Typical cyclic voltammograms of “thin” polybithiophene films deposited potentiostatically at a potential of (1) 1.3 V and (2) 1.25 V as well as (3) a film deposited potentiodynamically by scanning to a maximum potential of 1.3 V for 1 cycle at a rate of 100 mV•s⁻¹. The deposition charges for films 1 and 2 were 5.8 mC•cm⁻² and was selected so that the doping-undoping charges of the films would match that of film 3. The thicknesses of these films are ca. 30 nm. (c) A cyclic voltammogram of the “thick” polybithiophene film of Fig. 6.1a taken while increasing the anodic scan limit from 1.15 V to 1.45 V in intervals of 50 mV. The arrows A, B, and C indicate the positions of special points in the voltammograms at the potentials of 0 V, 0.91 V and 1.15 V, respectively.
Figure 4-9(a) presents typical cyclic voltammograms obtained in identical conditions for thick polymer films prepared using the two techniques. To ensure the accurate comparison, the deposition charges and other polymerization parameters were carefully adjusted so that the doping-undoping charges of all films would be the same. Three films are presented in the figure: two potentiostatic films with the deposition potentials of 1.25 and 1.3 V, and a potentiodynamic film. Potentiostatic films with higher deposition potentials were also tested and showed behavior identical to the film prepared at 1.3 V.

One can see that the voltammetric behavior of the films is quite different. Specifically, while the currents in the doping plateau region are quite similar for all films, the height of the doping peak is greater for the film prepared potentiostatically at 1.3 V, and the second undoping peak/shoulder at ca. 0.6 V is also better pronounced. The doping peak is also shifted towards less positive potentials. The height of the doping peak for the potentiodynamically prepared film is the lowest, and its position is shifted towards more positive potentials. The potentiostatic film prepared at low anodic potential shows intermediate behavior.

The same trend is observed for thin films (Fig. 4-9b): The height and the position of the doping peak change in the same manner for potentiostatic and potentiodynamic films and as dependent on the polymerization potential. Furthermore, the peak to plateau ratio is noticeably lower for thin films and the second undoping peak/shoulder at ca. 0.6 V is less pronounced. This means that these films are significantly less crystalline as compared to thicker films with sharper peaks.

Figure 4-9 (c) illustrates the voltammetric behavior of potentiodynamically deposited film with increasing the anodic scan limit. One can see a consistent pattern of broadening of the voltammograms and reducing of the doping peak height with an increase in the anodic scan limit.

For both potentiostatic and potentiodynamic deposition methods, it can be seen that films cycled to higher anodic potentials exhibit a rapid degradation of the charge storage capabilities over subsequent charge/discharge cycles. Likewise, when cycled to lower anodic potentials, the overall charge is decreased; however, the stability of films is much
greater for both types of films. At the same time, there is a pronounced difference in both cyclability and the charge storage capacity as well as the charge recovery rate between potentiostatically and potentiodynamically prepared films. Overall, potentiodynamically prepared films possess a much higher stability and charge/discharge recovery over multiple cycles (Fig. 4-7) in comparison to potentiostatically prepared films (Fig. 4-5). The origin of such a difference in the behavior of the polymer films synthesized using potentiodynamic and potentiostatic deposition methods lies in their nanoscale structural properties. The reasoning is supported by the results of our CV characterizations (Fig. 4-9). These results can be summarized as the following:

1. Potentiostatically deposited films have more pronounced doping peak and 2nd undoping peak/shoulder as compared to potentiodynamically deposited films;

2. Thin films prepared using both potentiostatic and potentiodynamic polymerization techniques show lower peak to plateau ratio and less pronounced 2nd undoping peak/shoulder as compared to thick film;

3. The same is true for potentiostatic films prepared at lower polymerization potentials as compared to films prepared at more anodic potentials.

4. Scanning with an increasing anodic limit results in a decrease in heights of both the doping peak and the 2nd undoping peak/shoulder, with the overall doping charge staying the same.

Furthermore, galvanic cycling data shows that for both potentiostatic and potentiodynamic deposition methods, films cycled to higher anodic potentials exhibit a rapid degradation of the charge storage capabilities over subsequent charge/discharge cycles. Likewise, when cycled to lower anodic potentials the overall charge is decreased, however the stability of films is much greater. At the same time, there is a pronounced difference in both cyclability and the charge storage capacity as well as the charge recovery rate between potentiostatically and potentiodynamically prepared films. Overall, potentiodynamically prepared films possess a much higher stability and charge/discharge recovery over multiple cycles (Fig. 4-7) in comparison to potentiostatically prepared
films (Fig. 4-5). The origin of such a difference in the behavior of the polymer films synthesized using potentiodynamic and potentiostatic deposition methods lies in their nanoscale structural properties.

Higher molecular weight (Mw) polymer produce more ordered/crystalline material, while the amorphous disordered regions are comprised of low Mw oligomers. Therefore, it can be concluded that at early stages of the potentiostatic deposition, the average molecular weight of the deposited polymer is significantly greater as compared to films deposited potentiodynamically. Furthermore, in potentiostatic deposition, the average molecular weight and the crystallinity decrease or stay the same, while in potentiodynamic deposition the average molecular weight and crystallinity of the polymer films increases in subsequent cycles.

The reason for this behavior is related to the concentration and reactivity of oligomers generated in the vicinity of the electrode in either of the electropolymerization techniques. For potentiostatic deposition, the potential is switched abruptly and thus a high concentration of reactive oligomers is generated in the electrode’s vicinity immediately after the potential step. These oligomers are quite reactive and can undergo rapid coupling and elongation, generating a considerably high content of high Mw polymer which then continue on to form primary crystalline nuclei on the surface of the substrate. As the deposition continues, the monomer oxidation current drops and so do the concentration and reactivity of oligomers at the electrode. The average molecular weight of the electrodeposited polymer decreases, and the disordered amorphous, low Mw grain periphery is formed. These trends can be seen in AFM (Figure 4-1).

This mechanism is also supported by the results of our electrochemical studies. In particular, for potentiostatic films prepared at lower electropolymerization potentials (Fig. 4-9). The electrochemical data clearly demonstrate that such films feature a lower crystalline content as compared to potentiostatic films prepared at higher anodic potentials. This can be seen in the potentiodynamically films’ lower, broader oxidation peak as compared to the sharper peaks of the more crystalline potentiodynamically deposited films. Again, the concentration and reactivity of electrogenerated oligomers is
decreased at lower electropolymerization potentials, which results in a decrease in the average molecular weight of electrodeposited polymer and its crystallinity.

As the thickness of the films increase, the properties and crystallinity of the films prepared using the two techniques become more similar. This can be attributed to a gradual conversion of low weight disordered phase into higher Mw polymer material through reaction of the electrodeposited polymer with oligomers from the solution.

However, even in this case, the degree of disorder in films prepared potentiodynamically remains higher, which explains the results of the charging-discharging experiments with polymer electrodes prepared using potentiostatic and potentiodynamic deposition.

Therefore, the observed differences in the electrochemical behavior of potentiostatic and potentiodynamic films clearly support our hypothesis that potentiodynamically prepared films feature lower crystallinity. They show lower doping peaks as compared to the doping plateau and less pronounced 2nd undoping peak/shoulder.

This data is also supported by the AFM data in figure 4-1. Taken together, this data shows that although potentiostatic films are more crystalline, they are not as well suited for use as electrodes in batteries. Our electrochemical and AFM results suggest that the differences in the polymer cyclability and charge storage capacity can be related to the differences in the observed nanoscale properties of these films. When a polymer undergoes charging, solvent enters the polymer matrix causing the polymer to swell. When the polymer film discharges, the opposite occurs; solvent is pushed out of the film causing the film to de-swell back to its original state. Unfortunately, the swelling and de-swelling is not a perfectly reversible effect. Upon deswelling, it is energetically favourable to maintain contact between polymer grains to reduce the surface energy. As a result, swelling-deswelling gives rise to redistribution of the polymer matter. Inevitably, such redistribution creates mechanical stresses in the film that eventually lead to fracturing and loss of some polymer mass from the electrode. More crystalline and thus more rigid films are more brittle in comparison to films with less crystalline structure. Therefore, the repeated swelling and de-swelling process and the associated build-up of mechanical stresses are more likely to cause more damage to films prepared using
potentiostatic electropolymerization. Likewise, potentiodynamically prepared films that exhibit a greater amorphous phase content should allow for a much greater flexibility in the polymer structure during the swelling and deswelling processes and thus would feature a greater reversibility of the repeated doping-undoping processes, greater cyclability and thus better charge storage performance, which is in fact observed experimentally.

4.4 Changes in the Redox Behavior of PBT Films Over the Course of Potential Cycling

Figure 4-10a-d shows representative cyclic voltammograms of PBT films of the same thickness deposited onto the surface of a HOPG electrode. The films were subjected to 50 doping and undoping cycles to anodic potentials limits of a) 1.3 V, b) 1.4 V, c) 1.45 V, and d) 1.5 V. The CVs were recorded after every fifth cycle during the scanning process.

One can see that all CVs show a remarkable feature that all voltammogram traces intersect around several specific points, which we will call quasi-isosbestic points, by analogy with isosbestic points defined in molecular spectroscopy15. Specifically, we can define the following quasi-isosbestic points in Figs. 4-10a – 4.10d:

- Figure 4-10a: Two quasi-isosbestic points are observed on the reverse scan denoted as “B” at ca. 0.8 V and “C” at ca. 0.6 V. There is an indication of an isosbestic point on the direct scan around 1.25 V; however, it is not well pronounced due to its closeness to the anodic scan limit.
- Figure 4-10b: Three well pronounced quasi-isosbestic points are observed at potentials of ca. 1.1 V (“A”, direct scan), ca. 0.75 V (“B”, reverse scan) and ca. 0.55 V (“C”, reverse scan). However, the quasi-isosbestic point “B” occurs only for the first 20 cycles (see Fig. 4-10b inset).
- Figure 4-10c: The isosbestic point at ca. 0.8 V on the reverse scan is no longer observed; however, the isosbestic points “A” on the direct scan at a potential of ca. 1.1 V and “C” on the reverse scan at ca. 0.55 V are still well pronounced. We still denote the potential of +0.75 V as a special point “B” for
the sake of discussion; however, this point is no longer a quasi-isosbestic point.

- Figure 4-10d: The quasi-isosbestic points “A” and “C” are still seen but their position now change slightly from 1.1 V to ca. 1.0 V and from 0.55 V to ca. 0.5 V, respectively. Again, as in Fig. 4-10c, we retain a special point “B” at 0.75 V for the sake of discussion.

Generally, by analogy with molecular spectroscopy, the occurrence of an isosbestic point on a cyclic voltammogram should suggest a co-existence of two redox-active forms with distinct redox potentials. Furthermore, one of the forms should be converted into the other but the total number of redox active sites should be preserved. The occurrence of any side reaction generally results first in a gradual shift in the position of the isosbestic point, and finally in its total disappearance.

Let us consider the CVs in Fig. 4-10b as showing the most typical behavior (features found in Fig. 4-10b can be to a certain extent found in all the other CVs of Fig. 4-10). The first quasi-isosbestic point “A” on the direct scan divides the overall doping process into two sections, before and after the quasi-isosbestic point. Specifically, in the course of scanning, the current before the point “A” gradually grows, whereas the current in the peak region including the peak height gradually decreases. On the reverse scan, the current before point “B” (on the right, at more anodic potentials) gradually increases, whereas the second undoping peak at ca. 0.6 V gradually diminishes and broadens transforming into a shoulder. This process also involves another quasi-isosbestic point denoted as “C”, the current past point “C” increases gradually in line with the already noted broadening and transformation of the second undoping peak.
Figure 4-10 (a) A typical cyclic voltammogram of a polybithiophene film subjected to 50 doping and undoping cycles to the anodic scan limit of 1.3 V. Two quasi-isosbestic points are observed on the reverse scan located at B (ca. 0.8 V) and C (ca. 0.6 V). There is an indication of an isosbestic point on the direct scan around 1.25 V; however, it is not well pronounced. (b) A typical cyclic voltammogram of a polybithiophene film subjected to 50 doping and undoping cycles to the anodic scan limit of 1.4 V. One quasi-isosbestic point on the direct scan is located at A (ca. 1.1 V). Two quasi-isosbestic points are observed on the reverse scan located at B (ca. 0.75 V) and C (ca. 0.55 V). An inset in the upper left hand corner shows a zoomed-in section of B and C. (c) A typical cyclic voltammogram of a polybithiophene film subjected to 50 doping and undoping cycles to the anodic scan limit of 1.45 V. One quasi-isosbestic point on the direct scan is located at A (ca. 1.1 V). One special point is observed on the reverse scan located at B (ca. 0.75 V) and one quasi-isosbestic point is seen at C (ca. 0.55 V). (d) A typical cyclic voltammogram of a polybithiophene film subjected to 50 doping and undoping cycles to the anodic scan limit of 1.5 V. One quasi-isosbestic point on the direct scan is located at A (ca. 1.0 V). One special point is observed on the reverse scan located at B (ca. 0.75 V) and one quasi-isosbestic point is seen at C (ca. 0.5 V). All samples were prepared under galvanostatic conditions at a current density of 1 mA cm$^{-2}$ for 50 s. All CVs were recorded after every fifth scan cycle.
While not all features as above are found in all CVs, the pattern still holds for all films scanned for various anodic potentials. Prolonged cycling gives rise to an increase in the currents in the region before the point “A” and a decrease in the current past this point, coupled with broadening and gradual disappearance of the second undoping peak. Moreover, scanning to higher anodic potentials results in a pronounced decrease in the current not only in the area of the second undoping peak but also before point “B”, in the area of the first undoping peak. In view of the relationship between the polymer redox behavior and nanomorphology/crystallinity discussed above, such behavior clearly indicates that cycling results in a change in the polymer morphology and a decrease in the amount of the crystalline phase. This should have a beneficial effect on the cyclability and charge storage capacity of polymer films if the potential scanning is limited to relatively low anodic potentials that do not allow pronounced polymer overoxidation. Taken together, our data suggest that nanomorphology is a major contributing factor to macroscopic electrochemical behavior and performance of polymer materials.

4.5 Conclusions

As follows from our electrochemical and AFM data, although the morphology of the polymer films prepared using the two techniques look similar, one can see a pronounced difference in the crystallinity and heterogeneity for potentiostatically and potentiodynamically deposited films, as revealed by nanoscale phase contrast data. Specifically, it can be concluded that at the early stages of film deposition, potentiodynamic films are predominantly amorphous and disordered whereas PBT films deposited potentiostatically are dominantly hard/crystalline. As the films increase in thickness, these initial differences gradually become less pronounced but the potentiodynamically synthesized films still remain less crystalline than the films of similar thickness prepared using potentiostatic method. Furthermore, the AFM results and electrochemical data clearly demonstrate that thin films, especially thin potentiodynamic films, show much lower crystallinity.

We also found that such a difference in nanomorphology unambiguously translates in a pronounced difference in the electrochemical behavior and charge storage performance of
the polymer films. More crystalline potentiostatic films clearly and consistently showed worse performance as compared to less crystalline potentiodynamically deposited films. This should be related to the difference in the mechanical properties of the films and their ability to maintain their properties upon repeated swelling-deswelling associated with the doping process.

We also conclude that the degradation of the conducting polymer electrodes upon repeated charging and discharging and the associated decline in the charge storage capabilities are not necessarily related to the process of over-oxidation, as is usually believed, but may to a great extent be related to significant morphology changes that take place in the polymer films upon redox cycling. The loss of capacity may be related to either direct loss of the active polymer mass from the electrode or inactivation of portions of the polymer, for instance, through the lost of accessibility of some polymer domain to solvent and dopant ions. Furthermore, if maintaining the electrode potentials within certain potential limits, the observed changes in nanomorphology can be even beneficial.

Therefore in order to achieve high cyclability and charge storage capacity in conjugated organic polymer films, one must decrease the crystalline content in these films and prepare films that are largely amorphous. Interestingly, this is opposite of the requirements to polymer materials for such important applications as organic solar cells and organic electronics, which require highly ordered and predominantly crystalline films to ensure high carrier mobility. Our results suggest that to ensure better performance in polymer-based charge storage applications, the active polymer material must be largely amorphous.
5 Examination of Carbon Nitride for Use as an Anode in Lithium-Ion Batteries

While many materials, including silicon, tin and various metal hydrides have been proposed or tested for use as an anode in a lithium-ion battery, the anode in all current practical batteries is still carbon. Because of this, there is a general interest in finding new carbon-based materials that demonstrate high specific capacities when used as an anode. One of the attractions of using new, unique forms of carbon-based material in lithium-anode batteries stems from the fact that minor variations to any of the various structures of carbon can lead to dramatic differences in battery performance. Recently, studies have been performed on a variety of materials ranging from carbon black to carbon nanotubes\textsuperscript{24,33-37}. Many carbon materials, and especially graphite, are quite brittle, which causes them to have low charging capacity and specific charge. Additionally, they contribute a lot of mass to a lithium cell by virtue of requiring a significant amount of carbon to contain a single lithium ion.

Because of distortions in the structure of amorphous carbon nitride created by the sp2 hybridized C-N centers, CN\textsubscript{x} has the potential to be a more effective electrode material than many other forms of carbon. Amorphous carbon nitride is also a much more robust, durable material as compared to graphite due to its unique features that match structures found in other allotropes such as diamond and fullerene structures. This is a favourable mechanical property in a battery due to the volume change that can occur as intercalation takes place.
Figure 5-1 demonstrates the shape of amorphous carbon nitride. The addition of nitrogen introduces a variety of sp$^3$ hybridized sites that distort the usual shape of graphite. Sections containing particularly high quantities of nitrogen centers can contain structures more similar to diamond (which is sp$^3$ hybridized throughout) or fullerenes. Varying the amount of nitrogen in a carbon nitride film can have a variety of effects affecting its durability, conductivity and other mechanical properties. Typically small amounts of nitrogen increase electronic conductivity while large quantities of nitrogen convert it into a semiconductor. Regardless, any nitrogen doping will cause the structure of the film to exhibit disordered clusters, rather than graphite’s highly ordered structure. In this work, carbon nitride was prepared by methods based on previously written work which has been demonstrated to be an effective method of creating CNx films.$^{29}$

Although the preliminary data shown here represents a work in progress, carbon nitride’s unique properties make it a very exciting material that is worth exploring for use as a cathode in lithium-ion intercalation cells.
5.1 Galvanic Studies of Lithium Ion Intercalation and Carbon Nitride

In order to determine carbon nitride’s efficiency as an electrode material, a variety of carbon nitride films were subjected to galvanic cycles. Figure 5-2 shows a typical galvanic cycle demonstrating the intercalation of lithium into carbon nitride. Very distinct and obvious charging and discharging steps can be seen in the galvanic cycle, and it appears to be highly reversible. Because galvanic cycles mimic the behavior of a battery cell, it can be seen that there is significant promise for carbon nitride to be effective when used as an anode in a lithium-ion cell.

![Galvanic Cycle Diagram](image)

**Figure 5-2** A typical galvanic cycle of lithium intercalation into carbon nitride. This is a film deposited under 5% nitrogen and cycled at a current density of 0.129 mA·cm$^{-2}$
5.2 Cyclic Voltammograms of Lithium Ion Interactions with CarbonNitride

Figure 5-3 demonstrates a CV comparison of three different carbon nitride films, deposited under 5, 50 and 75% nitrogen plasma on to aluminum substrates and Figure 5-4 shows a CV of a bare aluminum film with no deposition. It is immediately obvious that all of the peaks and interactions occurring happen only with samples on which carbon nitride has been deposited. Therefore, we can attribute these peaks to the interactions taking place between carbon nitride and the lithium ions in solution. Specifically, the CV starts in the anodic region, well above the point at which intercalation begins. As the cell potential becomes more cathodic, it passes a threshold potential (around 0.25 V in the CV) and lithium begins to intercalate into carbon nitride. The intercalation of lithium introduces structural changes to the carbon nitrides, as evidenced by the trace crossover that occurs on the reverse scan. The deintercalation step occurs slowly, with a peak occurring at approximately 0.7 V, which is several hundred millivolts higher than the potential at which intercalation began. One possible reason for this is that high nitrogen content films are semiconducting, and the intercalation of lithium increases conductivity. The change in the shape of the CV on the return sweep may be representative of a significant increase in the conductivity of the carbon nitride after intercalation. Other structural changes, including volume change, may occur too, but in any case the voltammetric behavior is quite stable. If anything, the peak currents increase, not decrease, with scanning, which can be attributed to the already mentioned changes in CNx conductivity.

As previously mentioned, none of these features are visible on the bare aluminum substrate in figure 5-4, indicating that the presence of carbon nitride is responsible for them occurring.
Figure 5-3 CVs of three CN$_x$ films in a solution containing lithium ions dissolved in propylene carbonate. The three films were deposited under identical conditions on to aluminum substrates, but with different nitrogen percentages in the plasma used for each. The percentages are 5% (red), 50% (black), and 75% (blue).
Figure 5-4 A cyclic voltammogram of bare aluminum. None of the typical intercalation peaks are visible, and the overall currents are much smaller, indicating that the intercalation must be due to carbon nitride.
5.3 Galvanic Cycling of Lithium and Carbon Nitride

In order to evaluate the performance of carbon nitride as a potential anode for lithium ion batteries, galvanic cycling was performed. This technique has been described in detail in the previous chapters. Figure 5-5 shows a collection of galvanic cycles for films created under three different plasma compositions. 5% (Black), 50% (red), and 75% (blue) nitrogen plasmas were used.

![Galvanic Cycling of CNx Films](image)

Figure 5-5 Galvanic cycles of CNx films made under similar conditions with three different nitrogen contents. These are 5% (black), 50% (red), 75% (blue), and 100% (green).
The galvanic cycles show a charging plateau near 0.25 V, which represents intercalation of lithium ions. In this case, intercalation continues until terminated by time, at which point the system begins discharging. Discharging is seen in the plateaus that occur around 0.75 V. The reason for the shape of the cycle is similar to the reasoning seen in chapter four. The cell plateaus at redox potentials for a particular species. That species must be converted to a reduced (charging) or oxidized (discharging) state before the cell potential moves to the next redox potential. In the case of lithium ions, rather than being reduced to lithium metal, they are intercalated into the carbon nitride electrode, and the plateaus will remain until that process is completed. The intercalation and deintercalation processes present themselves at different potentials because of the driving force required to begin those processes. The most important conclusion is that the length of the potential plateau increases with an increase in the nitrogen content in the CN$_x$ films.

Figure 5-6 A single film deposited with 75% nitrogen content run through galvanic cycles at 75 uA (black), 150 uA (red) and 300 uA (blue).
which seems to indicate that higher nitrogen content favors the intercalation. This may be due to higher sp$^3$ content in CN$_x$ films high nitrogen content.

Figure 5-6 demonstrates the effect of charging/discharging. The ability of a battery to sustain higher charging/discharging currents is very important since it allows the battery to produce more power and to be recharged more rapidly, thus greatly broadening the range of potential applications. A film deposited under plasma containing 75% nitrogen was run at currents of 75 (black), 150 (red) and 300 (blue) uA. One can see that the higher the current, the smaller the charge available for deintercalation, which indicates a decrease in the reversibility of the charging-discharging process at higher currents. The separation in the plateau potentials also changes with an increase in the charging-discharging current. However, even at high currents, the reversibility remains quite high. This is illustrated in fig 5-7.

Figure 5-7 demonstrates the dependences of the charges obtained from chronopotentiograms of Figs 5-5 and 5-6 during the charging and discharging processes, as well as the charge recovery rates for films of different nitrogen contents cycled at different currents. There are two issues which must be noted. First, as previously mentioned, none of the films complete their charging step, but rather have it terminated by the time constraint. This is visible in 5-7a, where it can be seen that all films at a given current density have identical charge values for any one charge density. Secondly, the film deposited under 5% nitrogen plasma was incapable of handling higher currents, and so only the data from the lowest current density is shown. Overall, we see that all films show good reversibility of the intercalation-deintercalation processes, approaching 100%. The values of the charges and the recovery ratio also are quite stable, indicating good cyclability of the CN$_x$ electrode, which is a requirement for an efficient battery material. In fact, there is even some increase in the values of the charge recovery ratio with cycling, which may be attributed to the already mentioned increase in the CN$_x$ conductivity upon intercalation.
5-7 charging, discharging and recovery ratios of a variety of carbon nitride films deposited with different nitrogen contents and cycled at a variety of currents. Approximate current densities are labelled. Nitrogen percentages are distinguished by colour.
At high currents, the efficiency of the charge recovery is lower, which is not surprising, but still remains quite high. Importantly, the films with the highest nitrogen content showed good stability and recovery rates over 80%. This should be attributed to the difference in the structure of CN\(_x\) films with different nitrogen content and, in particular, an increase in the sp\(^3\) hybridized carbon content. One should also note that the charging-discharging currents used here are very high as compared to those normally used in carbon-based lithium-ion batteries, yet the CN\(_x\) anodes perform well. Table 5.1 summarizes the charge capacity results for three of the films tested calculated per mass of CN\(_x\) deposited.

Table 5.1 - A sample set of summarized charge capacity data for films deposited under varied plasma compositions. The thickness of the films has been taken to be those shown in Table 3.1.

<table>
<thead>
<tr>
<th>Sample (by N(_2) in plasma)</th>
<th>Charging Current Used (uA)</th>
<th>Charge per 1000s cycle (C)</th>
<th>Charge per gram (C(\cdot)g(^{-1}))</th>
<th>Film capacity (mAh(\cdot)g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>5%</td>
<td>46.5</td>
<td>0.0465</td>
<td>7900</td>
<td>2195</td>
</tr>
<tr>
<td>50%</td>
<td>100</td>
<td>0.1000</td>
<td>9160</td>
<td>2545</td>
</tr>
<tr>
<td>75%</td>
<td>75</td>
<td>0.0750</td>
<td>5380</td>
<td>1495</td>
</tr>
<tr>
<td>100%</td>
<td>75</td>
<td>0.0750</td>
<td>4507</td>
<td>1252</td>
</tr>
</tbody>
</table>

One can see from the table that the films showed quite high specific capacities per gram of CN\(_x\) deposited, reaching 2500 mAh\(\cdot\)g\(^{-1}\). Another important feature which can be seen in all galvanic cycles is that during the charging step, the potential never starts to grow to a more negative potential than the charging plateau. This indicates that over the whole
range of intercalation, the capacity of the electrode to absorb lithium ions is not exhausted, even at very high charging levels, as has already been mentioned. At the same time, the efficiency of the intercalation-deintercalation process remains high in all experiments. This indicates that the charging/discharging corresponds to the intercalation of lithium, but probably involves not only CN\textsubscript{x} but also the aluminum support.

It should be noted that aluminum has been tested as an anode for lithium-ion batteries\textsuperscript{42} and it did show some activity due to the formation of intermetallic Li-Al alloys. However, such formation was extremely slow and would not occur to any considerable extent at the high current densities used in this work. Secondly, formation of such alloys was accompanied by very high degrees of volume change, which prevented aluminum electrodes from showing significant cyclability; the stored charge dropped to zero over just 2-3 charging cycles\textsuperscript{42}. Therefore, we must conclude that if the aluminum support is involved in the charging-discharging processes, it must be modified during the carbon nitride deposition and that it is this modified material, rather than aluminum itself, which is capable of supporting intercalation of lithium ions.

Such modification is likely to occur in the vacuum deposition chamber during the preparation of carbon nitride films. Specifically, in the vacuum deposition process, there are various reactive nitrogen and carbon species that are formed in the plasma. Such reactive species can modify the aluminum substrate. For instance, it is known that the nitrogen plasma can cause the formation of aluminum nitride\textsuperscript{43}. It is also possible that some aluminum carbides are formed as well. Therefore, it is likely that our electrodes are, in fact, complex systems that contain not only carbon nitride, but also aluminum nitride or carbide. Precise composition of the phases formed has yet to be obtained. However, our data suggests that aluminum modified with carbon nitride can serve an efficient system for lithium ion intercalation since it features good cyclability and is capable of supporting very high charging-discharging currents. Also, the reversibility of intercalation is high, even at high charge current densities, which makes the system very interesting and promising for future investigations, even though the specific capacitance will need to be revised.
5.4 Future Work

There are a variety of improvements that can be made to these experiments in order to provide a more accurate view of the storage capacity of carbon nitride. The first is the use of a different substrate that cannot participate in intercalation. Oxygen-free highly conductive copper may be appropriate to use in this case, preferably in a cell that prevents the exposure of any bare copper to solution to prevent lithium from depositing on the metal surface. In addition to this, a quartz crystal microbalance will be used to determine the specific mechanism of intercalation. Such experiments have been started but have not been completed at the time of writing.

Also, inert substrates could be coated with a thin film of aluminum with a known mass in our vacuum chamber, which could then be further coated with carbon nitride. This will allow correct evaluation of the specific capacities for our system.
6 Summary and conclusions

6.1 The structure of electronically active polymers

We compared the cyclability and the charge storage capacity of polymer electrodes prepared using potentiodynamic and potentiostatic electropolymerization techniques. It was shown that potentiodynamically prepared films featured a much higher stability and charge/discharge recovery rate approaching 100% over multiple cycles. Potentiostatically prepared films showed much lower performance and rapid deterioration in the charge storage capacity with cycling. Potentiodynamically prepared films showed little or no changes in their charge storage capacity over multiple cycles if the anodic potential limit was kept below +1.4 V. In contrast, potentiostatically prepared films displayed steady deterioration in the charge storage capacity even at the lowest anodic potential limit tested, +1.3 V. This behavior was related to the difference in the nanoscale morphology, crystallinity and degree of disorder of polymer films, as evidenced by AFM and AFM phase imaging.

Specifically, it was shown that potentiodynamically deposited films were more amorphous, which enabled the films to better withstand the mechanical stresses built up in the polymer phase due to repeated swelling-deswelling. This was also evidenced by electrochemical data. The difference in the degree of disorder and crystallinity in polymer films prepared using potentiodynamic and potentiostatic methods was related to different concentrations and reactivities of oligomers generated in the electrode vicinity. Our results point to structural factors and electrochemical over-oxidation being the dominant problems limiting the cycle life of polymer-based charge storage devices. Specifically, for charge storage applications, as opposed to solar cells and organic electronics, it is desirable to use materials with an increased amorphous content. Moreover, the results suggest that for polymer batteries, the issues of the purity of the electrolyte solution and the absence of oxygen and water may play a less crucial role, again, as opposed to polymer-based semiconductor devices and Li-based charge storage systems.
6.2 Carbon-Nitride as an Electrode for Lithium-Ion Batteries

We demonstrated some early results regarding the possible use of carbon nitride as an electrode material in lithium ion batteries. Carbon nitride’s unique structure and properties make it very exciting as a possible new material for use in such cells. Using films with different nitrogen content, we have shown that carbon nitride anodes feature reversible and stable charging-discharging response even at very high charging-discharging currents, and high charge storage capacities compared to the capacity of the graphite electrodes currently used. However, the exact mechanism of the intercalation-deintercalation processes and the chemical identity of the phases involved have yet to be determined.
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