ELECTROCHEMISTRY OF NANOSTRUCTURED CARBON MATERIALS IN AQUEOUS ELECTROLYTES AND ROOM TEMPERATURE IONIC LIQUIDS

By

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ABSTRACT

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Carbon is one of the most plentiful elements on the planet. From a materials perspective, carbon is unique because of the microstructurally distinct allotropes it forms. These include single and polycrystalline diamond, diamond-like carbon, glassy carbon, and graphite. All of these carbon materials are commonly used in electroanalysis, energy storage and conversion, separation, and chemical analysis, due to numbers of reasons, including low cost, high mechanical strength, wide usable potential range, rich surface chemistry, chemical inertness, and compatibility with a variety of solvents and electrolytes. For the optimal usage of carbon electrodes in electrochemistry, it is critical to fully understand and control the variables that impact background voltammetric current, capacitance, and heterogeneous electron-transfer kinetics at these materials. Over the years of carbon electrode usage in electrochemistry, much knowledge has been gained about the structure-function relationship at sp²- and sp³- bonded carbon electrodes. Nevertheless, as most of this knowledge pertains to aqueous electrolyte solution, there is still a significant gap about the properties of the electric double layer and the transport processes near the electrode interface in room temperature ionic liquids.

The room temperature ionic liquids are solvent-free medium, composed purely of ions, with a melting point near or below room temperature. In electrochemistry, they are appreciated for several of their excellent properties, such as wide working potential window, moderate electrical conductivity, high thermal and chemical stability, negligible vapor pressure etc. As the RTILs does not contain any solvent, their interfacial structure at an electrified interface

is significantly distinguished from the conventional Gouy-Chapman-Stern model describing the double layer in aqueous solutions. Additionally, also the redox analyte environment in RTILs is expected to different compared to those in aqueous solutions.

The work in this dissertation thesis is focused on the electrochemical performance of microstructurally different carbon electrodes in aqueous electrolytes and room temperature ionic liquids. The physical, chemical and electronic properties of glassy carbon, boron-doped diamond, and tetrahedral amorphous carbon electrodes are discussed. Furthermore, the microstructure of carbon electrodes is correlated to the heterogeneous electron transfer rate constants of soluble inorganic and organic redox couples in aqueous electrolytes and room temperature ionic liquids.

The attention was primarily focused on tetrahedral amorphous carbon electrode that can be doped with nitrogen, resulting in significant physical, chemical an electrochemical properties. Moreover, the electrode surface chemistry was alternated by an oxygen plasma modification and its effect on the electrochemical performance (background voltammetric current, capacitance and electron transfer kinetics), as well as potential surface damage was studied.

Lastly, as it is believed that the nitrogen incorporated tetrahedral amorphous material possesses an equally superb properties compared to the boron doped diamond, both electrode materials were used for determination of endocrine disruption compounds, specifically estriol, estradiol and estrone, using high-pressure liquid chromatography with electrochemical detection. The detection figures of merit for both boron doped diamond and nitrogen-incorporated tetrahedral amorphous carbon thin-film electrodes were determined.

To my grandma babička Jaruška

I wish more than anything you could be here and see that I made it!

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Where would I be, and what would I be without you?

I remember my first day at MSU very clearly. I entered the chemistry building and saw a big poster – an invitation to a seminar called *"What drives a success in research, hard work or luck?"*. I kept thinking about it for the rest of the day. Leaving the chemistry building later that evening, being happy with my new project, I was sure that hard work with a little luck always leads into success. And I thought that if I keep working hard, I can achieve whatever I want. Now, 5 years later, when finishing this thesis, I know how wrong I was. What really drove my success was an amazing combination of several factors, that I have found in Professor Swain's group.

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CHAPTER 1. INTRODUCTION

1.1. Carbon Electrodes

Carbon is one of the most plentiful elements on the planet. From a materials perspective, carbon is unique because of the microstructurally distinct allotropes it forms. These include single and polycrystalline diamond, diamond-like carbon, glassy carbon, and graphite.

Carbon materials are some of the most commonly used electrodes in electroanalysis, electrochemical storage and conversion, and electrosynthesis. ^{1–5} There are numbers of reasons for this including low cost, high mechanical strength, wide usable potential range, rich surface chemistry, chemical inertness, and compatibility with a variety of solvents and electrolytes. In order to optimally use carbon electrodes, it is critical to fully understand and control the variables that impact heterogeneous electron-transfer kinetics, capacitance and adsorption at these materials. It has been previously established that the variations in the sp² carbon electrode microstructure and surface chemistry can significantly affect the heterogeneous electron-transfer rate constant for some, (*e.g.* $Fe(CN)6^{-3/-4}$) but not all (*e.g.* $Ru(NH_3)6^{+3/+2}$), soluble redox systems, often by multiple orders of magnitude.^{6–11}

1.1.1. Glassy Carbon

The commonly used sp²-bonded carbons, *graphite* and *glassy carbon*, represent one extreme of the carbon microstructure spectrum. These materials consist of carbon atoms with σ and π bonds. The most microstructurally-ordered carbon, graphite, consists of layers of planar polycyclic aromatic sheets with the carbon atoms organized into a hexagonal lattice (Figure 1.1A). The edges of the individual sheets that are separated by 3.35 Å form very reactive sites for adsorption and electron transfer, so called "edge plane" sites. These carbon atoms react with oxygen and water to form a variety of surface oxygen functional groups, such as carboxylic acid,

carbonyls, phenols, ethers, etc. In contrast, the layer plane surface is the so-called "basal plane". Due to a lack of functional groups and a lower density of electronic states, the basal plane sites are unreactive with oxygen and water, and support weak molecular adsorption and sluggish electron-transfer.^{12–14} The edge plane sites are well known to exhibit significantly faster electron-transfer kinetics for many redox molecules in comparison with the basal plane sites.^{15,16} The capacitance of the edge plane sites is also greater than the basal plane sites.

Glassy carbon is a more microstructurally disordered graphitic carbon has a structure consisting of nanometer dimensioned graphitic domains that are randomly intertwined in a ribbon-like structure (Figure 1.1B). Glassy carbon has a relatively high ratio of edge plane sites exposed at the surface because of the microstructural disorder.^{17–19} Graphite has a hexagonal structure with the carbon atoms in 3-fold bonding configuration. There is a strong intraplanar bonding within the



Figure 1.1. Structure of various carbon materials: (A) graphite, (B) glassy carbon (C) diamond and (D) tetrahedral amorphous carbon. (Reprinted with a permission obtained from The Springer Nature).¹⁹

extended polycyclic aromatic rings and weak intraplanar bonding that allows the hexagonal sheet to slide across one another. Glassy carbon has a glassy-like appearance, hence its name. It is hard and brittle unlike graphitic forms of carbon. The material consists of a ribbon-like network of entangled nm-dimension graphitic carbon domains. The entanglement leads to the nano porosity of the material.²⁰ The material is made from the pyrolysis of polymer precursors. The material is classified by its post formation heat treatment temperature (e.g., 1000, 2000, 3000 °C). The higher the heat treatment temperature the more microstructural ordered the material becomes presumably die to a flattering and straightening of the ribbons. The microstructure order (nm dimensions) is characterized by the XRD-determined height of the graphite-like ribbons, L_e , of ~ 40 nm and length of the ribbons, L_a , of ~ 100 Å.²⁰ Importantly, glassy carbon has electrons in both σ and π orbitals that leads into a relatively small band gap between the valence and conduction gap, as well as high density of electronic states. It is nevertheless important to highlight that the presence of π orbitals possesses several unwanted features, such as specific adsorption, high background current, and microstructural changes at high positive potentials.¹⁵

1.1.2. Boron-Doped Diamond

Diamond represents the other extreme of carbon allotropes. (Figure 1.1C). Diamond has four-fold, sp³ hybridized carbon boundary consisting purely of σ bonds. Diamond is one of Mother Nature's best electrical insulator with a well-known large band gap of 5.5 eV and a low density of electronic states. The low electrical conductivity arises from a low number of free charge carrier as these it little thermal activation of electron in the conduction band at room temperature.²¹ To increase the electrical conductivity of diamond, the material can be doped using *p*- or *n*-type dopants. Boron is one of the most commonly used dopants that is incorporated from the gas phase during the growth process. for diamond material, commonly implemented into its growing process.

Boron atoms serve as electron acceptors and form an impurity band located ~0.35 eV, or less, above the valence band edge. Typical doping levels for diamond films used in electrochemistry are 10^{20} – 10^{21} cm⁻³.

Boron-doped diamond (BDD) is an increasing used carbon electrode material. ^{22–24} BDD electrode exhibits excellent electrochemical properties, such as a wide working potential window, low background current and noise, and rapid electron transfer kinetics for many redox species. The basic electrochemical properties of BDD have been reviewed extensively in publications dating back to early 1990s.^{25–30} Compared to the glassy carbon, BDD is microstructurally and morphologically stable even at high positive potentials and high currents and has weak molecular adsorption due to the lack of π bonds. Moreover, thanks to the large band gap, diamond is an optically transparent material, that can be advantageously used in for transmission spectroelectrochemical measurements in the UV/Vis^{31–35} and mid-IR³⁶ regions of the electromagnetic spectrum.

1.1.3. Tetrahedral Amorphous Carbon

Another carbon electrode that is receiving increase study is *tetrahedral amorphous carbon* (t*a*-C). *ta*-C is a type of 'diamond-like' carbon (Figure 1.1D). Microstructurally, it consists of a mixture of randomly arranged sp², and sp³ bonded carbon. The material can be generally tailored based on the required properties by controlling the ratio of sp² and sp³ content, as well as the hydrogen content. The ternary phase diagram conveniently displaying possible diamond-like carbon composition is shown in Figure 1.2.³⁷ The diamond-like material with a random arrangement of sp² and sp³ bonded carbon is defined as amorphous carbon. In this research, the focus is lying on the amorphous material, that can be deposited with a high portion of tetrahedrally bonded sp³ carbon, generally from 40 up to 85 %.³⁸ Films with such as high content of sp³ bonded carbon are denoted as *ta*-C. ³⁹ The sp³ hybridized atoms form a random network with neighboring



Figure 1.2. Amorphous carbon ternary phase diagram. The corners represent graphite, diamond and hydrocarbons. (Reprinted with a permission obtained from The Royal Society). ³⁶

atoms connected by strong σ bonds. Interspersed are sp² carbon domains that link the sp³ carbon regions. These sp² sites form π states which control the optical and electrical properties.⁴⁰

The structural and electronic properties of the *ta*-C are mainly a function of the fraction of the sp³-bonded carbon sites, ordering of the sp² sites, and hydrogen content. The atomic structure was described by Robertson et al⁴¹. A carbon atom has four sp³ orbitals that provides four strong σ bonds to the neighboring atoms. In contrast, in the sp² configuration, a carbon atom creates three trigonal sp² orbitals that forms three σ bonds in a plane. The remaining (fourth) electron of the sp² atoms lies in a p orbital that creates a weaker π bond with an adjusted atom.⁴¹ The amount of incorporated hydrogen is generally low in *ta*-C materials.

Due to the high percentage of sp³ bonded carbon, *ta*-C exhibits several properties akin to diamond, such as high chemical inertness, hardness, elastic modulus, optical transparency (band gap ~3.5 eV), and exceptional electrochemical behavior.^{42–47} Importantly, the *ta*-C electrode possesses a key benefit over the BDD, and that is the possibility of deposition at low temperatures (25 - 100 °C), as compare to the BDD (>600 °C). This makes possible deposition of *ta*-C on a variety of substrate materials. Moreover, the deposition of the *ta*-C electrode is significantly cheaper, and the deposition of continuous films takes in order of tens of minutes, compared to hours needed for a BDD film growth.

t*a*-C film generally have an sp²-rich layer on the surface because the material grows by a sub plantation process. In this process, incident carbon cations enter subsurface sites, densifying these and converting the bonding to sp^3 .^{38,48,49} This leaves behind an outer sp^2 carbon layer that could significantly impact the electrochemical properties. This outer sp^2 layer is a few nanometers thick.

1.1.3.1. Nitrogen Incorporation into the Tetrahedral Amorphous Carbon

Similarly to diamond , the *ta*-C material can be doped by incorporation of impurities. One of the most commonly used n-type dopants is nitrogen. The incorporation of the nitrogen into the film can be easily performed by adding the nitrogen gas flow into the chamber during the film deposition.⁵⁰ Electronic and optical properties are significantly affected by the nitrogen incorporation. While the pure *ta*-C film is considered to be a weak p-type semiconductor, it has been found that the controllable doping of *ta*-C with nitrogen increase the electrical conductivity.^{51–54}

Two main types of nitrogen incorporation have been described previously by Robertson at el.⁵⁵ and confirmed by other research groups.⁵⁶ For the implementation of nitrogen into the t*a*-C network at a partial pressure of nitrogen lower than 3.5 Pa, the nitrogen is incorporated mainly close to the already existing π bonded sites. Consequently, the bonds around nitrogen atoms undergo graphitization, accompanied by a significant narrowing of the band gap and an increase of electrical conductivity. Only a small fraction of all incorporated nitrogen atoms attributes to the conductivity. Nevertheless, for the nitrogen doping at partial pressure higher than 3.5 Pa, the optical gap gets wider and electrical conductivity of the resulting *ta*-C:N material begins to decrease. For example, for samples deposited at partial pressure of 7 Pa, the actual fraction of incorporated nitrogen atoms reaches up to 47%, while the optical gap rises to 4.05 eV and the electrical conductivity drops.⁵⁶ Such as reduction of conductivity is caused by a transformation of the initially bonded sp³ -CN matrix into a new sp² configuration containing a polymeric carbon nitride (>C=N-) film.^{43,56,57}

1.2. Characterization of Carbon Electrodes

If one wants to understand structure-function relationships at the nanostructured carbon electrodes, detailed electrode material characterization is necessary to know what the electrode morphology, microstructure, and bulk and surface chemical composition area. The microstructure, ratio of the sp² and sp³ carbon bonding and the chemical composition of the carbon at the surface and in the bulk play a key role in its properties. The most useful techniques for characterizing the material properties of carbon electrodes include electron microscopic and spectroscopic methods, such as transmission electron microscopy,⁵⁸ scanning electron microscopy,⁵⁹ x-ray photoelectron spectroscopy,⁶⁰ electron energy-loss spectroscopy,^{39,61} and Auger electron spectroscopy.⁶⁰ Optical spectroscopic methods are also useful including infrared spectroscopy,⁶² Visible and UV Raman spectroscopy.^{63,64} Lastly, other techniques such as ¹³C nuclear magnetic resonance,⁶⁵ inelastic neutron scattering spectroscopy,⁶⁶ and scanning probe microscopies (*e.g.*, AFM)⁶⁷ are also useful.

For determination of the sp^2 and sp^3 carbon bonding ratio in ta-C and ta-C:N electrodes visible and UV Raman spectroscopy, and x-ray photoelectron spectroscopy were used.

1.2.1. Raman Spectroscopy

Raman spectroscopy is one of the most commonly used techniques for carbon material microstructure characterization.⁶⁸ The technique can be used to distinguish the type of carbon bonding, the domain size, the doping level in boron-doped diamond films and the intrinsic internal stress of diamond.^{58,69}

The shape of the Raman spectrum for nanocrystalline BDD electrode is significantly affected by the boron content. Single crystal diamond is characterized by a sharp diamond line at 1332 cm⁻¹.^{68,70} The Raman spectra for low boron doped diamond film is characterized by a sharp band at 1329 cm⁻¹, attributed to the sp³ bonded carbon, and another peak presented at 519 cm⁻¹,

that is assigned to the phonon mode of the crystalline Si substrate on which the BDD film is deposited. At the low boron content (~500 ppm), the Si peak possess a Fano shape, given by the presence of boron in the substrate. With an increasing concentration of boron, the relatively symmetric Lorentzian band at 1332 cm⁻¹ changes towards an asymmetric Fano-like line shape and moves down to the 1290 cm⁻¹.⁷¹ Moreover, this shift is usually coupled with an increasing scattering intensity at ca. 500 and 1220 cm⁻¹. It has been previously reported that the 500 cm⁻¹ band is due to the vibrational modes of boron dimers and increases with an increasing level of boron doping. The peak positioned at 1220 cm⁻¹ is assigned to defects in the diamond lattice brought about by the high of boron doping or the boron-carbon complexes. The last peak presented at spectra of heavily doped BDD film is presented at around 1496 cm⁻¹. It is assigned to a presence of amorphous sp² carbon. The band is typical characteristics for BDD, and the intensity of the 1496 cm⁻¹ peak increases with an increasing boron level. ^{22,71-74}

The Raman spectra for tetrahedral amorphous carbons are characterized by an asymmetrical band centered between 1000 and 1800 cm^{-1} . This peak is attributed to the vibrational modes of sp²-bonded carbon clusters. The Raman scattering cross section for sp² bonded carbon (*e.g.*, graphite) is larger than the cross section for diamond with visible excitation so the Raman scattering is dominated by the sp² domains in the *ta*-C:N films.^{75,76} Two peaks of interest can be identified after deconvolution of the asymmetrical band. One component is the graphite 'G' band peak centered at 1550 cm⁻¹. The G band is attributed to the first-order phonon mode for pairs of sp² carbon sites in both rings and chains. A second component is the 'D' band peak centered approximately at 1358 cm⁻¹. This scattering is attributed to the breathing vibration modes of sp² carbon atoms in rings.^{62,77–79} In perfect graphite, this mode is forbidden, and therefore becomes active only for disordered materials.⁷⁵ Ferrari et al.⁷⁵ reported that the reason is the domination of

the sp² sites scattering. The π states are significantly more polarizable compare to the σ states because of their lower energy. Therefore, the sp² sites have about 50-230 times larger Raman cross section compared to the sp³ sites. ^{80,81} Consequently, the sp² sites dominate the Raman spectra of *ta*-C, even for those with low sp² content (10-15% of sp²). Ferrari and Robertson⁷⁵ also reported that the matrix element has a significantly stronger effect than in σ bonded structure. There have been several reports on the nitrogen incorporation and its effect on Raman spectra. ^{50,62,82} As the increasing nitrogen content causes an increasing fraction of sp² bonded carbon, intensity ratio of the D peak to G peak increase. The full-width-half-maximum of the G peak decreases with an increasing content, also due to the increasing content of sp² bonds. ^{50,78} Finally, the G band position was reported to shift to the lower wavenumbers with increasing nitrogen content. The observed trend is due to the increasing sp² bonded carbon content and an increasing number and/or size of clusters. ^{50,62,82}

The most commonly used fitting technique uses two Gaussians peaks centered around the theoretical D and G band positions. The focus for an characterization of tetrahedral amorphous carbon electrodes by visible Raman spectroscopy can be pointed at following spectra features: the G band position, the G band width and the intensity ratio of the D peak to G peak (I_D/I_G) .⁶², that are related to the structures, size, and density of the sp² clusters. Cui et al⁸³ found an unique correlation between the full-width-half-maximum of the G peak (FWHM) and the sp³ content for the hydrogen free diamond like carbon material. The following equation was reported⁸³:

$$sp^{3} content = -2.05 + 1.90 \times 10^{-2}W - 3.01 \times 10^{-5}W^{2} \pm 0.08$$
 (1.1)

where W is the FWHM(G) of Raman spectra measured at a wavelength of 514 nm. Ferrari et al.⁸⁴ reported a quantitative relation for Raman spectra measured at any excitation wavelength.

$$FWHM(G)@514 = FWHM(G)@\lambda + 0.21 \times (514 - \lambda) \ [cm^{-1}]$$
(1.2)

Combining both equations 1 and 2, a calculation of sp³ content in a hydrogen-free diamond-like carbon at any excitation wavelength can be performed.

1.2.2. X-ray Photoelectron Spectroscopy

Another method that can be used to estimate the sp^2 and sp^3 carbon bonding in diamond and tetrahedral amorphous carbon thin films is x-ray photoelectron spectroscopy (XPS). XPS is a powerful and surface-sensitive method that measures the uses the peaks position reflecting the electron binding energies for specific levels of atoms, further used for identification of the chemical states. XPS is a benefitial measurement technique because it not only reveal what elements are within a film but also what other elements they are bonded to. XPS spectra are received by irradiating a material with a beam of x-rays while simultaneously measuring the kinetic energy and number of electrons that escape from the top ~10 nm of the material being analyzed. For bulk chemical information, depth profiling XPS is used.

For boron-doped diamond and nitrogen-incorporated tetrahedral amorphous carbon, key elemental signals are the binding energies for B1s (185 eV), C1s (284 eV), N1s (402 nm) and O1s (532 nm). There are chemical shifts in these core peaks depending on what atoms the B, C, N and O are bonded to. In other words, shifts in the binding energies can be used to determine the atomic percentages of carbon atoms bonded to other carbon atoms, or to other boron, nitrogen or oxygen atoms. The chemical shift is also dependent on the lattice field of the material.^{85,86} Therefore, this can be used for an investigation of whether a carbon material is sp² or sp³ bonded. Moreover, the XPS can be used to investigate a surface composition, valence band density of states, etc.⁶⁰

Compared to some other methods, XPS can be used without any enormous damage of the material, and does not require a reference sample.

The core C1s position is sensitive to the sp² and sp³ bonded carbon in the material, so the technque can be used to estimate the ratio of sp² and sp³ carbon in *ta*-C and *ta*-C:N thin films.^{58,82,87,88} In order to analyze the spectra quentitatively, the deconvolution and fitting with a Gaussian peaks is neccesarry.^{60,89,90} The C1s position for a pure sp² material like graphite is 284.5 eV and the peak position for a pure sp³ material like diamond is 285.3 eV. Mizokawa et al.⁹¹ reported that the binding energy of the sp³ sites is shifted by 0.8 eV compared to the sp² sites. Another typically presented component found as a *ta*-C surface contamination is an oxygen. Panwar et al.⁶⁰ reported on diminishing of the oxygen peak after a cleaning process, proving that the oxygen is not presented in the film bulk, but only on the film surface.

For the nitrogen incorporated tetrahedral amorphous carbon, the characteristic N 1s line is also presented. It has been found that the nitrogen content affects also the C 1s peak. An increasing nitrogen content causes a shift of the C 1s line towards higher binding energy, as well as an increased broadening of the line. Moreover, the increasing intensity of the higher binding energy shoulder with an increased nitrogen content was reported.⁵⁶ According to Rodil et al, ⁸⁸ the N 1s peak can be deconvoluted and fit to three components, suggesting that the N in the film exists in three different chemical environments. The peaks are assigned to N bonded to sp³ carbon (398.56 eV), CN triple bonds (399.91 eV) and N-sp² carbon (401.41 eV).^{88.92} The XPS depth profiles has revealed that the nitrogen content is relatively constant with depth in the t*a*-C:N film).⁹²

Similarly to Raman spectroscopy, the XPS spectra must be deconvoluted to obtain a detailed information of the carbon material microstructure. The intensity of the core-level lines is

then directly proportional to the atomic density. For a calculation of the nitrogen concentration in the films, the ratio of the integrated intensities of the N 1s and C 1s lines can be used, with an implementation of sensitivity factors ($S_{nitrogen} = 0.42$ and $S_{carbon} = 0.25$).⁹³

1.3. Room Temperature Ionic Liquids (RTILs)

Room temperature ionic liquids (RTILs) are salts composed purely of ions with no solvent. These salts are liquids at room temperature due to their near room temperature melting point. ^{94–96} RTILs are composed of a large organic cation, such as imidazolium, pyridinium, and pyrrolidinium derivatives, and a small inorganic anion, such as [BF4], [PF6], [CF3SO3], and [(CF3SO3)2N]. Due to the numerous possible combinations of cationic and anionic structures, the physicochemical properties of the RTILs can be easily manipulated by changing the chemical composition.⁹⁷ From an electrochemical viewpoint, key properties of the RTILs are the viscosity, electrical conductivity and working potential window.

RTILs have attracted the attention of scientific word due to their many unique properties, such as negligible vapor pressure associated with high thermal stability, extraordinary chemical stability, moderate electrical conductivity, non-flammability, etc. ⁹⁶ RTILs possess advantageous properties when used in electrochemistry. When pure, many RTILs are stable over a wide potential range of approximately 5 to 6 V, which is in significant contrast with more aqueous electrolyte solutions (~2V). ^{98,99} The wide electrochemical window enables the study of redox reactions at extreme positive and negative potentials, something that is no possible in in aqueous electrolytes. Two limitations with their use, particularly in electrochemical studies of electron-transfer and mass-transport, are their high viscosity and the presence of impurities, such as water or reagents used in their synthesis.

The viscosity of RTILs is caused primarily by the strong van der Waals interactions between the cations and anions.^{99–101} It has been found that the viscosity is more affected by the structure of the anion compared to the cation. The viscosity increases with increasing size of the cation due to the strengthen cation-anion interactions. Typically, the viscosity of RTILs is significantly higher than water (η (H₂0) = 0.89 mPa s at 25 °C) ranging from 25 to 312 mPa s (Table 1.1). The variability of viscosity values in the table for a RTIL are likely due to variable levels of water contaminations. The high viscosity of RTILs suppresses diffusional mass transport and slows heterogeneous electron-transfer with an electrode. ^{102–104}

The presence of impurities in RTILs can have a significant effect on their physicochemical properties and on electrochemical processes using them. One of the most abundant contaminants is water. Both hydrophilic and hydrophobic RTILs can adsorb water.^{105–107} It has been reported that the water contamination in RTILs has a significant effect on their electrochemical properties by decreasing viscosity and density,^{95,107,108} while increasing the electrical conductivity.^{109,110} Water contamination causes a significant increase of voltammetric background current, reduces electrochemical potential window and affects the solubility and solvent environment around a redox molecule. The presence of water can also affect the structure of the electric double-layer formed at electrified interfaces.^{95,111} As the water removal process is somewhat time-consuming, the researchers often neglect trace level of such as contamination, as can be illustrated by the variable viscosity values reported for the same RTIL. For example, for [BMIM] [PF₆], values of 173, 207 and 312 mPa-s have been reported. Therefore, not only the experiments with RTILs require a fast and convenient water removal process.

RTILs	Structure	<i>Temperature</i> , °C	<i>Viscosity</i> , mPa s	Reference
[EMIM][BF4]	CH ₃	25	25	112
	F-B-F	25	37	113
	СН3	25	43	114
[BMIM][BF4]		25	92	115
	CH ₃	25	219	110
	F—B—F N F	25	233	116
	СН3	20	112	115
		20	154	117
[BMIM][PF6]	F F F F F F F F F F	25	173	115
		25	207	118
		25	312	116
		20	201	115
		20	286	118
[BMIM][OTF]	O^{-}	25	75	119
		25	90	112
		20	90	120
	~ `CH3	20	110	121

Table 1.1. Molecular structure and viscosity of RTILs used in this study.

RTILs consist purely of cations and anions with no solvent present. For the aqueous or organic electrolytes, the electrode – electrolyte interface, the so-called 'electric double layer,' has been intensively studied and can be described by Gouy-Chapman-Stern model (Figure 1.3). This model is most appropriate for dilute aqueous electrolyte solutions . It is questionable if this model is descriptive of the interfacial organization of a RTIL at an electrode. RTILs possess high total ion concentrations (3-6 M). The concentration of free ions is less due to ion pairing. Furthermore, at the electrified interface, the RTILs can form several layers of oscillatory charge density, which makes the typical uniform double layer model misleading. ^{96,102}

Over the last decade, several models of the electrical double layers in RTILs have been proposed and experimentally tested. In 1997, Borukhov et al.¹²² described a theory involving a binary electrolyte with a high ionic concentration. The model considers a Columbic interaction between the charged surface and the ions but there is a missing theory on the ion-ion correlation arising from the short range Coulombic interactions. The ionic correlations in concentrated electrolytes were later heavily investigated by Kornyshev et al. ¹⁰², who adapted the Borukhov's theory for the purposes of the RTILs. The resulting 'Lattice saturation model,' that suggests tightly packed multiple layers of ions (Figure 1.3B) is so far the most trustable model of the electrified layer in RTILs.¹²³

The absence of any solvent in the RTILs is important in several respects. First, in contrast with aqueous electrolyte solutions, the solution environment around a redox analyte in an RTIL is quite different. There is no solvation layer around the redox analyte but rather an organization of cations and anions. This means that there is likely a larger reorganizational barrier to overcome in an RTIL when a redox molecule undergoes electron transfer. For example, research in this project showed that when trying to measure electron transfer for the Fe(CN)₆^{-3/-4} redox system in RTILs,



Figure 1.3. Double layer in aqueous solutions (A) and room temperature ionic liquid (B).¹¹⁷

no current was measured voltammetrically in several RTILs even though the analyte was dissolved. However, when water was added to the RTIL, voltammetric current was observed for the redox reaction. This likely has to do with a very large reorganizational barrier in the pure RTIL, a barrier that is reduced when a dielectric solvent is added to the system. Second, the solubility of a redox molecule is affected by the presence of water. This is particularly true for highly charged redox molecules.

1.4. Research Objectives and Specific Aims

There is considerable knowledge about electron-transfer reactions for redox systems in aqueous and organic electrolyte solutions at carbon electrodes. In contrast, there is a limited information about electron-transfer reactions for redox systems in RTILs. The research presented in this dissertation focused on addressing this knowledge gap. The overall goal of the research was to advance the understanding of the material properties of sp³ (boron-doped diamond films) and hybrid sp³/sp² (nitrogen-incorporated tetrahedral amorphous carbon) nanostructured carbon electrodes and how these properties affect electrochemical processes (capacitance and

heterogeneous electron transfer) in RTILs. Comparison studies were performed using soluble redox systems in aqueous electrolyte solutions.

The research was conducted around three specific aims:

Specific Aim 1: To fully characterize the physical, chemical and electronic properties of the different carbon electrode materials used in the research: glassy carbon (GC), nitrogen-incorporated tetrahedral amorphous carbon (t*a*-C:N) and boron-doped diamond (BDD).

Specific Aim 2: To correlate the heterogeneous electron-transfer rate constants of soluble inorganic and organic redox couples with the RTIL type/structure at "as received" nanostructured carbon electrodes: boron-doped nanocrystalline diamond and nitrogen-incorporated tetrahedral amorphous carbon thin films. The goal was to determine if the electrode microstructure has a strong influence on heterogeneous electron-transfer rate constants in RTILs of different composition as is the case in aqueous electrolytes.

Specific Aim 3: To determine how various levels of nitrogen incorporation into the tetrahedral amorphous carbon thin films affect the physical, chemical and basic electrochemical properties of the materials. The electron-transfer kinetics for soluble inorganic and organic redox systems were investigated in both aqueous and RTILs solutions. Moreover, research was conducted to determine how changes in the surface chemistry of the ta-C:(N)_x electrodes affect the electron-transfer kinetics.

Specific Aim 4: To evaluate and compare the analytical detection figures of merit achievable with BDD and t*a*-CN electrodes for detection of various bioanalytes using high-pressure liquid

chromatography coupled with amperometric detection. The target analytes included estrogen and estrogen compound metabolites, and isatin.
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CHAPTER 2. EXPERIMENTAL METHODS

2.1. Electrode Preparation

2.1.1. Glassy Carbon Electrode

The GC working electrode (GC-20, Tokai Ltd.) was pretreated prior to use by mechanical polishing with successively smaller grades of alumina powder (1.0, 0.3 and 0.05 µm diameter) on separate felt polishing pads followed by ultrasonic cleaning. The powder was slurried with ultrapure water, and the polishing was performed by hand. After each polishing step, the electrode was rinsed copiously with ultrapure water and then ultrasonically cleaned for 10-20 min in ultrapure water to remove polishing debris.

2.1.2. Boron-Doped Nanocrystalline Diamond Thin Films

The BDD thin film was deposited on a boron-doped Si (111) substrate (~ 10^{-3} ohm-cm) by microwave-assisted chemical vapor deposition (CVD). A 1.5 kW reactor from Seki Technotron was used for the diamond growth. Prior to growth, the silicon substrate was seeded with nanodiamond particles (Opal Seed suspension, Adamas Nanotechnologies Inc., Raleigh, North Carolina). This was accomplished by a 30-min ultrasonic treatment in 10-30 nm nanodiamond powder slurried in DMSO. After seeding in a glass beaker, the substrate was cleaned by rinsing with ultrapure water in the beaker and then drying the substrate with nitrogen before placement in the CVD reactor chamber. For the BDD thin-film growth, a 1% CH₄/H₂ source gas was employed with 10 ppm of B₂H₆ added for boron doping. The microwave power was 800 W and the system pressure was 35 torr. The substrate temperature during the deposition was ~825 °C as estimated with a disappearing-filament optical pyrometer. These deposition conditions produced a diamond film ~2-4 µm thick (growth time 4-6 h) with a doping level in the low 10^{21} cm⁻³ range, based on Raman spectroscopic analysis.¹⁻³ The electrical resistivity was generally ≤ 0.01 ohm-cm. At the end of the deposition period, the CH₄ and B_2H_6 flows were stopped while the H₂ flow continued and the plasma remained ignited. The specimen was then cooled in the presence of atomic hydrogen by slowly lowering the power and pressure over a 30-min period to reduce the estimated substrate temperature to below 400 °C. This post-growth cooling is essential for maintaining a hydrogen surface termination and minimizing surface reconstruction from an sp³ to sp² hybridization.

2.1.3. Nitrogen-Incorporated Tetrahedral Amorphous Carbon Thin Films

The ta-C:N film was grown on a boron-doped Si (111) substrate (Virginia Semiconductor, Fredericksburg, VA; ~10⁻³ Ω -cm) using a Laser-Arc physical vapor deposition system at the Fraunhofer Center for Coatings and Diamond Technologies (MSU). The deposition method is based on laser-controlled, high-current cathodic vacuum arc deposition.^{4–8} In the process, a pulsedlaser beam is rastered across a rotating high-purity graphite target that serves as the cathode. Each laser pulse generates small localized plasma that delivers free charge carriers for the arc discharge. The arc discharge lasts only 125 µs before the laser triggers a new, staggered plasma across the graphite cathode. This discharge consists of highly ionized C atoms and small ionized carbon atom clusters that are accelerated toward the substrate (grounded anode). This process produces hard (30-60 GPa) and dense ta-C films. The substrate-target distance was approximately 30 cm. The substrates were rotated during the deposition to promote uniform film deposition. The arc evaporation is associated with the emission of macroparticles of carbon originating from the graphite drum (*i.e.*, cathode surface).⁸ These particles can be incorporated into the growing film and impact surface roughness. The nitrogen-incorporated films were deposited in the presence of N₂ gas at a flow rate of 10, 30 and 50 sccm (ta-C:N), a pulse rate of 350 Hz and a peak arc current of > 100 A. Increased levels of nitrogen in the chamber lead to increased nitrogen

incorporation into the film and increased electrical conductivity.^{9–12} The substrate temperature during the deposition was below 100 °C. The film growth rate was 2-3 μ m/h.

As a final cleaning step, all electrodes (GC, BDD and ta-C:N) were immersed for 20 min in ultrapure isopropanol daily before use.¹³ This was typically done with the electrodes mounted in the electrochemical cell. The isopropanol was purified first by distillation and then by storage over activated carbon. This ultrapure solvent cleans the surface by dissolving any remaining contaminants. After cleaning with the ultrapure isopropanol, electrodes were dried with the N₂. Before mounting the electrodes into the electrochemical cell, the back side of the Si substrate of the BDD and t*a*-C:N electrodes was then scratched with SiC paper, cleaned and coated with carbon from a graphite pencil in order to create an ohmic contact with the copper plate current collector.

2.2. Physical and Chemical Characterization of Electrodes and RTILs

2.2.1. Visible Raman Spectroscopy

Raman microscopy was performed using a Renishaw *in Via* Confocal Raman Microscope equipped with a Nd:YAG laser, controlled by a WiRE Interface commercial software package. Specimens were generally exposed to 4.5 W of laser power (45 W max. power laser with 10% of this focused at the specimen surface) with an integration time of 3-10 s. The excitation wavelength was 532 nm. Each spectrum was generated from an average of 3 spectral acquisitions at each point. The Raman spectra of ta-C:N_x thin-films were fitted with two peaks using Gaussian-Lorentzian functions. The Raman mapping images of ta-C:N_x films were constructed from the G band position, G band width, and the ratio of D-to-G band intensity ratio. The electrode area of 100 μ m² was mapped with a step size of 1 μ m. Before each sample measurement, the Raman spectrometer was calibrated with a Type IIa single-crystal diamond standard (one-phonon line at 1332 cm⁻¹).

2.2.2. Atomic Force Microscopy

The topography of the BDD and *ta*-C:N_x thin-film electrodes was investigated by atomic force microscopy. A Nanoscope IIa scanning probe microscope (Veeco Instruments, Inc., Santa Barbara, CA) operated in the contact mode was used for these measurements. Images were acquired in air at room temperature. The AFM tips (model SNL-10, Bruker, Billerica, MA) were etched Si₃N₄ on an Au-coated Si cantilever (100 µm triangular legs, 0.12 N m⁻¹ spring constant and a resonant frequency of 254 – 390.) The scanned area was 1 µm × 1 µm for *ta*-C:(N)_x and 3 µm × 3 µm for BDD. All microscopic images were generated and analyzed using NanoScope Analysis (version 1.5, Bruker) software. The images consisted of 254-line scans. The rms roughness (*R*) was calculated for at least three different spots on each film. Before the roughness calculation, the image was flattened. The flattening procedure is commonly used and does not affect the resulting *R* values. The procedure is used to account for the macroscopically titled samples with respect to the horizontal scan directions of the microscope. The roughness is defined herein as follows:

$$R = \left[\sum (h_i - h_{ave})^2 / N\right]^{1/2}$$
(2.1)

where h_i is the film height, h_{ave} is the average of the height values in the examined area, and N is the number of points measured.^{14,15}

2.2.3. Scanning Electron Microscopy

The morphology of the BDD and t*a*-C:N_x electrodes was examined using one of two fieldemission scanning electron microscopes (JEOL 6610LV and 7500F, Ltd., Tokyo, Japan), housed at the Center of Advanced Microscopy (MSU). Both a secondary and a back-scattered electrons were used to construct micrographs. Generally, micrographs were collected using an accelerating voltage of 10 kV.

2.2.4. X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy of the BDD and t*a*-C:N_x thin-film electrodes was carried out using a Perkin-Elmer Phi 5400 ESCA system (Perkin-Elmer, Waltham, MA) using a high intensity monochromatized Al K α (*hv* = 1486.6 eV) x-ray source. The experiments were performed at a take-off angle of 45° with a pass energy of 17.87 eV. The base pressure in the analysis chamber was near 10⁻⁹ torr, sufficient to ensure surface cleanliness during the measurement. The x-ray power was 350 W and scans were acquired over an area of 250 μ m². Prior to a measurement, the system was calibrated using the C1s line of graphite (*hv* = 284.6 eV). The resulting spectra were deconvoluted into several Gaussian peaks and evaluated using Multipak software.

2.2.5. Contact Angle Measurement

The wettability of the BDD and t*a*-C:N thin-film electrode surface was assessed by measuring the static water contact angle using an AST Products Video Contact Angle System 2000 with a 150 W light source, housed at the Fraunhofer Center for Coating and Diamond Technologies (MSU). The sessile drop method ($V = 0.1 \mu L$) at a minimum of three different spots in each sample was used. The measurement was carried out immediately after the liquid was dropped. All measurements were made using ultrapure water at room temperature and in ambient atmosphere.

2.2.6. Fourier Transform Infrared Spectroscopy

The FTIR spectra were obtained using a Mattson Galaxy 3020 (Mattson Instrument, Madison, WI). The spectra were recorded in the range from 600 to 4000 cm⁻¹. Samples were placed

on a potassium bromide disk (International Crystal Laboratories, Garfield, NJ). Each spectrum was generated from an average of 16 scans with a resolution of 4 cm⁻¹ and background subtracted. Background spectra were measured against the KBr disk.

2.3. Electrochemical Characterization

2.3.1. Cyclic Voltammetry

All electrochemical measurements were carried out in three-electrode, single-compartment glass cell (Figure 2.1)¹⁶. For aqueous solutions, a graphite rod served as the auxiliary electrode along with a home-made silver/silver chloride (3 mol L⁻¹ KCl) reference electrode. For all measurements in RTILs, a Pt wire (diameter 0.5 mm) counter electrode and an Ag wire pseudo-



outlet for reference electrode

Figure 2.1. The three-electrode single compartment glass cell.

reference electrode (~0.13 V vs. SCE measured in [EMIM][BF₄]) were used. The Ag wire pseudoreference electrode exhibited slight drift during the measurements. Various carbon working electrodes were used: BDD, t*a*-C:(N)_x and GC. The geometric area (0.2 cm²) of each in contact with the solution was determined by a Viton o-ring at the bottom of the cell. For the RTILs measurement, the electrode was mounted in the bottom of the glass cell outside of the glove box. The electrode and cell were then purged with nitrogen for several minutes before being placed in the glove box. The electrode and cell were then exposed to the dehydrated N₂ environment of the glove box for *ca*. 2 h before being filled with the RTIL solution. If not mentioned otherwise, all measurements were performed at room temperature (*ca*. 23-25 °C).

Cyclic voltammetry studies were performed using a computer-controlled electrochemical workstation (Model 650A CH Instruments Inc., Austin, TX). Cyclic voltammograms were recorded as a function of the scan rate from 0.1 to 0.5 V s^{-1} .

Temperature-controlled experiments were performed by wrapping heating tape around the electrochemical cell and using a Variac transformer (20 A and 110 V) for control of the electric power (resistive heating). The solution temperature was measured with a thermometer, ± 0.5 K.

The apparent heterogeneous electron-transfer rate constants (k^o_{app}) were determined from cyclic voltammetric ΔE_p -v data according to the method described by Nicholson⁶⁵:

$$k^{0} = \psi \frac{\left[\pi D_{0x} \upsilon (nF/RT)\right]^{1/2}}{(D_{0x}/D_{red})^{\alpha/2}}$$
(2.2)

where D_{ox} and D_{red} are the diffusion coefficients of the oxidized and reduced species, respectively, v is the scan rate, n is the number of electrons transferred, R is the ideal gas constant, T is the Kelvin temperature, α is the transfer coefficient (assumed to be 0.5). The parameter ψ is the transfer parameter, for practical usage (rather than producing a working curve) is given by:¹⁷

$$\psi = \frac{(-0.6288 + 0.0021 X)}{(1 - 0.017 X)} \tag{2.3}$$

where $X = \Delta E_P$ is used to determine ψ as a function of ΔE_P from the experimentally recorded voltammetry. The k^o_{app} was also determined by simulation with DigiSim[®] software (version 3.03).

2.3.2. High-Pressure Liquid Chromatography

The HPLC system (Schimadzu Scientific Corp) consisted of a CBM-20A system controller, a DGU-20A5R degassing unit, a LC-29ADXR high-pressure pump, a SIL-20ACXR autosampler, a SDP-M20A UV-VIS detector, and a CTO-20A oven. The reverse-phase column, an XTerraTM C18 (4.63100 mm, 5 mm), was placed inside of the column oven at 30 °C. The sample volume injected was 20 μ L. The mobile phase flow rate was 2 mL min⁻¹. The mobile phase consisted of a 10 mM phosphate buffer (pH 3)/acetonitrile (60:40%, v/v). The mobile phase was filtered using a polyamide membrane filter with a pore size of 0.2 μ m (Sartorius Stedim Biotech, Germany) prior to use. The mobile phase was degassed by ultrasonication using a PS 02000A ultrasonic bath (Powersonic, USA). The spectrophotometric detector was set at 281 nm.

The amperometric detector with a three-electrode arrangement was controlled by a CH Instrument 832A Electrochemical Workstation (Austin, Texas, USA). A home-made, cross-flow electrochemical detection cell was used (Figure 2.2).¹⁸ The cell consisted of two Kel-F pieces with the top portion having the entrance and the exit ports for the mobile phase, as well as a port for the Ag/AgCl reference electrode (-26 mV versus SHE electrode) (ET072-1, Dionex). The exit port was fitted with a short piece of stainless-steel tubing that also served as the counter electrode. The bottom piece of the cell served as the holder of the BDD or t*a*-C:N working electrode.



Figure 2.2. Diagram of the thin-layer, cross-flow electrochemical detection cell.¹⁷

The electrical contact was made to the back side of the working electrode with a piece of clean Cu foil. The volume of the flow channel was defined by a thin (0.1 cm) neoprene rubber gasket. A rectangular groove (1.13×0.1 cm) was cut into the gasket, and this defined the cell volume. Assuming a 50% compression of the gasket with the cell assembled, the cell volume was estimated to be ~10 µL. The potentiostat was electrically grounded and the cell was housed in a grounded Faraday cage to reduce electrical noise.

The HPLC system was cleaned regularly by flowing through ultrapure isopropanol followed by ultrapure water. If the system was to be left idle overnight, water was pumped through for 30 min, and the system (including column) was stored under ultrapure isopropanol.

2.4. Reagents

2.4.1. Electrochemical Measurements in Aqueous Electrolytes

The solutions of hexaammineruthenium(III) chloride (CAS No. 14282-91-8, 98%), potassium hexacyanoferrate(II) trihydrate (CAS No. 14459-95), potassium hexachloroiridate(IV) (CAS No. 16920-56-2, \geq 99.9%), methyl viologen dichloride hydrate (CAS No. 75365-73-0; 98%), ferrocenecarboxylic acid (CAS No. 1271-42-7, 97%), ferrocene (CAS No. 102-54-5, 98%), ferrocene methanol (CAS No. 1273-86-5, 97%), b-estradiol (CAS No. 50-28-2, \geq 98%), estriol (CAS No. 50-27-1, \geq 97%), estrone (CAS No. 53-16-7, \geq 99%), sodium phosphate monobasic (\geq 99.0%), methanol (HPLC grade, \geq 99.9%), and acetonitrile (HPLC grade, \geq 99.9%) were purchased from Sigma–Aldrich, and used without further purification when used for aqueous solutions experiments. Phosphoric acid (85%) was purchased from Spectrum Chemical (New Brunswick, NJ). All aqueous solutions were prepared using deionized water produced by a Barnstead E-Pure system (~18 M Ω cm, Millipore, USA), and stored in glass vessels and refrigerated in the dark at 5 °C when not in use.

2.4.2. Electrochemical Measurements in Ionic Liquids

1-butyl-3-methylimidazolium tetrafluoroborate (\geq 97.0 %, CAS No. 91508), and 1-ethyl-3-methylimidazolium tetrafluoroborate (\geq 98.0 %, CAS No.711721) were purchased from Sigma Aldrich (St. Louis, MO). 1-butyl-3-methylimidazolium hexafluorophosphate (99.5 %, CAS No. 174501-64-5), 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (99.0 %, CAS No. 174899-83-3), were purchased from IoLiTec (Tuscaloosa, AL).

Two techniques for RTIL purification were used. Each method consisted of three steps. In the vacuum drying method, (i) the as received RTIL was first stored over activated carbon for 3 days, (ii) after this period the liquid was then centrifuged to settle out the carbon powder, (iii) then stored over 5Å molecular sieves for a week, and (iv) most of the RTIL sample (several mLs) was then carefully removed and heated under vacuum (< 600 Pa) at 80 °C for 48 h. The round bottom flask used for this was heated in an oil bath. In the "sweeping" method, steps (i), (ii) and (iii) were the same. However, step (iv) involved heating the ionic liquid (approximately 0.5 mL) at 70 °C for 50 min while purging with ultrapure Ar (99.9995%, Linde). The sweeping method was performed with the liquid in the electrochemical cell in the nitrogen-purged vinyl dry box. The water content in the RTIL was assessed qualitatively by cyclic voltammetry (background current and working potential window) and FTIR, and quantitatively by thermogravimetric analysis (TGA). To remove any dissolved oxygen, the purified RTIL in the electrochemical cell was purged after any storage with ultrapure Ar for at least 10 min and remained blanketed with the gas during a measurement. To minimize water contamination, all glassware used was dried in oven at 150 °C for at least 24 h before use.

Solutions containing the different ferrocene redox probes in RTILs were prepared by diluting a stock solution. The stock solution of ferrocene carboxylic acid, ferrocene methanol or ferrocene was prepared by dissolving the analyte in ultraclean (distilled and stored over activated carbon) isopropanol (\geq 99.5, CAS No. 67-63-0, Macron, Croydon, PA) at the designated concentration. The ferrocene derivative + RTIL solution was prepared by quantitatively transferring a specific volume of the IPA solution into a 1 mL volumetric flask and then evaporating to dryness in an oven at 100 °C for 1 h. The volumetric flask was then filled to the mark with the purified RTIL. This solution was then stirred for 12 h before use. All sample preparation and the electrochemical measurements were performed inside of a nitrogen-purged vinyl dry box (Coy Laboratories, Grass Lake, MI). The relative humidity in the box was at or below the 0.1% level, as measured with a hygrometer. All purified RTILs were stored over

activated (heat treated at 400 °C in a furnace) 5 Å molecular sieves in a glass-stoppered bottle and kept in the dry box. Ultrapure water was used for the water contamination measurements.

2.4.3. Water Samples for the HPLC Estrogen Compound Analysis

Well water was collected unfiltered from a home well (Owosso, MI) in a clean polypropylene bottle. The tap water samples were collected in the Chemistry Building at MSU using clean polypropylene bottles. The river water sample was collected from Red Cedar River on the MSU campus (East Lansing, MI). In terms of sample preparation, the water samples were first filtered (8 μ m, Whatman) to remove large particles. The water samples were then analyzed by HPLC–EC for estrogen and estrogen metabolites as received and after spiking with estrone, estradiol, and estriol, followed by dilution with phosphate buffer (pH 3)/ acetonitrile at a 25:75 v/v% ratio. The final concentration of the estrogenic compounds in the different spiked water samples was 7 μ molL⁻¹.

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CHAPTER 3. ASSESSMENT OF HETEROGENEOUS ELECTRON-TRANSFER RATE CONSTANT FOR SOLUBLE REDOX ANALYTES AT TETRAHEDRAL AMORPHOUS CARBON, BORON-DOPED DIAMOND AND GLASSY CARBON ELECTRODES

3.1. Abstract

The electrochemical properties of a nitrogen-incorporated tetrahedral amorphous carbon (t*a*-C:N) thin-film electrode were investigated. Cyclic voltammetry was used to investigate the background current response as a function of potential, scan rate, and electrolyte composition. Cyclic voltammetry and digital simulation were used to determine the heterogeneous electron-transfer rate constants (k^o) for IrCl₆^{2-/3-}, Fe(CN)₆^{3-/4-}, ferrocene carboxylic acid, Ru(NH₃)₆^{3+/2+}, and methyl viologen. The results revealed that the background current for the *ta*-C:N electrode falls between that of BDD and GC. k^o values for all the redox analytes at *ta*-C:N were comparable to the values at BDD and GC. k^o values were lower for Fe(CN)₆^{3-/4-}, 10⁻³ cm s⁻¹, than for the other four redox systems, 10⁻²–10⁻¹ cm s⁻¹. k^o for Ru(NH₃)₆^{3+/2+} was insensitive to the electrolyte cation (Li⁺, Na⁺, K⁺, and Cs⁺) at all three electrodes. In contrast, k^o for Fe(CN)₆^{3-/4} was sensitive to the cation type with the greatest sensitivity seen for the *ta*-C:N electrode suggestive of more significant double layer effects. The *ta*-C:N electrode supports relatively rapid electron transfer for a wide range of redox systems with formal potentials from *ca*. 0.9 to –1.0 V vs. Ag/AgCI.

3.2. Introduction

Carbon electrodes are routinely used for the electrochemical detection of electroactive analytes in a variety of media.^{1–5} By electroactive, one is referring to molecules that are easily oxidized or reduced at an electrode surface. Generally speaking, electrochemical measurements typically involve recording the current that flows in response to a potential perturbation, which is reflective of the local analyte concentration. Carbon is one of the most abundant elements found on the planet. From a materials perspective, carbon is unique because of the microstructurally

distinct allotropes it forms. These include from single and polycrystalline diamond, diamond likecarbon (mixtures of sp² and sp³ carbon bonding), microstructurally disordered glassy carbon, and the graphitic carbons (nanotubes, single sheet graphene, and highly ordered pyrolytic graphite). The graphitic carbons have been investigated extensively for over four decades now so much is known about the structure–function relationships that govern their behavior.^{6–10} The diamond and diamond-like carbon materials have been less studied by comparison. Generally speaking, carbon materials are used today in various technologies because of some common attributes: high mechanical strength, good thermal conductivity and stability, chemical inertness, high carrier mobility and good electrical conductivity, and rich surface chemistry.

Boron-doped diamond (BDD) is one type of carbon electrode that performs well in electroanalytical measurements, often providing superior detection figures of merit compared with conventional carbon electrodes, like glassy carbon.^{11–15} t*a*-C:N electrodes, like BDD, are characterized by a wide working potential window, low background current and noise, rapid electron-transfer kinetics for many redox systems without conventional pretreatment, excellent morphological and microstructural stability at positive potentials and high currents, and weak molecular adsorption.¹⁶ The basic electrochemical properties of BDD have been reviewed extensively in publications dating back to the early 1990s.^{3,11–15} In addition, BDD can function as an optically transparent electrode for transmission spectroelectrochemical measurements in the UV/Vis^{17–21} and mid-IR²² regions of the electromagnetic spectrum.

BDD electrodes can be prepared as a single crystalline or a polycrystalline material as we recently documented.²³ Polycrystalline diamond films can be one of three types: microcrystalline, nanocrystalline (NCD), or ultrananocrystalline (UNCD).²⁴ Microcrystalline diamond thin films are typically grown by chemical vapor deposition (CVD) in a hydrogen-rich environment and are

composed of well-faceted crystallites that are micrometers in dimension.²⁵ The roughness of these films increases with film thickness; so-called grain coarsening. NCD thin films are also deposited in a hydrogen-rich environment. Key for preparing such a film morphology is proper seeding of the substrate surface to produce a high initial nucleation density. This leads to growth of a uniform and pin-hole free nanocrystalline diamond film. NCD films have grains or crystallites with dimensions of tens of nanometers.²⁶ Finally, UNCD thin films are grown in an Ar-rich environment. This type of polycrystalline diamond was pioneered by Gruen and coworkers at Argonne National Laboratory back in the early 1990s.²⁷ These films consist of 50–100 nm aggregates of diamond grains (~15 nm diam.) and are grown under conditions where a high rate of renucleation exists. Unlike NCD, UNCD films have high energy, high-angle grain boundaries that contain π -bonded carbon.^{27,28} The roughness of UNCD films is independent of the film thickness as renucleation events interrupt crystal growth such that no one crystalline has a chance to grow very large.

Over the years, our group has reported extensively on the heterogeneous electron-transfer rate constants of soluble redox analytes at boron-doped microcrystalline,^{3,29–32} NCD, and $UNCD^{33,34}$ thin-film electrodes. Two limitations of diamond as an electrode are the relatively high deposition temperatures (>600 °C) and the limited number of substrate materials that can be used due to thermal stability and stress considerations.

We recently reported on some of the basic electrochemical properties of nitrogenincorporated tetrahedral amorphous carbon (ta-C:N) thin-film electrodes,¹⁶ and on the application of this material in flow injection analysis with amperometric detection.³⁵ The use of ta-C electrodes in electroanalysis is a rather new area of research. There have been some recent studies reported^{36–40} but the original reports were from Miller and coworkers back in the 1990s.^{41,42}

These films are formed by filtered cathodic vacuum arc or laser arc plasma deposition. Tetrahedral amorphous carbon films can be deposited with a high portion of tetrahedrally-bonded sp³ carbon (~80% max.) and therefore, can exhibit high hardness (>70 GPa) and a wide band gap $(\sim 3.5 \text{ eV})$.⁴³⁻⁴⁵ Nitrogen can be incorporated into the films by deposition in the presence of a N₂ gas flow. The electrical resistivity decreases with increasing N incorporation due to increased formation of sp^2 carbon bonding. The hardness, band gap, and electrochemical properties of these coatings can be tailored by controlling the ratio of sp²-sp³ bonded carbon in the film.⁴³⁻⁴⁵ The ta-C:N electrodes investigated by our group so far had an sp³ carbon content of 40–60%; the balance being sp^2 carbon. Even with this level of sp^2 carbon, the films exhibit electrochemical properties that more closely resemble those of boron-doped diamond rather that glassy carbon¹⁶: microstructural stability, weak molecular adsorption, and good activity for several redox systems without conventional pretreatment. The electrochemical behavior of the ta-C:N films bear some similarities to the nanocarbon films reported on extensively by Niwa and co-workers.⁴⁶⁻⁴⁹ A motivation for studying the ta-C:N films is the fact that they can be deposited at or near room temperature on a wide variety of substrate materials.

We report herein on an investigation of the electrochemical properties of t*a*-C:N thin film electrodes, specifically the voltammetric background current as a function of scan rate and electrolyte composition, the voltammetric response of multiple redox systems spanning a 2 V potential window, and heterogeneous electron-transfer rate constants for these redox systems as determined from ΔE_p -v trends and digital simulation. Comparison data are reported for freshly polished glassy carbon (GC) and boron-doped diamond (BDD).

3.3. Results

3.3.1. Material Characterization

Figure 3.1A and B shows SEM images of a BDD and t*a*-C:N thin-film electrode, respectively. Inspection of multiple images revealed a continuous film coverage over the entire substrate. The polycrystalline BDD film consists of faceted and randomly oriented crystallites. Most of them are less than 1mm in dimension. The film was largely pin hole and defect free.

Figure 3.1B shows that the t*a*-C:N film consists of a nodular morphology overall with larger carbon clusters decorating the surface. The clusters are on the order of 50–100 nm in size. In prior work, we reported that the roughness of a film deposited with this level of N₂ in the source gas was 14 ± 3 nm (30 sccm N₂) recorded by AFM over a 3×3 mm² area.¹⁶ This represents the surface roughness between the larger clusters. Over larger areas, the true roughness of the film is greater than this due to the presence of the carbon clusters. Importantly, the overall roughness of the *ta*-C:N films increases with increasing nitrogen content.¹⁶ These cluster result in part from the formation of the charge carbon cluster in the Laser Arc pulses used to deposit these films. This system has no filtering to remove these large particles.



Figure 3.1. SEM images of (A) a boron-doped nanocrystalline diamond (BDD) film and (B) a nitrogen-incorporated tetrahedral amorphous carbon (t*a*-C:N) thin film. Notice the difference in scale bars on the two images: 1 μ m for BDD and 0.1 μ m for t*a*-C:N.

Figure 3.2 shows Raman spectra (visible excitation) for BDD (black) and t*a*-C:N (red) thin films. The spectrum for BDD consists of multiple peaks at 519, 1220, 1323, and 1496 cm⁻¹. These spectral features are consistent with those seen for nanocrystalline diamond films formed on quartz²⁰, and reflect a high boron-doping level.^{50,51} For heavily boron-doped films, the firstorder diamond phonon line shifts from 1332 cm⁻¹ to lower wavenumbers with increasing boron concentration. This shift is typically accompanied by increases in scattering intensity at ca. 500 and 1225 cm^{-1.50,51} In this spectrum, the diamond peak is shifted down to 1323 cm⁻¹ as a single fraction of the carbon atoms are bounded to the lighter boron atoms. There is also significant scattering intensity at 1220 cm⁻¹. The scattering at 519 cm⁻¹ is associated with the phonon mode of the crystalline Si substrate. However, this peak sits on a broader scattering peak centered around 500 cm⁻¹. Given that the intensity of the 500 cm⁻¹ band increases with boron-doping level, this peak has been assigned to the vibrational modes of boron dimers^{51–54} and pairs or clusters.⁵⁵



Figure 3.2. Visible micro-Raman spectra for a BDD thin-film (black) and a t*a*-C:N thin film (red). Integration time = 10 s. Excitation wavelength = 532 nm.

The 1220 cm⁻¹ peak has been assigned to defects in the diamond lattice brought about by the high boron doping, possibly boron–carbon complexes.^{50,51} Finally, the 1496 cm⁻¹ peak is presumed to be caused by some amorphous sp² carbon that becomes more prominent with increasing boron dopant incorporation.^{50,51} In other words, the addition of large amounts of boron is accompanied by increasing carbon graphitization in the grain boundaries. Even with the sp² carbon impurity, the electrochemistry of the BDD film is controlled by the "diamond" and not the sp² carbon, which is low in abundance. The spectral features of this film suggest the doping level on the order of 10^{21} cm⁻³.^{56,57}

The spectrum for the *ta*-C:N thin film is characterized by a broad asymmetric scattering profile between 1000 and 1700 cm⁻¹ with a single peak maximum at ca. 1510 cm⁻¹. Such a spectrum is typical for *ta*-C films.^{58,59} The peak becomes more asymmetric with increasing nitrogen incorporation as the scattering intensity near 1350 cm⁻¹ increases.¹⁶ This trend is indicative of an increasing fraction of sp²-bonded carbon. The Raman spectrum for amorphous carbons, like *ta*-C, is dominated by modes of the graphitic lattice; the so-called D and G modes.^{58,59} This domination is because of the sizably larger (230×) scattering cross-section coefficient for the sp²-bonded as compared to the sp³ carbon.^{58,59} The G mode for amorphous carbons arises from the bond stretching vibrations of pairs of sp² sites, and the D mode is due to the breathing mode of six-fold sp² rings.^{58,59}

To approximate the sp²/sp³ carbon ratio in the film, the spectrum was fit with two Gaussian peaks: the D-mode centered at 1351 cm⁻¹ and the G-mode at 1550 cm⁻¹. Robertson et al. reported that the I_D/I_G intensity ratio and the line width of G peak are good indicators of the t*a*:C film microstructure.^{58,59} Prior work showed that the I_D/I_G ratio increases with increasing N content. The

G-mode width decreases and the band position shifts to lower wave numbers with increasing N content. For the present film, the I_D/I_G ratio is 0.79 and the width of the G-band, W_G , is 176 cm⁻¹.

3.3.2. Background Cyclic Voltammetric Curves

Background cyclic voltammetric *i–E* curves for the three electrodes (GC, BDD, and ta-C:N) in 1 mol L⁻¹ KCl are presented in Fig. 3.3. The curve shapes for all three were unchanged with cycle number from 2 to 20. The current for BDD is approximately 7× lower than the current for GC and about 5× lower than the current for t*a*-C:N in this potential range. The lower background current for BDD, as compared to GC, is presumed due to a combination of (i) a slightly lower density of electronic states, and (ii) the absence of pseudocapacitive current associated with electroactive and or ionizable surface carbon-oxygen functionalities over this potential range. ^{60,61}



Figure 3.3. Background cyclic voltammetric *i*-*E* curves for GC, BDD and t*a*-C:N electrodes in 1 mol L^{-1} KCl. Scan rate = 0.1 V s⁻¹.

GC surface.^{60–62} The lower back ground current, especially for BDD, leads to increased signal-tobackground ratios in electroanalytical measurements. Generally, the background current for ta-C:N electrodes lies between that for GC and BDD with the magnitude depending on the level of sp² carbon in the film.¹⁶ The greater the sp² carbon content, the closer the background current is to that for GC for the same geometric area.



Figure 3.4. Background cyclic voltammetric *i*–*E* curves for (A) BDD, (B) ta-C:N, and (C) GC electrodes as a function of scan rate in 1 mol L^{-1} KCl. Scan rates of 0.1, 0.2, 0.3, 0.4, and 0.5 V s⁻¹ are shown.

Figure 3.4 A–C shows background cyclic voltammetric *i–E* curves recorded at different scan rates for (A) BDD, (B) *ta*-C:N, and (C) GC electrodes in 1 mol L⁻¹ KCl. Curves for scan rates from 0.1 to 0.5 V s⁻¹ are presented. The currents for all three electrodes increase with the scan rate over the potential range probed. For GC, there are oxidation and reduction waves centered at 0.2 V. These are associated with redox-active functional groups (quinone/hydroquinone) on the GC surface at the exposed edge plane sites.^{60–62} These redox-active functional groups are largely absent on the BDD and *ta*-C:N electrodes. For all the electrodes, the current at multiple potentials in the 0.1–0.5 V window increases proportionally with the scan rate. This is expected for capacitive current. For example, the positive current at 0.4V increases linearly with the scan rate for all the electrodes with linear regression correlation coefficients of 0.9994 for GC, 0.9999 for BDD, and 0.9989 for *ta*-C:N.

Further evidence for the current-scan rate linearity is presented in Fig. 3.5. The plots show the positive current measured at 0.2 V for each electrode versus the scan rate. The curves are linear



Figure 3.5. Cyclic voltammetric background current (positive or anodic) at 0.2 V as a function of the scan rate for BDD, ta-C:N, and GC electrodes in 1 mol L⁻¹ KCl.
consistent with the current being capacitive and not Faradaic in nature. The difference in slope is related to the difference in electrode capacitance. Log–log plots of the background current at this potential versus the scan rate were linear with a slope near 1 consistent with capacitive current.

The slope of the current-scan rate plots is related to the electrode capacitance, $C_{dl} = i_{ch}Av = slope \times A$. Calculating the capacitance from these plots assumes the background current is exclusively capacitive in nature. Based on the slopes of the plots in Figure 3.5, the electrode capacitance at 0.2 V was calculated for each electrode. The results are presented in Table 3.1. The low capacitance for BDD of 10 μ F cm⁻² is consistent with previous reports for this electrode.^{3,60,61,63} Therefore, CV is a reliable method for determining the capacitance of BDD electrodes in this potential range as the background current is purely capacitive. The capacitance for GC of 71 μ F cm⁻² is larger than what is typically observed for a clean and smooth electrode.⁶¹ The larger capacitance is likely due to the pseudocapacitance (*i.e.*, larger background current) arising from electroactive and ionizable surface carbonoxygen functionalities over the potential range probed. The capacitance for t*a*-C:N of 42 μ F cm⁻² is consistent with what we have previously reported.¹⁶ It should be noted that all capacitance values are normalized to the geometric and not the real surface area. This measurement was made on only one electrode of each material so a detailed statistical analysis is not possible.

Table 3.1. Slopes of background current (0.2 V) - scan rate plots and the calculated electrode capacitance for GC, BDD, and ta-CN electrodes in 1 mol L^{-1} KCl.

Electrode	Slope (A V ⁻¹ s)	Capacitance (F cm ⁻²)
GC	14.22	7.11×10^{-5}
BDD	1.98	$9.91 imes10^{-5}$
ta-C:N	8.36	$4.18 imes 10^{-5}$

3.3.3. Cyclic Voltammetric Curves for Different Redox Analytes

Cyclic voltammetric studies were performed using the following redox systems at all three electrodes: $Fe(CN)_6^{3-/4-}$, $IrCl_6^{2-/3-}$, $Ru(NH_3)_6^{3+/2+}$, methyl viologen, and ferrocene carboxylic acid (FCA). Figure 3.6 A–C shows cyclic voltammetric *i*–*E* curves for 0.1 mmol L⁻¹ Fe(CN)₆⁴⁻, in 1 mol L⁻¹ KCl recorded at (A) t*a*-C:N, (B) BDD, and (C) GC electrodes as a function of the scan



Figure 3.6. Cyclic voltammetric *i*–*E* curves for 0.1 mmol L⁻¹ Fe(CN) $_{6}^{3-/4-}$ in 1 mol L⁻¹ KCl at (A) t*a*-C:N, (B) BDD, and (C) GC electrodes at varying scan rates (0.1, 0.2, 0.3, 0.4, and 0.5 V s⁻¹). (D) Corresponding Randles–Sevcik plots of i_p^{ox} and i_p^{red} vs. $v^{1/2}$ calculated from *i*–*E* curves for each of the three electrodes. R² ≥ 0.99. No error bars are shown with the data in D.

rate. Well-defined, peak-shaped curves are seen with peak currents that increase with the scan rate. The curves reflect the chemically reversible redox reaction, $Fe(CN)_6^{4-} \leftrightarrow Fe(CN)_6^{3-} + e^-$. The peak potential separation, ΔE_p , ranges from 97 to 143 mV for t*a*-C:N, 70–85 mV for BDD, and 61–65 mV for GC. These trends indicate the electron-transfer kinetics are nearly reversible for GC and quasi-reversible for t*a*-C:N and BDD. Figure 3.6 D shows Randles–Sevcik plots of i_p (ox) and i_p (red) vs. scan rate^{1/2} for all three electrodes. For all three, the oxidation and reduction peak currents increase linearly with the scan rate^{1/2}. This indicates the redox reaction rate is limited by semi-infinite linear diffusion of the reactant to the electrode interface. Analysis of the slopes reveals similar value s for all three electrodes: 13.26 (t*a*-C:N), 12.90 (BDD), and 13.26 (GC) μ A $V^{-1/2} s^{1/2}$. From the slopes, the diffusion coefficient (D_{red}) was calculated to nominally be $6.1 \times 10^{-6} cm^2 s^{-1}$. This is close to the generally accepted value of $6.3 \times 10^{-6} cm^2 s^{-1}$.⁶⁴

Figure 3.7 shows comparison voltammmograms for 0.1 mmol L⁻¹ Ru(NH₃)₆³⁺ in 1 mol L⁻¹ KCl at (A) ta-C: N, (B) BDD, and (C) GC electrodes. Well defined reduction and oxidation peaks are seen for this redox system at all three electrodes. The curves reflect the chemically reversible redox reaction, Ru(NH₃)₆³⁺ + e⁻ \leftrightarrow Ru(NH₃)₆²⁺. Unlike the results for Fe(CN)₆^{3-/4-} the ΔE_p for all three electrodes ranges from 60 to 70 mV. The near-Nernstian response for all three electrodes indicates that the electron-transfer kinetics are equally as fast for this redox analyte. Figure 3.7 D shows that both the reduction and oxidation peak currents very linearly with the scan rate^{1/2}, consistent with a reaction rate control by semi-infinite linear diffusion. Analysis of the slopes of the plots reveals similar values for all three electrodes: 19.25 (ta-C:N), 20.47 (BDD), and 19.18 (GC) μ AV^{-1/2} s^{1/2}. From the slopes, the diffusion coefficient (D_{ox}) was calculated to nominally be 1.3×10^{-6} cm² s⁻¹. This value is a little lower than the reported value of 5.5×10^{-6} cm² s⁻¹ in pH 7

phosphate buffer.⁶⁵ D_{ox} was also found to be independent of the solution concentration in 1 mol L⁻¹, 1.27 (± 0.15) × 10⁻⁶ cm² s⁻¹.



Figure 3.7. Cyclic voltammetric *i*–*E* curves for 0.1 mmol L⁻¹ Ru(NH₃) $_{6}^{3+/2+}$ in 1 mol L⁻¹ KCl at (A) t*a*-C:N, (B) BDD, and (C) GC electrodes at varying scan rates (0.1, 0.2, 0.3, 0.4, and 0.5 V s⁻¹). (D) Corresponding Randles–Sevcik plots of i_p (ox) and i_p (red) vs. $v^{1/2}$ calculated from current–potential curves for each of the three electrodes. R² ≥ 0.99. No error bars are shown with the data in D.

Figure 3.8 shows cyclic voltammograms for all five redox systems tested at a t*a*-C:N thinfilm electrode. Chemically and electrochemically reversible responses were observed for all the redox systems, ΔE_p values of 59–65 mV at this scan rate, except for Fe(CN)₆^{3-/4-} which exhibited a ΔE_p of 95 mV. All redox analytes undergo a 1e⁻ redox reaction except for methyl viologen, which undergoes two 1-electron transfers (MV²⁺ \leftrightarrow MV⁺ and MV⁺ \leftrightarrow MV⁰). Clearly, the t*a*-C:N electrode is active for electron transfer over a wide potential range with relatively rapid kinetics for these redox systems.



Figure 3.8. Cyclic voltammetric *i*–*E* curves for 0.1 mM methyl viologen, Ru(NH₃) $_{6}^{3+/2+}$, Fe(CN) $_{6}^{3-/4-}$, FCA and IrCl $_{6}^{2-/3-}$, all in 1 mol L⁻¹ KCl, at a *ta*-C:N thin-film electrode. Scan rate = 0.1 V s⁻¹.

3.3.4. Heterogeneous Electron-Transfer Rate Constants

The heterogeneous electron-transfer rate constants were determined from the cyclic voltammetric ΔE_p -scan rate dependences⁶⁶ and digital simulation (DigiSim 3.1). As expected, both methods produced similar results. In order to use cyclic voltammetric data for rate constant determination, one has to verify that the voltammetric ΔE_p values are unaffected by ohmic or



Figure 3.9. Cyclic voltammetric i-E curves for (A) $Fe(CN)_6^{3-/4-}$ and (C) $Ru(NH_3)_6^{3+/2+}$, in 1 mol L⁻¹ KCl at a *ta*-C:N thin-film electrode as a function of the analyte concentration from 0.1 to 1 mmol L⁻¹. (B) Plots of i_p (ox) and i_p (red) as a function of the Fe(CN)₆⁴⁻ solution concentration. $R^2 \ge 0.99$. Scan rate = 0.1V s⁻¹.

uncompensated resistance effects, specifically resistance of the BDD or ta-C:N thin-film electrodes. To verify this, we measured cyclic voltammograms for 0.1 mM Fe(CN)₆⁴⁻ and Ru(NH₃)₆³⁺ as a function of the solution concentration from 0.1 to 1 mM. Figure 3.9 A and C shows the curves for Fe(CN)₆⁴⁻ and Ru(NH₃)₆³⁺, respectively, at a t*a*-C:N electrode. Identical behavior was seen for the BDD electrode (data not shown). The peak currents for both redox analytes increase with concentration. The linear relationship for the Fe(CN)₆^{3-/4-} couple is shown in Fig. 3.9 B. It is clear that the ΔE_p for both compounds is unchanged with concentration consistent with there being negligible ohmic effects arising mainly from resistance through the electrode. If ohmic effect had been contributing to the curve shapes, one would expect the ΔE_p values to increase with increasing concentration. This result confirms that the voltammetric data can be accurately used for rate constant calculations.

The voltammetric data were recorded in high supporting electrolyte concentration (1M KCl) to minimize any double layer effects on the rate constants. Table 3.2 provides a summary of the k^o values determined by digital simulation for all five redox analytes. It can be seen that the t*a*-C:N thin-film electrode supports rate constants for all four redox systems that are close to the values for BDD and GC. There are no statistically significant differences in the k^o values at the three electrodes for any of the redox system.

Data for methyl viologen are not presented due to the fact that the redox system behaved in an electrochemically reversible manner (fast ET) at the scan rates tested for all three electrodes. The lowest rate constant for all three electrodes is seen for $Fe(CN)_6^{3-/4-}$.

Heterogeneous electron-transfer rate constants (k^o) were also calculated from the $\Delta E_p - v$ relationships according to the following equation⁶⁶:

$$k^{0} = \psi \frac{\left[\pi D_{0x} \upsilon (nF/RT)\right]^{1/2}}{(D_{ox}/D_{red})^{\alpha/2}}$$
(3.1)

where D_{ox} and D_{red} are the diffusion coefficients of the oxidized and reduced species, respectively, v is the scan rate, n is the number of electrons transferred, R is the ideal gas constant, T is the Kelvin temperature, α is the transfer coefficient (assumed to be 0.5). The parameter ψ is the transfer parameter and is calculated from the $\Delta E_p - v$ data using equation 2.3. k^o values were calculated from voltammetric data at scan rates from 100 to 1000 mVs⁻¹. Similar values to those reported in Table 3.2 were calculated with a variability in the value at any scan rate of less than 7 % (RSD) for any electrode.

Figure 3.10 A and B shows examples of the fit between the simulated curves for a selected value of k^o and the experimental curves for 0.1 mmol L⁻¹ Fe(CN)₆⁴⁻ and (B) 0.1 mmol L⁻¹ Ru(NH₃)₆³⁺, both in 1 mol L⁻¹ KCl. It can be seen that there is excellent agreement between the simulated and experimental traces. The differences between the simulated and experimental currents at the tail end of each peak are due to inaccuracies in the simulated background current.

Redox system	Electrode	Rate constant (cm s^{-1})
	ta-C:N	$6.31 (\pm 0.81) \times 10^{-3}$
Fe(CN)6 ^{3-/4-}	BDD	$5.66(\pm 1.17) \times 10^{-3}$
	GC	$8.86 (\pm 1.24) \times 10^{-3}$
	ta-C:N	$1.28~(\pm 1.21) imes 10^{-1}$
Ru(NH ₃) ₆ ^{3+/2+}	BDD	$3.59~(\pm 0.96) imes 10^{-1}$
	GC	$1.27~(\pm 1.50) imes 10^{-1}$
	ta-C:N	$4.48~(\pm 0.42) \times 10^{-2}$
IrCl ₆ ^{2-/3-}	BDD	$2.39~(\pm 0.71) imes 10^{-1}$
	GC	$7.19(\pm 1.35) \times 10^{-2}$
	ta-C:N	$3.77 (\pm 1.82) \times 10^{-2}$
FCA	BDD	$7.82 (\pm 0.62) \times 10^{-2}$
	GC	$2.60 \ (\pm 1.21) imes 10^{-2}$

Table 3.2. Heterogeneous electron-transfer rate constants for different redox systems at t*a*-C:N, BDD, and GC electrodes.

Values reported as mean and standard deviation for n = 3 electrodes of each type



Figure 3.10. Experimental and digitally simulated cyclic voltammetric *i*–*E* curves for (A) 0.1 mmol L^{-1} Fe(CN) $_{6}^{3-/4-}$ and (B) 0.1 mmol L^{-1} Ru(NH₃) $_{6}^{3+/2+}$, both in 1 mol L^{-1} KCl. Scan rate = 0.1 V s⁻¹. The transfer coefficient, α , was assumed to be 0.5. n = 1 electron for both redox molecules.

3.3.5. Electrolyte Effects on the Heterogeneous Electron-Transfer Rate Constant

Preliminary experiments were performed to learn how the electrolyte type affects the background current and the k^o values for Fe(CN) $_6^{3-/4-}$ and Ru(NH₃) $_6^{3+/2+}$ at a t*a*-C:N electrode. Similar studies were performed with BDD and GC electrodes. Figure 3.11 A–C shows background cyclic voltammetric *i–E* curves for all three electrodes in 0.1 mol L⁻¹ solutions of LiCl, NaCl, KCl, and CsCl. Clearly, for BDD (Fig. 3.11 A), changing the cation has little effect on the background current at any of the potentials or the electrode capacitance. For the t*a*-C:N (Fig. 3.11 B) and the GC (Fig. 3.11 C) electrodes there is some variation on the background. current with electrolyte. Slightly larger background current is seen for KCl. For GC, there is also some slight variation in the background current with the largest current recorded in CsCl.

Figure 3.12 A and B shows cyclic voltammetric i-E curves for 0.1 mmol L⁻¹ Ru(NH₃)₆³⁺ and Fe(CN)₆⁴⁻ at a t*a*-C:N thin-film electrode as a function of the electrolyte composition. A nearly



Figure 3.11. Background cyclic voltammetric *i*–*E* curves for (A) BDD, (B) t*a*-C:N, (C) GC electrodes in 0.1 mol L⁻¹ LiCl, NaCl, KCl, and CsCl. Scan rate = 0.1 V s⁻¹. Geometric area =



Figure 3.12. Cyclic voltammetric *i*–*E* curves for (**A**) 0.1 mmol L^{-1} Ru(NH₃) $_{6}^{3+}$, and (**B**) 0.1 mmol L^{-1} Fe(CN) $_{6}^{4-}$ in 0.1 mol L^{-1} LiCl, NaCl, KCl, and CsCl at a *ta*-C:N thin-film electrode. Scan rate = 0.1 V s⁻¹. Geometric area = 0.2 cm².

electrochemically reversible or Nernstian response is seen for Ru(NH₃) $_{6}^{3+/2+}$ with a ΔE_p of 70mV and a formal potential, $E^{o'}$, of -0.145 V. Both are invariant with the electrolyte cation type. In contrast, significant changes in both ΔE_p and $E^{o'}$ are seen for the Fe(CN) $_{6}^{3-/4-}$ couple with cation type. A poorly defined curve is seen in LiCl. The peaks sharpen with an increasing peak current and decreasing ΔE_p when moving from NaCl to KCl. In KCl, the ΔE_p is 120mV and $E^{o'}$ is 0.230 V. A smaller ΔE_p of 100mV is seen in CsCl but $E^{o'}$ is shifted positive by 100 mV. There is clearly a strong effect of the cation on the redox chemistry of the Fe(CN) $_{6}^{3-/4-}$ couple at this electrode.

Figures 3.13 and 3.14, A and B, shows voltammetric data for BDD and GC, respectively, in the same electrolytes. For BDD, ΔE_p for Ru(NH₃) $e^{3+/2+}$ is about 70mV in all the electrolytes with an unchanging $E^{o'}$. Similar peak currents are seen in LiCl, NaCl, and CsCl but slightly larger peak currents are seen in KCl. ΔE_p is largely invariant with the cation type for Fe(CN) $e^{3-/4-}$. This is similar to previously reported results.⁶⁷ $E^{o'}$ is similar in all the electrolytes except CsCl for which there is a few tens of millivolt positive shift. For GC, both ΔE_p and $E^{o'}$ for Ru(NH₃) $e^{3+/2+}$ are invariant with the cation type. The peak currents are also similar in all the electrolytes. In contrast,



Figure 3.13. Cyclic voltammetric *i*–*E* curves for (**A**) 0.1 mmol L^{-1} Ru(NH₃)₆³⁺, and (**B**) 0.1 mmol L^{-1} Fe(CN)₆⁴⁻ in 0.1 mol L^{-1} LiCl, NaCl, KCl, and CsCl at a BDD thin-film electrode. Scan rate = 0.1 V s⁻¹. Geometric area = 0.2 cm².



Figure 3.14. Cyclic voltammetric *i*–*E* curves for (**A**) 0.1 mmol L^{-1} Ru(NH₃)₆^{3+,} and (**B**) 0.1 mmol L^{-1} Fe(CN)₆⁴⁻ in 0.1 mol L^{-1} LiCl, NaCl, KCl, and CsCl at a GC electrode. Scan rate = 0.1 V s⁻¹. Geometric area = 0.2 cm².

 ΔE_p for Fe(CN)₆^{3-/4-} decreases as one moves from LiCl to CsCl. There is also a slight positive shift in $E^{o'}$ in KCl as compared to the other electrolytes.

3.4. Discussion

The t*a*-C:N thin-film electrode is attractive for electroanalysis because of the lower background current and wider potential window, as compared to GC, the weak adsorption (resistance to fouling) that occurs on the surface, and the microstructural stability particularly at positive detection potentials.^{16,35} As more is learned about the basic electrochemical properties of this material and how to control them through manipulation of the growth conditions, a wide range of electroanalytical applications will emerge. Prior work showed that the magnitude of the background current scales with the sp² carbon content in the film, which is directly related to the amount of incorporated nitrogen.¹⁶ This prior work also revealed that the *ta*-C:N electrodes, even with sp² carbon levels of 40–60%, exhibit electrochemical properties more resembling those of BDD rather than GC. Background currents are low and stable even at potentials positive of 1V where GC undergoes microstructural alterations and surface oxidation, the electrochemical activity

for $Ru(NH_3)_6^{3+/2+}$ and $Fe(CN)_6^{3-/4-}$ is comparable to BDD and GC without conventional surface pretreatment, and there is little to no adsorption of methylene blue.¹⁶

The detailed electrochemical characterization of the t*a*-C:N thin-film electrode conducted in this work produced some interested findings on the material's electrochemical behavior. The results reveal that the background current for t*a*-C:N falls between that of GC and BDD, consistent with prior published work.¹⁶ The background current is stable with cycle number at potentials from -0.3 to 1.0 V vs. Ag/AgCl and is capacitive in nature for both t*a*-C:N and BDD.

The t*a*-C:N electrode capacitance of ~40 μ F cm⁻² is higher than the typical value for BDD of ~10 μ F cm⁻². More work is needed to evaluate the capacitance-potential trends for t*a*-C:N but one can infer at this point the larger capacitance is related to the greater level of sp² carbon (*i.e.*, higher potential-dependent electronic state density).¹⁶

The voltammetric results presented herein for the different redox systems reveal that the *ta*-C:N electrode supports relatively rapid rates of electron transfer over a wide potential range. The formal potentials of the redox systems used span about 2V. Recall that the cyclic voltammetric response for methyl viologen (data not shown) was electrochemically reversible at all the scan rates tested. Therefore, the electrode has a high density of electronic states (DOS) over this potential range, which supports rapid electron transfer. IrCl₆^{2-/3-}, Ru(NH₃)₆^{3+/2+}, FCA, and methyl viologen are all surface-insensitive redox probe molecules on GC and BDD ^{3,6–8,10,29–33} as well as *ta*-C:N. This means that the heterogeneous electron-transfer rate constant for these redox systems is most strongly affected by the DOS across the potential range and less so by surface microstructure or surface chemistry. The rate constant for Fe(CN)₆^{3-/4-} is approximately 10× lower than the rate constants for the other redox systems and it exhibits more sensitivity to the surface chemistry of *ta*-C:N electrodes. This is similar to what has been observed for BDD ^{3,29–32}.

The lower k^o for BDD and ta-C:N could be due in part to the presence of surface carbon-oxygen functionalities, which are known to inhibit electron transfer for this redox couple at BDD.²⁹

The preliminary voltammetric results for the electrolyte effects on $Fe(CN)_6^{3-/4-}$ electron transfer show that there is a strong cation electrolyte effect on the formal potential, $E^{o'}$, and electron transfer rate based on increases in ΔE_p , particularly for t*a*-C:N. There is no electrolyte cation effect for $Ru(NH_3)_6^{3+/2+}$ at any of the electrodes, as expected. The cation electrolyte effect for $Fe(CN)_6^{3-/4-}$ is much less at BDD and GC generally consistent with prior results.⁶⁷ The data suggest that there may be a significant difference in the organization of the electrolyte double layer at the *ta*-C:N electrode as compared to BDD and GC. It is difficult to infer much from these preliminary results but ΔE_p depended on the electrolyte cation type, decreasing in order of Li⁺ >Na⁺ >K⁺ >Cs⁺. This is attributed to the decrease in cation hydration sphere, as the cation size increases.⁶⁷

3.5. Conclusions

The following are the key findings from the work.

(1) The t*a*-C:N electrode exhibited a background voltammetric current that falls between than of GC and BDD for similar geometric areas.

(2) Normal capacitance values determined from voltammetric background currents were $10 \,\mu\text{F} \,\text{cm}^{-2}$ for BDD, $41 \,\mu\text{F} \,\text{cm}^{-2}$ for t*a*-C:N, and $71 \,\mu\text{F} \,\text{cm}^{-2}$ for GC at 0.2 V vs. Ag/AgCl. These values are normalized to the geometric area. More work is needed to evaluate the *C*_{dl}-*E* trends of this electrode in different media. The relatively high value for GC may be due to unaccounted for surface roughness or currents from surface faradaic processes such as redox-active carbon-oxygen functional groups.

(3) The t*a*-C:N electrode exhibited a high density of electronic states over a wide potential range based on the observation that the electrode supports rapid rates of electron transfer for four surface

insensitive redox systems (IrCl₆^{2-/3-}, FCA, Ru(NH₃)₆^{3+/2+}, and methyl viologen) with widely varying $E^{o'}$ values. k^{o} ranged from 3×10^{-2} to 1×10^{-1} cm s⁻¹ at t*a*-C:N. The rate constants are very similar to those found for BDD and freshly polished GC.

(4) Slightly slower electron-transfer kinetics were seen for the surface-sensitive $Fe(CN)_6^{3-/4-}$ at the t*a*-C:N electrode. k^o was 6×10^{-3} cm s⁻¹ with similar values observed at BDD and freshly polished GC.

(5) There was no significant effect of the electrolyte cation type on the voltammetric response $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ at any of the three electrodes based on similarities in ΔE_p , $E^{o'}$ and i_p .

(6) In contrast, significant effects were seen for $Fe(CN)_6^{3-/4-}$ particularly at t*a*-C:N. The voltammetric peaks sharpen with an increasing peak current and decreasing ΔE_p when moving from LiCl to NaCl to KCl. In KCl, the ΔE_p is 120 mV and $E^{o'}$ is 0.230 V. A smaller ΔE_p of 100 mV is seen in CsCl but $E^{o'}$ is shifted positive by 100 mV.

(7) ΔE_p for Fe(CN)₆^{3-/4-} at t*a*-C:N decreased in order of Li⁺ >Na⁺ >K⁺ >Cs⁺.

(8) The data suggest that there may be a significant difference in the electrolyte double layer structure at the *ta*-C:N electrode.

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CHAPTER 4. RAPID PREPARATION OF ROOM TEMPERATURE IONIC LIQUIDS WITH LOW WATER CONTENT AS CHARACTERIZED WITH A ta-C:N ELECTRODE

4.1. Abstract

Room temperature ionic liquids (RTILs) provide an ionic, solvent-free medium for electrochemical reactions. RTILs are appreciated for their many unique properties; nevertheless, it is precisely these qualities that can be very easily debased by water and organic impurities.¹ Water, as a major contaminant in hygroscopic RTILs, has a strong effect on the physical and electrochemical properties (*e.g.*, viscosity and dielectric constant, hence the background voltammetric current, diffusion coefficient of redox analytes and electron-transfer kinetics). In this work, a simple and relatively rapid purification process was investigated that involves sparging ultrahigh purity Ar through the RTIL while being heated at 70 °C (so-called sweeping). A more conventional vacuum drying method at 80 °C was used for comparison. The electrochemical properties of two RTILs, [BMIM][BF4] and [EMIM][BF4], were assessed voltammetrically using a nitrogen-incorporated tetrahedral amorphous carbon (t*a*-C:N) thin-film electrode. It was found that the found the sweeping purification method was superior to vacuum drying in terms of more timely and effective removal of water. In addition, we present for the first time some of the basic electrochemical properties of novel t*a*-C:N electrodes in contact with RTILs.

4.2. Introduction

Room temperature ionic liquids (RTILs) are pure salts with melting points near or below room temperature.^{2,3} Many ILs are composed of a bulky organic cation, like 1-ethyl-3- ethylimidazolium, and a smaller inorganic anion, such as tetrafluoroborate. Equal numbers of positive and negative ions are present so the whole liquid is electrically neutral. Importantly, there is no solvent so the interfacial structure of an RTIL at an electrified interface is expected to be quite distinct from that of a typical aqueous electrolyte solution. It is also likely that the interfacial structure will depend on the carbon electrode microstructure and surface chemistry.⁴ The conventional Gouy-Chapman-Stern model used to describe the electric double layer in aqueous or organic electrolytes probably does not represent the interfacial structure formed in an ionic liquid.⁵ In addition, the solution environment around a redox analyte will be different in an RTIL than in an aqueous electrolyte. How this environment affects electron-transfer kinetics and mechanisms at carbon electrodes is the focus of our ongoing research. RTIL properties useful for electrochemical applications include negligible vapor pressure, high thermal and chemical stability, moderate electrical conductivity, non-flammability and a wide working potential window or breakdown voltage. They are appreciated in many areas of chemistry and electrochemistry as a "green"^{6–8} recyclable alternative to traditional organic solvents for batteries^{9,10} and fuel cells.^{11,12}

Depending on the electrode and the RTIL, the electrochemical potential window or breakdown voltage can be on the order of 5–6 V.^{2,3,13,14} This is dependent on the purity of the RTIL because the nature and concentration of contaminants may significantly affect its physicochemical properties. The potential window is typically reduced by common impurities such as water, unreacted organic reagents from the synthesis and residual organic solvents. Redox processes will arise from dissolved gases such as oxygen or carbon dioxide.¹⁵ Water is typically the most abundant contaminant. Hydrophilic RTILs can absorb water as can hydrophobic ones.^{15,16} Water has a significant effect on the electrochemical properties of an RTIL by increasing the conductivity,^{2,3,15,17} decreasing the density¹⁸ and viscosity,^{1,2,14,19} and reducing the electrochemical potential window. ^{1,2,14,20}

The purification of RTILs involves the use of a sorbent material, such as activated carbon, alumina and silica that can be employed for the removal of organic impurities and water.¹⁵ The conventional method for removing traces of water is vacuum drying. This process often

requires lengthy times of 12 h or more and temperatures from 60 to 120 °C. However, this method of drying is not appropriate for many protic RTILs since the conjugated acid and base species may be volatile.¹⁵ The disadvantages of this drying method are the requirements for the vacuum heating apparatus and the lengthy time needed for adequate water removal (*i.e.*, slow diffusive transport of water out of the liquid due to the high viscosity). The time needed for vacuum purification will increase with the volume of RTIL. In addition, prolonged heating of some RTILs can cause degradation when the temperature is held at an elevated level for more than 10 h.²¹

We investigated the effectiveness of what we term a "sweeping method" for more rapid and complete water removing from an RTIL. This method, originally reported by Ren et al.,²² involves sparging the RTIL in the electrochemical cell with ultrahigh purity Ar while heating at 70 °C. We compared the performance of this method with conventional vacuum drying. The electrochemical properties of two RTILs, 1-ethyl-3-methylimidazolium tetrafluoroborate, [EMIM][BF₄], and 1-butyl-3-methylimidazolium tetrafluoroborate, [BMIM][BF₄], were investigated using a tetrahedral amorphous carbon (t*a*-C:N) electrode after the two purification processes. Specifically, we studied the effect of the water content on the cyclic voltammetric background current, the electrochemical potential window, and the cyclic voltammetric response for ferrocene carboxylic acid (FCA).

4.3. Results and Discussion

4.3.1. Background Current and Potential Window

All electrochemical measurement reported on in this chapter were made in a N₂-filled vinyl glove box (Coy Laboratories). Cyclic voltammetric curves for the *ta*-C:N electrode in contact with purified [EMIM][BF₄] are shown in Figure 4.1. Curves are shown for the RTIL purified by vacuum drying (dashed line) and the "sweeping" (solid line) method. On the positive-going sweep, a small anodic peak is seen at about 1.5 V. The peak has greater magnitude in the ionic liquid purified by vacuum drying. It is believed that this peak is associated with the oxidation of water and the larger current in the vacuum dried ionic liquid indicates a greater impurity level. There is also slightly greater current on the negative-going sweep for the RTIL purified by vacuum drying. Importantly, the working potential window at this electrode is approximately 6 V in [EMIM][BF₄]. This is significantly larger than the 3 V window typical for this electrode in H₂SO₄.²³ Nearly identical



Figure 4.1. Background cyclic voltammetric i-E curves for a t*a*-C:N electrode in [EMIM][BF₄] (A) after vacuum drying (dashed) and the "sweeping" (solid) purification procedure. The effect of intentional water contamination (10 wt. % = 10 ppt added) is also shown (dotted line). The background voltammetric curves shown in (B) are for [EMIM][BF₄] purified by the "sweeping" method with scans recorded over a narrow (solid line) and wide potential range (dashed line). Scan rate = 0.1 V s⁻¹. Geometric area = 0.2 cm².

background current magnitudes and working potential windows were observed in [BMIM][BF4] (curves not shown). The background current in both ionic liquids in the 0-1 V range increased proportionally with the scan rate. This indicates the current at these potentials is capacitive in nature. The difference in water contamination in the two RTILs does not have a significant impact on the background current level or the working potential window. TGA results revealed an estimated water concentration at or below 10 ppm after the "sweeping" method (see Fig. 4.4 A below). The water concentration was determined from the mass change of the ionic liquid during heating from 30 to 325 K at 5 K min⁻¹ with the assumption that the mass loss is due to water removal. After purification by the "sweeping" method, no mass change was observed during TGA analysis at least to the 0.001 wt. % (10 ppm) level, which is the lower limit measurable with the instrument. In some cases, TGA measurements of the [EMIM][BF4] revealed a mass change as high as 0.1–0.2 wt. % after vacuum drying, ca. 1000 ppm. In the example shown in Figure 4.1 A, the water oxidation peak current for the vacuum dried RTIL is ca. 2 times greater than the current for the ionic liquid after purifying by the sweeping method. This would make the estimated concentration about 20 ppm or so.

In order to understand how water contamination affects the voltammetric curve shape, the purified [EMIM][BF₄] (sweeping method) was spiked with a large amount of water (10 wt. % or 10 ppt). The resulting curve is shown in Figure 4.1 A (dotted line). Clearly, water has a significant effect on the curve shape by causing an increase in the background current (*e.g.*, increased dielectric constant of the RTIL so increased capacitive current) and a reduced working potential window (*e.g.*, breakdown of water).

An advantage of the "sweeping" purification method is the lower water level that can be achieved, as compared to the vacuum drying method. Another advantage is the short treatment time, 50 min vs. multiple hours or days. Finally, the sweeping method is easily performed directly in the electrochemical cell prior to a measurement, which eliminates the possibility of water contamination during the transfer of the RTIL from the vacuum apparatus to the glove box.

A rather unexpected result is presented in Figure 4.1 B. Cyclic voltammetric *i*-*E* curves are shown for [EMIM][BF₄], purified by the "sweeping" method, recorded over a narrow and a wide potential range. Similar behavior was seen for [BMIM][BF4] (data not shown). When scanning from 0 to 1.2 V, the curve exhibited a relatively low and constant background current. However, when the potential range was expanded to the full 6 V window, the small anodic peak due to water oxidation was detected at 1.5 V. Most importantly though, the background current in the 0 to 1.2 V range increased by a factor of ~ 3 . When the scan range was reduced back to the 0 to 1.2 V limits, the original low background current was re-established. This indicates the increased background current is not due to some change in the electrode microstructure brought about by the high positive potentials. The calculated capacitance (C_{dl}) of the ta-C:N electrode at 0.4 V, assuming the voltammetric current is capacitive, was 13 and 11 μ F cm⁻² for [EMIM][BF₄] when purified by the vacuum drying and sweeping method, respectively. Again, the differences in water level in the two ionic liquids had little effect on the background current magnitude. However, when the scan range was increased to the 6 V window, the calculated capacitance increased by 3 times to 33 μ F cm⁻². Additional work is needed to better understand this unusual effect which typically is not seen in aqueous electrolytes.

4.3.2. Effect of Water on the Voltammetric Response for FCA

As shown above, water contamination tends to increase the voltammetric background current and reduce the working potential window in the RTIL. Water affects the RTIL's physical properties by lowering of the viscosity, which results in an increase in the diffusion coefficient of a dissolved redox analyte.^{2,3,15} This is apparent when considering the Stokes – Einstein equation:²⁴

$$D = \frac{k_B T}{6\pi a\eta} \tag{4.1}$$

The RTIL viscosity, η , is typically 10–100 times greater than water. [BMIM][BF4] has a reported viscosity of 112 mPa s.²⁴ The viscosity of [EMIM][BF4] is lower with a value of 37 mPa s. Figure 4.2 A presents cyclic voltammograms for ferrocene carboxylic acid (FCA) dissolved in [EMIM][BF4] that was purified by vacuum drying (dotted line) and the "sweeping" (solid line) method. In contrast to the background voltammetric response, the difference in water level after the two purification methods has a more profound effect on the response for this redox system.



Figure 4.2. Cyclic voltammetric i-E curves for a 0.5 mM ferrocene carboxylic acid (FCA) in [EMIM][BF₄] at a t*a*-C:N electrode after (A) employing the vacuum drying (dotted) and sweeping (solid line) purification methods. (B) demonstrating the effect of air humidity on the electrochemical behavior.

The peak potential separation, $\Delta E_{\rm p}$, is 121 mV at this scan rate and the diffusion coefficient, $D_{\rm ox}$, calculated using the Randles-Sevcik equation based on the measured oxidation peak current was 6.03×10^{-7} cm² s⁻¹ in the ionic liquid after vacuum drying. As seen, the oxidation peak current is ca. 7 µA. In contrast, a larger peak splitting and lower oxidation peak current are seen for FCA recorded in [EMIM][BF₄] after the "sweeping" purification (Fig. 4.2 A). ΔE_p increased to 173 mV, which reflects more sluggish electron-transfer kinetics, and the peak current decreased to *ca.* 4 μ A. The calculated diffusion coefficient decreased to 1.08×10^{-7} cm² s⁻¹. This value is close to the value, 2.55×10^{-7} cm² s⁻¹, reported for the same redox system in (EMIM)(NTf₂).²⁵ The more viscous medium not only lowers the diffusion coefficient but it also reduces the electron-transfer kinetics. Tachikawa et al.²⁶ have shown that a linear relationship exists between the heterogeneous electron-transfer rate constant and η^{-1} . The reason for the more sluggish kinetics is that the nuclear frequency factor, v_n , which is the effective frequency of passing through the transition state, decreases with increasing viscosity of the solution medium.²⁶ Although not presented herein, similar results were obtained for [BMIM][BF4] after vacuum drying and the "sweeping" purification. To assess how long the purified ionic liquid can be used outside of the controlled environment of the nitrogen-purged dry box, cyclic voltammograms for 0.5 mM FCA in [EMIM][BF4] purified by the "sweeping" method were recorded as a function of time during exposure to the laboratory air. Representative curves are shown in Figure 4.2 B. With increasing time and presumably greater water uptake, ΔE_p progressively decreases from the initial 170 mV value and the peak currents progressively increase. After 2h, ΔE_p decreased to 82 mV and, based on the peak current magnitude, the diffusion coefficient, $D_{\rm ox}$, increased to 3.73×10^{-7} cm² s⁻¹. After 12h, ΔE_p decreased to 82 mV and D_{ox} increased to 6.21×10^{-7} cm² s⁻¹. Similar behavior was observed when purified $[BMIM][BF_4]$ was used. The uptake of moisture is remarkably rapid. After the 12h period, the electrochemical behavior of FCA in [EMIM][BF4] approaches the behavior seen in an aqueous electrolyte such as 1M KCl, $\Delta E_p \approx 62$ mV and $D_{ox} = 2.17 \times 10^{-7}$ cm² s⁻¹. These results further confirm what has been reported in the literature that the preparation, storage and measurement environment for ionic liquid has a significant effect on the measured electrochemical response.^{2,3,24}

4.3.3. Effect of Water on the Background Voltammetric Response

In Figure 4.1, the difference in water contamination of [EMIM][BF₄] after vacuum drying and the "sweeping" method did not significantly affect the voltammetric background current or the working potential window. Experiments were performed to see how rapidly the background voltammetric current and working potential window change upon exposure of the purified RTIL to the laboratory air. Figure 4.3 shows curves for [EMIM][BF₄] at a t*a*-C:N electrode during a 1h exposure to the laboratory air. It can be seen that the water concentration, and presumably



Figure 4.3. Background cyclic voltammetric i-E curves for a t*a*-C:N electrode in [EMIM][BF₄] purified by the "sweeping" method at different times during exposure to the laboratory air. Scan rate = 0.1 V s^{-1} . Geometric area = 0.2 cm^2 .

dissolved oxygen, increased progressively with time. The background voltammetric current increased and the working potential window decreases with increasing water contamination during the exposure period. The water oxidation peak at ~1.5 V increased proportionally with the exposure time. The increasing cathodic current negative of -2 V is likely due to the reduction of dissolved oxygen. These results clearly show that water contamination can occur quickly with some of the RTILs so care should be taken when working with these outside of the controlled environment of the dry box. Figure 4.4 A shows a mass change versus temperature profile for [EMIM][BF₄] purified by the "sweeping" method recorded during a thermogravimetric analysis. Up to 250 °C, no significant mass change was seen consistent with low water and volatile contaminant levels.

The lower limit of mass change observable with the instrument is 0.01% so this corresponds to 100 ppm. Therefore, the TGA analysis is consistent with a water content \leq 100 ppm. Figure 4.4 B shows an FTIR transmission spectrum for the purified [EMIM][BF₄].^{27,28} The peaks between



Figure 4.4. (A) TGA mass change versus temperature profile during the heating of $[EMIM][BF_4]$ purified by the "sweeping" method. (B) FTIR transmission spectrum for the purified ionic liquid.

2800–3000 cm⁻¹ originate from the ethyl side chain (*i.e.*, the butyl side chain of BMIM) attached to the imidazolium ring. These peaks are attributed to symmetric and asymmetric stretches of sp³-bonded CH₂ and CH₃ groups. The peaks above 3000 cm⁻¹ arise from sp²-bonded C-H modes of the imidazolium ring. The prominent peak at 1570 cm⁻¹ is attributed to the C-C stretch of the imidazolium ring. The intense peak centered at 1160 cm⁻¹ arises from the C-N stretch. Finally, the two peaks at 750 and 850 cm⁻¹ are attributed to B-F stretches of the anion. These spectral features reflect the purity of the [EMIM][BF₄] as no peaks are present characteristic of impurities. Very weak intensity near 3300 cm⁻¹ is evident (O-H stretch) due to the low level of water.

4.4. Conclusion

We demonstrated that a "sweeping" method is more effective than conventional vacuum drying for rapidly removing of water contamination from room temperature ionic liquids. The purification can be performed directly in the electrochemical cell. The following conclusions were reached:

1. The "sweeping" method removes water contaminant from [EMIM][BF₄] and [BMIM][BF₄] more rapidly and effectively than does vacuum drying. Water levels were reduced to \leq 100 ppm after a 50 min heating of the RTIL in the electrochemical cell while purging with ultrahigh purity Ar.²⁰

2. The *ta*-C:N thin-film electrode exhibits a working potential window of 6V in both purified RTILs, and a low and stable background current between the potential limits. The background current within the window appears capacitive in nature.

3. The higher water level in the RTILs after vacuum drying estimated to be on the order of 100–500 ppm, as compared to the lower level after the "sweeping" method, had little effect on the

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background voltammetric current and the working potential window of the t*a*-C:N thin-film electrode.

4. The difference in water level did have a more profound effect on the voltammetric response for FCA. In the RTIL with the higher water content, Ep was smaller, reflective of more rapid electron transfer kinetics, and the oxidation peak current was greater due to the larger diffusion coefficient.
5. Both purified RTILs pick up water rapidly during exposure to the laboratory air and this impacts the voltammetric response for FCA as well the background current magnitude and working potential window. The water levels during this exposure apparently exceed the level after the vacuum drying.

6. Great care should be taken when working with RTILs outside of a controlled environment as the uptake of water can have a significant impact on the mass transport and electron transfer for soluble redox systems and on the voltammetric background current.

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CHAPTER 5. TEMPERATURE DEPENDENCE OF THE HETEROGENEOUS ELECTRON-TRANSFER RATE CONSTANT AND DIFFUSION COEFFICIENT FOR FERROCENE CARBOXYLIC ACID

5.1. Abstract

The apparent heterogeneous electron-transfer rate constant (k^{o}_{app}) for ferrocene carboxylic acid (FCA \rightleftharpoons FCA⁺ + e⁻) in two ionic liquids, (1-ethyl-3-methylimidazolium tetrafluoroborate [EMIM][BF₄] and 1-butyl-3-methylimidazolium tetrafluoroborate [BMIM][BF₄]), was measured at boron-doped diamond (BDD), and nitrogen-incorporated tetrahedral carbon thin-film (ta-C:N) electrodes as a function of temperature from 298-338 K. Comparison measurements were made using glassy carbon (GC). The goal was to learn how the microstructure of the different carbon electrodes influences capacitance and electron transfer in RTILs. Capacitance-potential curves were recorded in the two RTILs at room temperature. The capacitance magnitudes for BDD and ta-C:N ranged from 5-12 μ F cm⁻² in both RTILs. Cyclic voltammetric measurements were made as a function of scan rate and temperature using 0.5 mmol L⁻¹ FCA. The results demonstrate that both the carbon electrode microstructure and the RTIL's physical properties have an effect on the electron-transfer kinetics for this traditionally-viewed, surface-insensitive redox system. Both D (~10⁻⁷ cm²/s) and k^{o}_{app} (10⁻³-10⁻⁴ cm s⁻¹) increase with increasing temperature. The temperature dependences of k^0 , the activation energy, E_a , and the diffusion coefficient, D, were studied. In both RTILs, the largest k^o and smallest E_a values were found for BDD followed by ta-C:N and GC. k^{o}_{app} was ~2-3x larger and E_a was 2-3x lower in the less viscous [EMIM][BF₄] (6-14 kJ mol⁻¹) than in [BMIM][BF₄] (16-28 kJ mol⁻¹) at all three electrodes.

5.2. Introduction

Carbon electrodes, specifically sp²-bonded materials (HOPG, glassy carbon, carbon fibers nanotubes and more recently graphene), are used extensively in electroanalysis, electrochemical

energy storage and conversion, and electrosynthesis.^{1–5} There are a number of reasons for this including the materials' relatively low cost, wide usable potential range, rich surface chemistry, chemical inertness, and compatibility with a variety of solvents and electrolytes. A challenge with optimally using carbon electrodes is understanding and controlling the variables that impact heterogeneous electron-transfer kinetics at these materials. Variations in the carbon material type and the surface pretreatment protocol can cause significant changes in rate constant for a given redox system, often by multiple orders of magnitude.^{6–11} It is well established that electron-transfer rate constants for surface-sensitive redox systems in aqueous media are differentially influenced by the carbon electrode surface cleanliness, microstructure and chemistry. ^{6–11}

The electrochemical behavior of sp² carbon electrodes in aqueous electrolytes (*e.g.*, electron-transfer kinetics, capacitance, adsorption) very much depends on the surface microstructure of the carbon and the method of pretreatment. ^{6–11} Surface pretreatment is virtually always necessary to activate a carbon electrode prior to use in an electroanalytical measurement. A variety of pretreatments have been investigated over the years including ultraclean polishing,¹² electrochemical polarization,¹³ vacuum heat treatment,¹⁴ solvent cleaning,¹⁵ and laser exposure.¹⁶ These pretreatments alter surface cleanliness, surface microstructure and surface chemistry, and therefore affect capacitance, molecular adsorption and electron-transfer kinetics. The challenge is that the extent to which any or all these key variables are affected depends on the carbon type and the pretreatment method used. Stated another way, the same pretreatment applied to distinct carbon materials will produce differences in surface cleanliness, microstructure and chemistry. It remains to be determined if the same structure-function relationships hold in room temperature ionic liquids (RTILs). This was the focus of the work reported on in this chapter.

A major amount of what is known about sp^2 carbon electrode structure-function relationships in aqueous electrolytes has come from work by the McCreery group.^{1,5–11,15,16} Their efforts over the years have focused on well characterized HOPG, glassy carbon and pyrolyzed photoresist electrodes.^{1,5–11,15–17} Recent work with e-beam deposited carbon has shown that it is also a viable electrode material.^{18,19} Key findings include: (i) rate constants for some redox systems (e.g., $Ru(NH_3)_6^{+3/+2}$ and $IrCl_6^{2-/3-}$) are relatively insensitive to surface cleanliness and adsorbed monolayers, while the rate constants for others (e.g., $Fe(CN)_6^{3-/4-}$ and O_2) are very sensitive to the surface condition of the surface, (ii) the exposed electrode microstructure can have a significant effect on rate constants for electron transfer, capacitance and molecular adsorption with the basal plane of HOPG supporting much slower electron transfer, lower capacitance and weaker adsorption than glassy carbon, which has a relatively high fraction of exposed edge plane $(e.g., Fe(CN)_6^{3-/4-})$, ascorbic acid and catecholamines), and (iii) rate constants for some redox systems are very sensitive to the presence of surface oxides (e.g., $Fe^{+3/+2}$ and $V^{+3/+2}$). The potentialdependent density of electronic states (DOS) of the elecrode influences all redox reactions. A lower DOS correlates with lower k^o values. If properly activated and kept clean, sp² carbon electrodes can exhibit k^o values >10 cm s⁻¹ for some redox systems.^{19,20}

Over the past 20 years, boron-doped diamond (BDD) has been studied as an electrochemical electrode.^{21–26} BDD is quite attractive for electroanalytical measurements because of the (i) wide working potential window in aqueous electrolytes ($\geq 3V$), (ii) relatively rapid electron-transfer kinetics for some aqueous redox systems ($10^{-2} - 10^{-1}$ cm s⁻¹) without conventional surface pretreatment, (iii) superb microstructural stability, (iv) a rich surface chemistry (its carbon!) and (v) resistance to the adsorption of polar molecules. The negligible adsorption is both good and bad. This property allows the electrode to be used stably in complex environments

with minimal fouling.²⁶ This property also means that redox reactions proceeding through a surface confined state will be kinetically sluggish (*e.g.*, catecholamines).^{24,25} Our group has been actively involved over the years in studying structure-function relationships of boron-doped microcrystalline, nanocrystalline and ultrananocrystalline diamond thin films. Factors known to influence the electron-transfer kinetics at BDD electrodes in aqueous and organic solvent/electrolyte systems include the (i) boron-doping level, (ii) sub-surface H content, and (iii) surface chemistry (H vs. O termination). ^{21–30}

Another type of carbon electrode that shows promise in electroanalysis is nitrogenincorporated tetrahedral amorphous carbon (ta-C:N).^{31,32} Thin-film ta-C:N is diamond-like and consists of a mixture of sp^2 and sp^3 -bonded carbon. The hardness, optical properties and electronic structure can be tailored from those of graphite to diamond by controlling the ratio of non-diamond (sp²) to diamond (sp³) carbon atom bonding as well as the hydrogen content in the film. Depending on the deposition method, ta-C films can have high hardness (~70 GPa), a wide bandgap (~3.5 eV) and a high proportion of sp³-bonded carbon (~80% max.).^{33–43} There is always some residual sp²bonded carbon in ta-C. This is important because this carbon increases the π states in the bandgap which increases the electrical conductivity of the material.^{35,37,41–43} In other words, increasing the sp^2 carbon content in ta-C films increases the electrical conductivity. The sp^3 hybridized atoms form a random network in which neighboring atoms are connected by strong σ bonds.³⁶ An sp³ site forms tetrahedral σ bonds with four adjacent atoms. This gives the material its "diamond" character.³⁷ An sp² site forms trigonal σ bonds with three neighboring atoms in a plane and a weaker π bond normal to the plane. Factors affecting electron transfer at these carbons have not yet been fully elucidated.

The electronic properties of thin-film t*a*-C can also be altered by impurity incorporation. Nitrogen is a common impurity incorporated during the film deposition. The incorporation of N by adding N₂ gas flow during deposition can have at least two effects. First, adding the element dopes the film making it an *n*-type semiconductor.^{35,41–43} Second, adding the element can increase the amount of sp²-bonded carbon in the film, which adds π electronic states in the bandgap.^{35,41–43} Hence, nitrogen incorporation also alters the electronic properties of t*a*-C (*i.e.*, increases the electrical conductivity).

The electrochemical behavior of these two sp^3 carbon electrodes has not been extensively investigated in room temperature ionic liquids (RTILs).^{44–48} RTILs are finding ever increasing use in batteries and capacitors, fuel cells, separations, electrodeposition of metals with very negative standard reduction potentials (below the water decomposition potential), solar cells, electrochemical sensors and tribology.⁴⁹⁻⁵⁵ RTILs exhibit behavior that is very distinct from common molecular liquids as they are composed entirely of charged species (large organic cation and smaller inorganic anion) solvent. Two limitations with their use, particularly in electrochemical studies of electron-transfer and mass-transport processes, are their high viscosity (ca. 100x greater than H₂O) and the presence of impurities, such as water or reagents used in their synthesis. Water is particularly problematic in the more hydroscopic RTILs as this impurity causes increased voltammetric background current, a reduced potential window, and a redox peak in the 1-1.5 V vs. Ag QRE region if the concentration is in the 100's of ppm.⁴⁵ The high viscosity of RTILs is caused primarily by the large organic cationic size and strong inter-ionic van der Waals interactions between the cations and anions. The high viscosity suppresses diffusional mass transport and slows heterogeneous electron-transfer with an electrode.

We report herein on the temperature dependence of the heterogeneous electron-transfer rate constant and diffusion coefficient for ferrocene carboxylic acid (FCA) in two different RTILs, 1-ethyl-3-methylimidazolium tetrafluoroborate [EMIM][BF4] and 1-butyl-3-methylimidazolium tetrafluoroborate [BMIM][BF4], at sp³ carbon electrodes of distinct microstructure. These two RTILs have a common anion, a different organic cation structure and similar electrical conductivity and density. A significant difference is the higher viscosity of [BMIM][BF4] compared to [EMIM][BF4]. FCA was selected because its surface insensitive at sp² carbon and metal electrodes and its ability to undergo heterogeneous electron transfer in RTILs. The use of charged redox systems (e.g., $Fe(CN)_6^{3-/4-}$) to probe electrode activity is problematic because of either poor solubility in RTILs and or electrochemical inactivity presumably due to large activation barriers. Cyclic voltammetric measurements were performed at temperatures from 298-338 K (25-65 °C) using boron-doped nanocrystalline diamond (BDD) and nitrogen-incorporated tetrahedral amorphous carbon (ta-C:N) thin-film electrodes with glassy carbon (GC) used for comparison. Rate constants were determined from both cyclic voltammetric vs. scan rate (ΔE_p -v) trends and digital simulation using DigiSim[®] 3.30. Activation energies (E_a) of electron transfer were determined from the temperature dependence of the rate constants. The temperature dependence of the FCA coefficient was also investigated. Both k^{o} and D increase with increasing temperature, and k^o and E_a depend on the sp³ carbon electrode microstructure in both RTILs.

5.3. Results and Discussion

5.3.1. Background Current Capacitance

Table 5.1 provides a comparison of the room temperature viscosity, dielectric constant, density and electrical conductivity reported for the two ionic liquids. [BMIM][BF₄] is about $3 \times$ more viscous than [EMIM][BF₄] and both are $30 - 100 \times$ more viscous than water. The dielectric constants are essentially the same for the two ionic liquids, and both are $5 \times$ lower than water. Both RTILs are slightly more dense than water and both are significantly more electrically conducting than deionized water. The conductivity of [EMIM][BF₄] is 4-5× greater than the conductivity of [BMIM][BF₄] due to the higher mobility of the smaller [EMIM] cation. The total concentration of both RTILs is ~6 mol L⁻¹.

Background cyclic voltammetric *i*–*E* curves (~25 °C) for GC, BDD and t*a*-C:N in purified (A) [BMIM][BF4] and (B) [EMIM][BF4] are presented in Figure 5.1. All three electrodes exhibit a potential window of *ca*. 6 V in both RTILs using limits of \pm 40 µA cm⁻². This means that extreme positive and negative potentials are required to breakdown down the RTIL. Similarly wide potential windows have been reported previously for BDD electrodes in RTILs.^{44–48} The breakdown products of the RTILs at the two potential extremes are unknown. Fabiánska et al. examined the electrooxidation of various imidazolium ionic liquids in aqueous electrolyte solutions and found that OH• radicals generated presumably from water impurity introduce oxygen functional groups into the imidazolium ring.⁵⁶ The wide window is also qualitative evidence that

Analyte	Viscosity (η) (mPa s)	Dielectric Constant (ɛ)	Density (g cm ⁻³)	Conductivity (S m ⁻¹)	Reference
Water	1	80.4	1.00	<10-6	
[EMIM][BF4]	38	12.9	1.28	1.38 - 1.58	53,54
[BMIM][BF4]	112	11.7	1.26	0.35	53,54

Table 5.1. Physical property data for the ionic liquids at 298 K (25 °C).

the RTIL possesses relatively low water content.^{45,57} The actual water content in these particular purified RTILs was not measured, although measurements of other selected RTIL samples after the sparging pretreatment revealed levels below 100 ppm. As the water contaminant level



Figure 5.1. Background cyclic voltammetric i-E curves for GC (red), BDD (black) and ta-C:N (blue) electrodes in (A) [BMIM][BF₄] and (B) [EMIM][BF₄]. Scan rate 0.1 V s⁻¹. Geometric area for all three electrodes = 0.2 cm².

increases, the voltammetric background current increases and the potential window decreases.^{45,57} What is most interesting about these data is the fact that all three carbon electrodes exhibit similar potential windows in the RTILs. This is noteworthy because their windows in aqueous electrolytes are quite distinct. For example, the working potential window for BDD and t*a*-C:N is \geq 3V in 0.5 M H₂SO₄, while the window for GC is < 2 V.^{21–26,58,59}

The background current in these two RTILs between the potential limits scales as follows: GC > ta-C:N > BDD. For example in [BMIM][BF4] at 0 V, the background current for GC is 2.8 μ A, for ta-C:N is 1.2 μ A, and for BDD is 0.6 μ A. The small peak seen for BDD and ta-C:N on the positive-going scan between 1 and 2 V is believed due to the oxidation of some residual water.^{45,57}This peak is not seen with GC because it is masked by a large background current. In principle, this peak could be used to quantify the water level in an RTIL and the BDD and ta-C:N electrodes could be quite useful for this purity check.^{45,57}The small peak seen for BDD and ta-C:N on the negative-going scan between -1 and -3 V is presumed due to the reduction of residual dissolved oxygen. Again, the peak is not seen with GC because of the large background current. The current traces for all the electrodes were stable with cycle number and generally reached an unchanging shape after the third scan.

Background cyclic voltammetric curves were recorded as a function of the scan rate in both RTILs over a narrow potential range between -0.5 to 0.5 V vs. Ag QRE. Figure 5.2 shows plots of the current at 0.4 V versus the scan rate for all three electrodes in the two different RTILs. Even with the increased viscosity of the RTILs, the background voltammetric current at multiple potentials, including 0.4 V, increased linearly ($R^2 > 0.997$) with the scan rate from 0.1 to 0.5 V s⁻¹. This trend is consistent with the current being capacitive in nature. The slope of the plots, which is related to C_{dl} , decreases in the following order: GC > ta-C:N > BDD in both RTILs.



Figure 5.2. Background cyclic voltammetric i-E curves for GC, BDD and ta-C:N electrodes in (A) [BMIM][BF4] and (B) [EMIM][BF4]. i_{meas} at 0.4 V. Scan rate = 0.1 V s⁻¹. Geometric area = 0.2 cm².

This is the same trend that is seen in aqueous electrolyte solutions and is attributed to slight differences in the electronic properties of each electrode.^{21–26,58,59} In other words, the slightly lower density of potential-dependent electronic states in *ta*-C:N and BDD leads to less excess surface charge at a given potential and therefore less counterbalancing charge on the solution side of the interface. This results in lower currents as compared to that measured for GC. The voltammetric background current for GC in aqueous electrolytes can also include a contribution from redoxactive surface carbon-oxygen functional groups that terminate the exposed graphitic edge plane sites.^{60,61} The redox activity of these surface functional groups in RTILs remains unclear. These functional groups (quinone-hydroquinone) are expected to be greater in coverage on GC than on *ta*-C:N or BDD, especially after polishing the former in air as part of the activation protocol. Very similar *C*_{dl} values were calculated from the voltammetric data for both *ta*-C:N and BDD in the two RTILs (6-12 μ F cm⁻²).

5.3.2. Cyclic Voltammetric Studies of FCA as a Function of Temperature

Representative cyclic voltammetric *i-E* curves for FCA in [BMIM][BF4] at a t*a*-C:N electrode are shown in Figure 5.3 A. Curves are presented for different scan rates between 0.1 and 0.5 V s⁻¹ at 338 K (65 °C). Well-defined curves are observed at all the scan rates with anodic and cathodic peak potentials near 0.465 and 0.295 V, respectively. ΔE_p is 170 mV and E^{o^*} is 0.380 V (vs. Ag QRE) for the curve recorded at 0.1 V s⁻¹. The anodic $(i_p{}^a)$ and cathodic $(i_p{}^c)$ peak current ratio is slightly greater than one $(i^a{}_p/i^c{}_p > 1)$ at all of the scan rates due to the lower diffusion coefficient of FCA⁺, as compared to FCA, in the highly charged RTIL. The oxidation peak is also sharper than the reduction peak, qualitatively consistent with a transfer coefficient, α , being less than 0.5. The curves presented are the fifth scan at each scan rate and they were generally unchanging in shape after the third scan. Similar trends were observed for FCA in [EMIM][BF4] at this electrode (data not shown).



Figure 5.3. (A) Cyclic voltammetric *i-E* curves for a ta-C:N electrode showing the effect of scan rate on the response of 0.5 mmol L⁻¹ FCA in [BMIM][BF4] at 338 K. Curves were recorded at scan rates from 0.1 to 0.5 V s⁻¹. (B) Randles–Sevcik plots of i_P vs. $v^{1/2}$ for 0.5 mmol L⁻¹ FCA in [BMIM][BF4] at the *ta*-C:N electrode for various temperatures: 298 K (•), 313 K (•), 323 K (•) and 338 K (•).

Plots of the oxidation and reduction peak currents as a function of the scan rate^{1/2} at different temperatures are presented in Figure 5.3 B. Linear regression analysis revealed i_p - $v^{1/2}$ plot linearity for both peaks at all the temperatures. The currents at each scan rate, and therefore the slopes of the curves, increase with increasing temperature due to a progressively larger diffusion coefficient (D) according to the Stokes-Einstein equation:

$$D = \frac{k_B T}{6\pi a \eta} \tag{5.1}$$

where k_B is the Boltzman constant, *T* is the temperature (K), *a* is spherical shape parameter (m), and η is the viscosity (kg m⁻¹s⁻¹). The correlation between i_p and $v^{1/2}$ indicates the redox reaction rate is limited by planar diffusion of the analyte to the electrode surface under these measurement conditions.

Figure 5.4 A shows cyclic voltammetric *i*-*E* curves for 0.2 to 1.0 mmol L^{-1} FCA in [BMIM][BF₄] at a t*a*-C:N electrode. The scan rate was 0.1 V s⁻¹ and the temperature was 298 K.



Figure 5.4. (A) Cyclic voltammetric *i*-*E* curves for a t*a*-C:N electrode for different concentrations of FCA in [BMIM][BF₄] at 298 K. Curves are shown for concentrations from 0.2 to 1.0 mmol L⁻¹. Curves were recorded at a scan rate of 0.1 V s⁻¹. (B) Plots of $i_P{}^a$ and $i_p{}^c$ vs. *concentration* for FCA in [BMIM][BF₄].

The anodic and cathodic peak potentials are 0.565 and 0.405 V ($\Delta E_p = 160$ mV), respectively, and are invariant with the concentration. Importantly, the results of this experiment verify that ohmic effects are not influencing the voltammetric peak splitting. If ohmic resistance was influencing the curve shapes, then the oxidation peak would have shifted positive and the reduction peak would have shifted negative with increasing concentration due to increased *iR* potential loss. Therefore, the ΔE_p -v trends seen here and those discussed below can be ascribed solely to electron-transfer kinetic effects. Similar ΔE_p invariance with concentration was seen for FCA at both GC and BDD in [BMIM][BF₄] (data not shown). Figure 5.4 B indicates that both $i_p{}^a$ and $i_p{}^c$ increase linearly with the FCA concentration at the ta-C:N electrode. The oxidation current at each concentration is slightly larger than the reduction current due to the larger diffusion coefficient of FCA as compared to FCA⁺.⁶² The BDD and GC electrodes also exhibited peak currents that increased linearly with the FCA concentration, with ΔE_p values being independent of the concentration. A similar trend of unchanging ΔE_p with increasing concentration of FCA in [EMIM][BF₄] was also observed at the ta-C:N electrode, indicative of minimal ohmic resistance effects on the cyclic voltammogram curve shapes.

Figure 5.5 A and B show cyclic voltammetric *i*-*E* curves for 0.5 mmol L⁻¹ FCA in (A) [EMIM][BF₄] and (B) [BMIM][BF₄] at a *ta*-C:N electrode as a function of temperature from 298-338 K (25-65 °C). The scan rate was the same for all the curves, 0.3 V s⁻¹. The $i_p{}^a$ and $i_p{}^c$ values increase and the ΔE_p values decrease with increasing temperature. The increasing peak current with temperature is due to a progressively larger diffusion coefficient for both FCA and FCA⁺. The reduction in ΔE_p with increasing temperature is due to an increasing heterogeneous electron-transfer rate constant. The peak currents at all temperatures are slightly larger in [EMIM][BF4]



Figure 5.5. Cyclic voltammetric *i*-*E* curves 0.5 mmol L⁻¹ for FCA in (A) [EMIM][BF₄] and (B) [BMIM][BF₄] at a t*a*-C:N electrode as a function of temperature. Scan rate = 0.3 V s^{-1} .

than in [BMIM][BF₄] due to the lower viscosity of the former ΔE_p is also slightly smaller in [EMIM][BF₄], again due to the lower viscosity. The experimental cyclic voltammetric data for the *ta*-C:N electrode as well as calculated diffusion coefficients for FCA in [BMIM][BF₄] at different temperatures are summarized in Table 5.2. Values for the diffusion coefficient increase with increasing temperature and are 10-100× lower than the typical value for small molecules in aqueous electrolyte solutions (10⁻⁵ cm² s⁻¹) due to the higher viscosity of the RTIL. The calculated diffusion coefficients for FCA are similar to literature values reported for this and other RTILs of comparable viscosity.^{62–66}

Temperature-dependent cyclic voltammetric *i-E* curves for 0.5 mmol L⁻¹ FCA in [EMIM][BF₄] and [BMIM][BF₄] are presented for GC (Fig. 5.6 A and B) and BDD (Fig. 5.6 C and D). As was the case for the t*a*-C:N electrode, the peak currents increase and the ΔE_p decrease with increasing temperature.

Temperature, K	υ, V s ⁻¹	<i>i_p^a</i> , µA	<i>i_p^c</i> , µA	$E_p{}^a, \mathbf{mV}$	$D, 10^{-7} \mathrm{cm}^2 \mathrm{s}^{-1}$
298	0.1	2.34	-2.01	529	$\boldsymbol{0.71 \pm 0.03}$
	0.2	3.32	-2.89	517	
	0.3	3.92	-3.42	524	
	0.4	4.47	-3.98	532	
	0.5	4.98	-4.42	523	
	0.6	5.39	-4.81	528	
313	0.1	3.01	-2.58	502	$\boldsymbol{1.27\pm0.08}$
	0.2	4.38	-3.81	499	
	0.3	5.17	-4.58	508	
	0.4	5.89	-5.28	506	
	0.5	6.59	-5.79	519	
	0.6	7.27	-6.40	520	
323	0.1	3.53	-2.94	487	$\boldsymbol{1.81 \pm 0.05}$
	0.2	4.95	-4.44	481	
	0.3	6.09	-5.33	484	
	0.4	6.82	-5.98	485	
	0.5	7.55	-6.61	486	
	0.6	8.03	-7.03	487	
338	0.1	3.82	-3.38	452	$\textbf{2.32} \pm \textbf{0.18}$
	0.2	5.54	-5.22	452	
	0.3	6.98	-6.26	449	
	0.4	7.33	-6.93	453	
	0.5	8.19	-7.58	456	
	0.6	8.66	-8.19	457	

Table 5.2. Experimental cyclic voltammetric data and calculated diffusion coefficients for 0.5 mmol L^{-1} FCA in [BMIM][BF₄] at a *ta*-C:N electrode as a function of temperature.

Example cyclic voltammetric data presented for on t*a*-C:N electrode. Diffusion coefficients are reported as an mean \pm standard deviation (n = data for 3 electrodes). Values determined by cyclic voltammetry from the slope of i_p^a vs. $v^{1/2}$ plots.



Figure 5.6. Cyclic voltammetric *i*-*E* curves for 0.5 mmol L^{-1} FCA in (**A**) [EMIM][BF₄] and (**B**) [BMIM][BF₄] at GC and (**C**) [EMIM][BF₄] and (**D**) [BMIM][BF₄] at a BDD thin-film electrode as a function of temperature. The scan rate was 0.3 V s⁻¹.

Figure 5.7 overlays cyclic voltammetric *i-E* curves for GC, BDD and t*a*-C:N electrodes for 0.5 mmol L⁻¹ FCA in (A) [EMIM][BF₄] and (B) [BMIM][BF₄] (Ag QRE scale). In 1 mol L⁻¹ KCl, for example, a near-Nernstian response ($\Delta E_p = 60$ mV) was observed for FCA at all three electrodes with a midpoint potential of *ca*. 0.350 V vs. Ag/AgCl. The near reversibility was seen for scan rates from 0.1 to 0.5 V s⁻¹. In contrast, ΔE_p is significantly larger in the RTILs and the peak currents are smaller. The midpoint potential in [BMIM][BF4] is *ca.* 0.450 V and [EMIM][BF4] is *ca.* 0.550 V vs. Ag QRE. The dielectric constants of both RTILs are similar so this is not the cause for the shift (see Table 5.1). The more negative midpoint potential maybe due to reduced activity of FCA⁺ in [BMIM][BF4] due to complex ion pairing. The lowest peak currents are seen in [BMIM][BF4] as it is the more viscous of the two RTILs. Looking closely at the two curves, it can be seen that the oxidation peaks are sharper than the corresponding reduction peaks consistent with a transfer coefficient value, α , of less than 0.5.



Figure 5.7. Cyclic voltammetric *i*-*E* curves for 0.5 mmol L⁻¹ FCA in (**A**) [EMIM][BF₄] and (**B**) [BMIM][BF₄] at GC, BDD and t*a*-C:N electrodes. Scan rate = 0.3 V s^{-1} . T = 298 K.

5.3.3. Rate Constants and Activation Energies for Electron Transfer as a Function of Temperature

 k^{ρ}_{app} and E_a for FCA in the two RTILs were determined from cyclic voltammetric ΔE_p - υ trends (so-called Nicholson treatment⁶⁷) as a function of temperature at the three distinct carbon electrodes. The cyclic voltammetric curves at the different temperatures were also fit by digital simulation (DigiSim 3.0) to determine k^{ρ}_{sim} . Examples of experimental and simulated cyclic voltammetric *i*-*E* curves for 0.5 mmol L⁻¹ FCA in [BMIM][BF4] and [EMIM][BF4] at a *ta*-C:N electrode are presented in Figure 5.8 A and B, respectively. It can be seen that the simulated curves match the peak currents and peak splitting well in both RTILs, but there is poor fitting of the currents, particularly for [BMIM][BF4] in the diffusion-controlled region past each peak and in the rising portion of the oxidation peak where the rate of electron transfer limits the current flow. The simulations best fit the entire experimental curve peak shapes in [EMIM][BF4]. This misfit is greater in the more viscous [BMIM][BF4], particularly on the rising portion of the oxidation peak.



Figure 5.8. Cyclic voltammetric i-E curves for 0.5 mmol L⁻¹ FCA in (A) [BMIM][BF₄] and (B) [EMIM][BF₄] at a *ta*-C:N thin-film electrode. Experimental (solid line) and simulated (circles) curves are presented. Scan rate = 0.5 V s⁻¹, temperature = 338.15 K and area = 0.2 cm². Simulation parameters used were $D_{red} = 2.3 \times 10^{-7}$ cm² s⁻¹, $C_{dl} = 2.2 \mu$ F and $\alpha = 0.36$.

The experimental curves are asymmetrically shaped with relatively sharp oxidation peaks and a broader reduction waves, consistent with an α value < 0.5. Simulated curves best fit the experimental ones in both RTILs when using $\alpha = 0.36$. Generally, the simulation fit was much better at all potentials when matching voltammetric curves for FCA in aqueous electrolyte (*e.g.* 1 M KCl), as compared to the RTILs. For all of the RTIL data, the fitting parameters (α and k^{o}) that produced the best matched peak splitting and peak currents were applied.

Table 5.3 presents D_{red} , k^o_{app} and k^o_{sim} data for FCA in both ionic liquids as a function of the temperature. k^{o}_{app} is the rate constant determined from ΔE_{p} vs. v trends according to the Nicholson treatment⁶⁵ while k^{o}_{sim} is the rate constant determined by digital simulation. D_{red} , k^{o}_{app} and k^{o}_{sim} all increase with temperature. All three parameters are smaller in the more viscous [BMIM][BF4] than in [EMIM][BF4]. k^{o}_{app} and k^{o}_{sim} are ca. 2-3x lower in [BMIM][BF4]. The key finding, however, is the fact that there is an electrode dependence of k^{o}_{app} with the rate constant decreasing in the following order: BDD > ta-C:N > GC. The k^{o}_{sim} values are larger than the nominal k^{o}_{app} values with the difference being most pronounced for BDD in [BMIM][BF₄]. This difference may be due to the difficulty in fitting entire voltammetric curve shape by digital simulation (see Fig. 5.8). Consistent with the lower k^{o}_{app} and k^{o}_{sim} values in [BMIM][BF4] are the E_a values which are a factor of 2-3× higher than in [EMIM][BF₄]. For example, E_a values in [EMIM][BF₄] range from 6-13 kJ mol⁻¹ while the values in [BMIM][BF₄] range from 16-29 kJ mol⁻¹, depending on the carbon electrode. The values in parentheses are the E_a values determined from ln k^{o}_{sim} vs. 1/T plots. The magnitude of E_a in [EMIM][BF₄], 6-13 kJ mol⁻¹, is similar to E_a values for Fe(CN)₆^{-3/-4} (14-17 kJ mol⁻¹ in 1 mol L⁻¹ KCl) at BDD electrodes.⁶⁸

Analyte/ solvent	Electrode	<i>Т</i> , К	D _{red,} 10 ⁻⁷ cm ² s ⁻¹	<i>k⁰_{app}</i> , 10 ⁻⁴ cm s ⁻¹	<i>k⁰sim</i> , 10 ⁻⁴ cm s ⁻¹	<i>E_a</i> , kJ mol ⁻¹
FCA/	GC	298.15	1.30 ± 0.04	3.11 ± 0.87	5.23	12.88 ± 1.98
[EMIM][BF4]		313.15	1.76 ± 0.08	4.14 ± 0.24	6.87	(14.03*)
		323.15	2.02 ± 0.15	4.65 ± 0.40	7.12	
		338.15	2.10 ± 0.15	6.01 ± 0.38	9.26	
	BDD	298.15	1.84 ± 0.06	7.99 ± 0.34	14.80	6.02 ± 0.31
		313.15	2.76 ± 0.09	8.90 ± 0.47	16.80	(8.87*)
		323.15	3.46 ± 0.13	9.48 ± 0.36	17.40	
		338.15	4.03 ± 0.11	10.71 ± 0.56	21.30	
	ta-C:N	298.15	$1.52\ \pm 0.05$	$4.08 \hspace{0.1 cm} \pm \hspace{0.1 cm} 0.41$	6.96	10.47 ± 0.95
		313.15	2.11 ± 0.09	$5.25\ \pm 0.51$	8.11	(9.98*)
		323.15	$2.46\ \pm 0.11$	5.92 ± 0.44	9.28	
		338.15	$3.28\ \pm 0.26$	$6.72 \hspace{0.1cm} \pm \hspace{0.1cm} 0.48$	10.36	
FCA/	GC	298.15	0.68 ± 0.04	1.09 ± 0.28	3.00	28.35 ± 2.36
[BMIM][BF4]		313.15	1.23 ± 0.08	1.97 ± 0.15	4.09	(19.13*)
		323.15	1.65 ± 0.06	3.00 ± 0.52	5.21	
		338.15	2.59 ± 0.09	4.12 ± 0.49	6.23	
	BDD	298.15	0.93 ± 0.04	3.39 ± 0.19	5.61	16.89 ± 1.11
		313.15	1.55 ± 0.07	5.03 ± 0.23	6.88	(12.32*)
		323.15	1.86 ± 0.04	5.87 ± 0.37	7.82	
		338.15	3.53 ± 0.08	7.68 ± 0.41	9.11	
	ta-C:N	298.15	0.71 ± 0.03	2.09 ± 0.33	4.11	25.23 ± 1.51
		313.15	1.27 ± 0.08	3.29 ± 0.62	5.02	(15.03*)
		323.15	1.81 ± 0.05	4.88 ± 0.63	5.92	
		338.15	2.32 ± 0.18	6.71 ± 0.59	7.40	

Table 5.3. Diffusion coefficients and heterogeneous electron-transfer rate constants for FCA in [EMIM][BF4] and [BMIM][BF4] at different temperatures for the three distinct carbon electrodes.

Diffusion coefficients and rate constants are reported as an mean \pm standard deviation. Activation energy values calculated from $\ln k^o_{app}$ vs. 1/T plots. *Activation energy values calculated from the slope of plots of $\ln k^o_{sim}$ vs. 1/T plots, where k^o_{sim} values were determined from digitally simulated fits of the experimentally recorded cyclic voltammograms. Values is parentheses are calculated from the simulated *i-e* curves.

 E_a was calculated by plotting ln k^o_{app} vs. 1/T according to the Arrhenius equation:

$$\ln k^{o}_{app} = \ln A + \left(-\frac{E_{a}}{R}\right) \left(\frac{1}{T}\right)$$
(5.2)

where E_a is an activation energy (kJ mol⁻¹) and *A* is the frequency factor (s⁻¹). Figure 5.9 presents plots of ln k^0_{app} versus 1000/*T* for FCA in (A) [BMIM][BF4] and (B) [EMIM][BF4]. There is good linearity for all the plots at each electrode over this temperature range. In [BMIM][BF4], the least squares correlation coefficients were 0.9316, 0.9916 and 0.9769 for GC, BDD and t*a*-C:N, respectively. In [EMIM][BF4], the correlation coefficients for GC, BDD and t*a*-C:N were as follows: 0.9795, 0.9872 and 0.9811. The greatest uncertainty in the slope, hence E_a , was observed for GC in both ionic liquids and the least was for BDD. The results indicate a larger E_a (greater negative slope) in the more viscous ionic liquid ([BMIM][BF4]) for all three electrodes. Most interesting is the fact that E_a varies with the carbon electrode material in each RTIL for this traditionally-viewed, surface-insensitive redox probe. BDD electrodes exhibited the lowest activation energy (6 and 17 kJ mol⁻¹ for [EMIM][BF4] and [BMIM][BF4], respectively), while the



Figure 5.9. Arrhenius plots of $\ln k^{0}_{app}$ versus 1000/T in (A) [BMIM][BF4] and (B) [EMIM][BF4] in the range of 298.15 – 338.15 K for GC (•), BDD (•) and ta-C:N (\blacktriangle) electrodes.

highest activation energy was found for GC (13 and 28 kJ mol⁻¹ for [EMIM][BF4] and [BMIM][BF4], respectively). This means that in these two RTILs, the heterogeneous electron-transfer rate constant and activation energy for electron transfer for FCA depends on the carbon electrode microstructure.

5.4. Discussion

A goal of this work was to better understand the temperature dependence of redox analyte/solvent dynamics and interfacial structure in RTILs at sp³ carbon electrodes. To date there has been very little reported research on the study of electrochemical reactions in RTILs at BDD^{44,46-48} and ta-C:N electrodes.⁴⁵ The FCA/FCA⁺ redox system, like ferrocene and other ferrocene derivatives, is generally considered to be a surface-insensitive, outer-sphere redox system in aqueous and organic electrolytes.⁶³ In other words, as long as an electrode is a good conductor, then rapid electron transfer will be observed in aqueous and organic solvent/electrolyte systems. However, the chemical environment around a soluble redox system in an RTIL is considerably different from that in an aqueous or organic solvent/electrolyte system. RTILs are viscous and heterogeneous with microscopic segregation.^{49–55}Large organic cations and smaller inorganic anions exist as ion pairs or clusters in the solvent-less media. The chemical environment around neutral (FCA) and charged (FCA⁺) in an RTIL will consist of an extended organization of these ion pairs or clusters rather than organized solvent dipoles shielding the redox moiety from discrete anions and cations as in an aqueous electrolyte solution. The dynamics for solution reorganization around a redox system in response to an electron transfer will be slower due to the more viscous medium.

In conventional solvent/electrolyte systems, k^o can be expressed as follows:⁶⁹

$$k^{0} = K_{p} \kappa_{el} \upsilon_{n} exp\left(-\frac{\Delta G^{*}}{RT}\right)$$
(5.3)

where ΔG^* is the Gibbs activation energy, K_p is the precursor equilibrium constant, κ_{el} is the electronic transmission coefficient, v_n is the nuclear frequency factor, and R and T are the gas constant and temperature, respectively. There are a couple of variables that will be affected by the higher viscosity of the RTILs and the absence of a dielectric solvent. The first is v_n . This parameter represents the frequency of attempts the reactant makes to reach the transition state and transfer an electron. The frequency of attempts will vary inversely with the viscosity, as has been shown by Tachikawa et al.⁶⁹ A lower v_n value leads to a lower k^o . The second is ΔG^* . This term includes the reorganization energy necessary to transition from the reactant, FCA, to the product, FCA⁺. In conventional solvent/electrolyte systems, the monocationic species is effectively shielded from electrolyte ions by solvent molecules so it is relatively insensitive to ion pairing effects. The same is not the case in RTILs. There is no solvent so the monocationic species will then ion pair with the counter anion, and the anion will in turn electrostatically interact with neighboring organic cations in an extended fashion. In an RTIL, it is expected that a more substantial reorganization of the RTIL ions would be needed when transitioning from the neutral to the monocationic species so there should be a larger ΔG^* , as compared with an aqueous electrolyte solution, and hence a smaller k^{o} . The rate of this reorganization will be slower in the more viscous RTIL. Movement of one ion in an RTIL in response to an electrostatic attraction by FCA⁺ causes the reorganization or movement of all the ions in the medium with the greatest reorganization in the vicinity of the redox probe. In other words, the electrostatic environment around a monocation will likely not involve just one counter ion but many organized ions and ion pairs. It is reasonable to expect therefore that the reorganization energy in RTILs will be larger than in aqueous or organic electrolyte solutions, and that k^o will decrease accordingly.

There is high charge density present in RTILs (total ion concentration 5 - 6 M). RTILs should not be considered as discrete ions but rather as ion-paired polarizable moieties.^{49–55} Recently, the Shaw⁷⁰ and Blanchard groups^{71,72} have independently identified organization in RTILs that extends over micrometer distances. This is consistent with the idea above that the movement of one ion in an RTIL necessarily causes the reorganization of all others. The Shaw group demonstrated, for example, that organization evolved slowly in RTILs at either gas or solid interfaces, where the media would organize into crystal-like (liquid) phase over periods of minutes to days, and this structural order persisted at least one micron into the bulk RTIL. This order was seen using infrared spectroscopy (IRRAS) and second order nonlinear spectroscopy. Their findings demonstrated clearly the (slow) evolution of crystal-like order in RTILs.

The Blanchard group has found that exposing RTILs to a planar charged surface induces a charge density gradient in the ionic liquid normal to the charged surface plane, and the extent of the gradient is on the order of 100 μ m. ^{71,72} This was found using spatially-resolved fluorescence lifetime decay measurements of cationic, neutral and anionic chromophores. These two separate and important findings point to the fact that ionic liquids behave very differently than either ionic crystals or dilute electrolyte solutions, specifically with their propensity for exhibiting organization over macroscopic length scales. This extended organization is important when considering the ionic reorganization that would be necessary in an RTIL when FCA undergoes electron transfer to form FCA⁺. What remains to be determined is how the extended charge density gradient affects the interfacial capacitance at different carbon electrodes, the electric field distribution at the

electrode surface, and the electron-transfer kinetics for different surface-insensitive and surfacesensitive redox systems.

Studies have shown that for ferrocene and ferrocene derivatives, k^{o} varies inversely with the solution viscosity, η .^{69,73} k^o values for ferrocene and the various derivatives generally range from 10⁻³ to 10⁻⁴ cm s⁻¹ depending on the RTIL with viscosities of 10-100 cP^{44,69,73} and on the electrode material. Our data are consistent with most of these limited reports. For example, Fontaine et al. reported a k^o for ferrocene of $(2.1 \pm 0.3) \times 10^{-2}$ cm s⁻¹ in EmiTFSI ($\eta = 34$ cP) at a Pt disk electrode.⁶⁵ Xiao et al. reported a k^o for ferrocene of 2.3 x 10⁻⁴ and 3.2 x 10⁻⁴ cm s⁻¹ in [BMIM][PF₆] at GC and edge plane pyrolytic graphite. k^{o} values were 10x lower for low-defect pyrolytic graphite.⁶⁶ The results indicate a correlation between exposed edge plane density and k^{o} in an RTIL, similar to what is observed in aqueous electrolyte solutions.^{6–11} Pan et al. reported larger k^{o} for ferrocene of 0.05 to 0.18 cm s⁻¹ in three common ionic liquids based on the bis-(trifluoromethylsulfonyl)imide anion at a Pt disk electrode.⁷⁴ Brinis et al. reported k^o for ferrocene of $(4.82 \pm 0.38) \times 10^{-3}$ cm s⁻¹ in a toluene/phosphonium-based ionic liquid at a Pt disk electrode.⁷⁵ Bentley et al. reported k^o values for ferrocene at a Pt microdisc electrode in multiple ionic liquids with viscosities ranging from 30-620 cP.⁷³ Values from 0.007 to 0.21 cm s⁻¹ were determined. A plot of ln k^o vs. ln η was linear with a slope of -1.0. Fietkau et al. reported quite high k^o values for ferrocene, FCA and ferrocene carboxaldehyde in [EMIM][NTf₂] of 0.1 to 0.2 cm s⁻¹ at a Pt channel electrode.⁶³ The k^o values reported herein for FCA are comparable to originally reported values at BDD electrodes in [BMIM][BF₄].⁴⁴

A unique finding from this work is that k^o_{app} and E_a for this redox system depend on the carbon electrode material in the two RTILs. The highest k^o values and the lowest E_a values in both ionic liquids are seen for BDD. This behavior is opposite of what is observed for outer-sphere,

surface-insensitive redox systems (e.g., $Ru(NH_3)6^{+3/+2}$, $IrCl6^{2-/3-}$, FCA, methyl viologen) in aqueous electrolytes at BDD, ta-C:N and GC electrodes.^{23–25,32,76} For these systems, k^{o}_{app} is very similar at all three carbon electrodes (0.1-0.5 cm s⁻¹). For other more surface-sensitive redox systems (e.g., Fe(CN) $_{6}^{3-/4-}$), k^{o}_{app} is lower by a factor of 10x at BDD and ta-C:N as compared to GC.²³⁻ 25,32,76 Furthermore, E_a for Fe(CN) $_6^{3-/4-}$ was found to be 14.3, 15.6, and 16.5 kJ mol⁻¹, respectively, for KCl, NaCl, and LiCl at BDD.⁶⁸ A much greater dependence of E_a on the cation type of the supporting electrolyte was seen for GC. The temperature-dependent k^o data reported herein are the first for BDD and ta-C:N electrodes. Ea values for FCA in [EMIM][BF4] are similar to the values for $Fe(CN)_6^{3-/4-}$ in aqueous electrolytes, although the k^o_{app} for the former is 100x lower. This difference in k^{o}_{app} is attributed to a lower v_n in the more viscous ionic liquid. The values in [BMIM][BF4] are 2-3x higher indicating a possible cation effect. Fawcett et al. reported rate constants and activation energies for ferrocene in different 1-alkyl-3-methyl-imidazolium [BF4] ionic liquids.⁷⁷ They reported E_a of 15 kJ mol⁻¹ independent of the cation type. Their predicted E_a values in [EMIM][BF₄] are similar to our experimental data. However, their predicted E_a values in [BMIM][BF₄] are lower than our experimental data. Additionally, their predicted k^{o} values (0.1-0.5 cm s⁻¹) are 100-1000x larger than our experimentally determined rate constants.

5.5. Conclusions

The temperature dependence of the diffusion coefficient and heterogeneous electrontransfer rate constant for FCA in 1-ethyl-3-methylimidazolium tetrafluoroborate and 1-butyl-3methylimidazolium tetrafluoroborate were investigated by cyclic voltammetry at three microstructurally-distinct carbon electrodes. The following are the key findings from the work:

- 1. The capacitance of BDD and t*a*-C:N electrodes varied from 5-12 μ F cm⁻² in both [EMIM][BF₄] and [BMIM][BF₄] with a distinct capacitance minimum at *ca.* -0.55 V vs Ag QRE.
- 2. k_{app}^{o} (10⁻³ 10⁻⁴ cm s⁻¹) and *D* (10⁻⁷ cm² s⁻¹) both increase with the temperature consistent with a lowering of the RTIL viscosity.
- 3. In both RTILs, k^{o}_{app} decreased in the following order: BDD > ta-C:N > GC. This trend is opposite that seen for multiple surface-insensitive and surface-sensitive redox systems in aqueous electrolyte solutions. This difference in behavior may be linked to the electric double layer structure and electric field distribution in RTILs vs. aqueous electrolyte solutions.
- 4. *D* increased linearly with *T* as predicted by the Stokes-Einstein equation. $\ln k^{o}_{app}$ varied inversely with 1/T as predicted by the Arrhenius equation at all three carbon electrode types.
- 5. k^{o}_{app} is lower and E_a (6-13 kJ mol⁻¹ vs. 16-28 kJ mol⁻¹) is higher in the more viscous [BMIM][BF₄] than in [EMIM][BF₄].

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CHAPTER 6. EFFECT OF THE NITROGEN CONTENT AND OXYGEN PLASMA TREATMENT ON THE HETEROGENEOUS ELECTRON-TRANSFER KINETICS AT THE TETRAHEDRAL AMORPHOUS CARBON ELECTRODES IN AQUEOUS ELECTROLYTES AND ROOM TEMPERATURE IONIC LIQUIDS

6.1. Introduction

An objective of this research was to understand the factors that affect the electron transfer at tetrahedral amorphous carbon thin-film electrodes (t*a*-C). t*a*-C, which is a mixed sp² and sp³-bonded material, is challenging to investigate due to variations in the material microstructure. The basic electrochemical properties of t*a*-C electrodes have been previously reported.¹ It has been confirmed that the unique electrochemical properties of the material are granted by the high content of sp³ bonded carbon, that makes the electrochemical properties resembling more of those of BDD, and it also makes it a pseudo band gap semiconductor. Nevertheless, the electrochemical behavior of the t*a*-C is not simply directly related to the fraction of the sp³-bonded carbon. Rather, the electrochemical properties are influenced in a complex manner by (i) the sp³ content, (ii) the clustering and ordering of the sp² phase (iii) the dopant type and concentration, if used (iv) the hydrogen content and (v) the surface termination (O, H, F, etc...) In other words, the electrochemical properties of t*a*-C material are highly complex and need to be further investigated.

As mentioned, the electrical properties, as well as the structure of the t*a*-C electrode material are strongly affected by the dopant incorporation. One of the most commonly used dopants is nitrogen. According to the literature, an increasing level of nitrogen leads to an increase in the sp²/sp³ ratio, as well as a decrease in the bond gap.² Therefore, controlling the level of nitrogen doping is an effective way to control the material electronic properties and thus enhance electron-transfer processes.^{1,3} Yang et al.¹ reported on electrochemical behavior of tetrahedral amorphous carbon material in aqueous solutions as a function of nitrogen content. The authors found that as the nitrogen content increase, the sp² carbon content increases. The reported

electrochemical behavior for Fe(CN)₆^{-3/-4} indicating decreasing ΔE_p values with increasing nitrogen content and therefore a faster electron-transfer kinetics. The reported k^{0}_{app} values were increasing with a nitrogen content ranging from 0.005 ± 0.001 cm s⁻¹ for the ta-C film to 0.015 ± 0.009 cm s⁻¹ for the 50 sccm t*a*-C:N film.¹ The incorporated nitrogen does give the natural n-type electrical conductivity, but the main effect on the electronic properties is the π states in the σ - σ^* gap that incorporated nitrogen introduces.⁴

Another factor affecting the electron transfer is the electrode surface termination. It has been previously reported that the electron-transfer kinetics on sp³ carbon material (BDD electrodes) is significantly affected by the surface termination for specific redox species, for example, $Fe(CN)_{6}^{-3/-4}$. Such as behavior is ascribed to the electrostatic repulsion between dipoles at the oxygen-terminated surface and the charges on the redox ion. ^{5–7} For instance, at the BDD electrode, the electron transfer rate of $Fe(CN)_6^{-3/-4}$ has been found to be more sluggish at the oxygen-terminated surface compared to the as deposited BDD surface. For example, the ΔE_p was 198 mV and 70 mV for the oxygen-terminated, and as deposited BDD surfaces.⁸ On the other side, for the sp² carbon (GC), McCreery et al⁹ reported that even though the $Fe(CN)_6^{-3/-4}$ is surface sensitive redox molecule, the modification has only minor effect on the electron transfer kinetics. Considering that the ta-C:N electrodes are a mixture of an sp² and sp³ bonded carbon, the expectation is that the behavior would partially follow those of BDD electrodes and the surface oxygen species would change the electrochemical properties of the ta-C:(N)_x electrodes. There have been several reports regarding the effect of the oxygen surface treatment of BDD electrodes on the electron transfer kinetics. Nevertheless, in our knowledge, this has not been reported for the ta-C:N electrodes in RTILs electrolytes.

The electrochemical activity of t*a*-C:N electrodes as a function of incorporate nitrogen level was investigated using the outer and inner-sphere redox species. Fe(CN)₆-^{3/-4} is a commonly used redox system used to probe the reactivity of the electrodes, as a representative of inner-sphere redox couples. The heterogeneous electron-transfer rate constant (k^0) for this redox couple is strongly affected by i) surface cleanness ii) electronic properties of the electrode (density of electronic states near E^0) and iii) surface chemistry.

On the other hand, second investigated redox couple, $Ru(NH_3)6^{+3/+2}$, is classified as an outer-sphere redox couple. It generally involves simple electron transfer on most electrodes including diamond,^{10,11} and sp² carbon.^{12,13} Compare to the first examined Fe(CN)6^{-3/-4}, $Ru(NH_3)6^{+3/+2}$ is relatively insensitive to the microstructure surface, surface oxides and adsorbed monolayers on sp² carbon electrodes.¹⁴ In the ideal case, the heterogeneous electron transfer rate constant is mainly controlled by the electronic properties of the electrode (*i. e.*, carrier concentration, and mobility).

Even though the $Fe(CN)_{6}^{-3/-4}$ and $Ru(NH_3)_{6}^{+3/+2}$ are the two of the most commonly used redox species for investigation of the electrode electrochemical behavior in aqueous solutions, it has been problematic in RTILs solutions. One of the reasons might be either poor solubility in RTILs or electrochemical inactivity presumably due to large activation barriers. Therefore, the ferrocene (Fc) and its derivates ferrocene methanol (FeMeOH) and ferrocene carboxylic acid (FCA) has been selected due to its ability to undergo heterogeneous electron transfer processes in RTILs. In most aqueous and non-aqueous systems (such as organic solvents), the ferrocene/ferricenium (Fc/Fc⁺) redox reaction undergo a reversible or Nernstian redox behavior. This seems not to be the same scenario in the room temperature ionic liquid.¹⁵ Several reports on the diffusion and kinetics of the Fc/Fc⁺ in RTILs have been published.^{16,17} Notwithstanding, in our knowledge, there is no systematic investigation of the electron transfer rate of ferrocene and its derivates in RTILs as a function of i) the electrolyte composition, ii) ta-C(:N)_x nitrogen level incorporation, and iii) the oxygen surface termination.

In the enclosed chapter, the microstructure of ta-C(:N)_x thin-film electrodes with various nitrogen content are reported on using Raman spectroscopy, X-ray photoelectron spectroscopy, atomic force microscopy, and static contact angle measurements. The material properties are correlated with the basic electrochemical properties. Redox systems in aqueous electrolytes and RTILs were used to investigate the *ta*-C:N electrode activity. Cyclic voltammetry was the main electrochemical method used. Preliminary work looking at the effect of the oxygen plasma treatment on the *ta*-C(:N)_x electrode activity is also reported on.

6.2. Results and Discussion

6.2.1. The Nitrogen Content Effect

6.2.1.1. Characterization of ta-C(N)_x Electrode Surfaces

X-Ray Photoelectron Spectroscopy

XPS analysis was carried out for two purposes. The first was to determinate the ratio of sp² and sp³ carbon in t*a*-C(:N)_x thin-film electrodes. The second was estimation of nitrogen content in ta-C(:N)_x films deposited with various N₂ gas flows in the deposition chamber. The films characterized below were 200 – 300 nm thick. The XPS analysis provides information on the elemental composition of the film in the top ~10 nm.

Figure 6.1 shows XPS spectra for t*a*-C:N thin films deposited with a varying levels of nitrogen incorporation. The nitrogen levels in the films were controlled by the flow rate of N_2 gas into the deposition chamber. Flow rates from 0 to 50 sccm were used. Three primary peaks are present in all spectra. The first peak at 284 eV is the C 1s core. The second peak at 532 eV is



Figure 6.1. XPS spectra for ta-C(:N)_x thin films deposited with 0, 10, 30 and 50 sccm of N₂ added to the reaction chamber.

associated with the O 1s core. The third peak at 398 eV associated with the N 1s core. The intensity of this peak generally increases with increasing N₂ flow rate during the deposition. All the films contain C and O in the near surface region, and the N 1s signal intensity increases with the N₂ flow rate indicating increased N incorporation into the films. Prior work has shown that the N content with depth in the *ta*-C:N film is uniform with depth.¹⁸

Figure 6.2 shows an expanded view of the C 1s peak for the *ta*-C film deposited with 0 sccm N₂. Deconvolution was used to fit the primary peak with five sub-peaks reflective of carbon atoms in different bonding states. The five peak maxima are at 283.5, 284.1, 285.0, 286.1 and 287.7 eV. According to the literature, the deconvoluted peaks are ascribed to sp² and sp³-bonded carbon, and to carbon atoms bonded to surface oxygen (C-OH, C=O, and O-C=O).¹⁹ The relative concentration of sp² and sp³ hybridized carbon was calculated from the area of the respective sub-peaks for all *ta*-C(:N)_x films.^{20,21} In agreement with the hypothesis, the fraction of sp²-bonded carbon increased with an increasing N content in the film (Table 6.1). The values were found to



Figure 6.2. The C 1s core peak and its sub-peaks (sp^2 , sp^3 , C-OH, C=O, O=C-C) for t*a*-C thinfilm electrode grown with no added N₂. The red line represents the measured raw data.

Electrode	sp ² (%)	sp ³ (%)
ta-C	70.3	29.7
ta-C:N 10sccm	72.4	27.6
ta-C:N 30sccm	83.0	17.0
ta-C:N 50sccm	76.4	23.6

Table 6.1. Summary of XPS data for the ta-C(:N)_x films deposited with a flow of 0, 10, 30 and 50 sccm of N₂ gas flow.

be 70.3, 72.4, 83.0, and 76.4 % for the film deposited with 0, 10, 30 and 50 sccm of nitrogen, respectively. Furthermore, as the nitrogen flow increased, the position of the C 1s peaks shifted towards the higher binding energy, and broadening of the C1s line was observed. Therefore, it can be assumed that the incorporation of nitrogen during the deposition process forms sp^2 hybridized C=N bonds, that consequently leads to a higher concentration of sp^2 -bonded carbon.

Figure 6.3 shows the variation of nitrogen content in the near surface region of the films as a function of the N_2 flow rate used during the deposition. The nitrogen concentration increases proportionally with the N_2 flow rate, which is consistent with previously published results.¹ The atomic concentrations of nitrogen in the films were 1.8, 3.4, 7.9 and 9.1 at. % for films deposited with 0, 10, 30, and 50 sccm of N_2 . It is presumed that the nitrogen concentration near the surface in the films is the same as the concentration in the bulk. Prior XPS depth profiling has revealed constant N levels through the bulk of t*a*-C:N films.¹⁸

Finally, all films had a relatively high level of O near the surface ranging from 12.4 - 16.0 at. %. Surface O is typically detected on t*a*-C:N films exposed to the atmosphere.^{1,22} The O content is most likely confined to the near-surface region and is not present in the bulk of the films. t*a*-C thin films generally consists of a layer of amorphous, graphite-like carbon on the surface. No attempts were made to remove this layer before performing the XPS measurements. Therefore,



Figure 6.3. Atomic concentration of nitrogen in the ta-C(:N)_x thin films as a function of nitrogen flow used during the deposition.

the XPS data presented herein may not reflect the elemental composition of the bulk of the films but rather reflect the near-surface region. It is because of this that the fraction of sp^3 hybridized carbon in these films is so apparently low and the fraction of sp^2 hybridized carbon is rather high. Generally speaking, t*a*-C and t*a*-C:N films consist of greater than 50% sp³ hybridized carbon. In terms of the electrochemical properties reported on below, the carbon microstructure on the t*a*-C:N film surface and the surface functional groups are expected to play a dominate role.

Visible Raman Spectroscopy

The incorporation of N into the films significantly alters the carbon-carbon bonding and leads to more sp² hybridized carbon . Ferrari et al. have reported, that the clustering of sp² phases in t*a*-C films can be identified by the D band (~1360 cm⁻¹), specifically by the D to G intensity ratio I_D/I_G .²³ The tetrahedral amorphous carbon 'cluster model' develop by Robertson⁴ describes

the C network as an sp³-bonded matrix with implanted sp² clusters. The properties of the film are then controlled by both structures. The mechanical properties are affected by the sp³ -bonded matrix, while the electronic structure and optical bond gap are dominated by the sp² clusters, namely by the π states.²⁴

The visible Raman spectra of t*a*-C thin film electrodes deposited on Si with different N₂ gas flows are documented in Figure 6.4. The range of $450 - 2000 \text{ cm}^{-1}$ is shown. All obtained spectra are characterized by an asymmetric peak centered at ca. 1550 cm⁻¹. The intensity of the peak decreased with increasing N₂ gas flow (i.e., increasing N content) due to reduced optical transparency to the visible excitation light. In other words, the Raman scattering volume decreased with increasing N content. This asymmetric peak can be fit with two components: the G (~1560 cm⁻¹) and D (~1360 cm⁻¹) bands. No peak associated with nitrogen (carbon double bonded or triple bonded with nitrogen) was found in the visible Raman spectra. An example of the deconvoluted peak for *ta*-C:N 30 sccm is shown on Figure 6.5.



Figure 6.4. Raman spectra of *ta*-C and *ta*-C:(N)_x electrodes with various nitrogen level.



Figure. 6.5. Raman spectra deconvolution example for t*a*-C:N 30 sccm. Red line represents the measured raw data, blue line the D band, and pink line the G band.



Figure 6.6. Variation of D to G peak intensity ratio with the N₂ gas flow used during the deposition of the ta-C:(N)_x thin film electrodes (n = 10 000).

The dependence of the I_D/I_G intensity ratio on the N₂ flow used during the deposition is shown in Figure 6.6. The results show that as the N content in the film increases, the I_D/I_G intensity ratio increases. The pure tetrahedral amorphous carbon thin film electrode (0 sccm N₂content has the I_D/I_G value of 0.53 ± 0.01, while the t*a*-C:N thin film deposited with 50 sccm N₂ has the maximum I_D/I_G value of 0.87 ± 0.05. Following the Robertson 'cluster model' with an sp³-bonded matrix with few embedded sp² clusters, such an increase in the I_D/I_G values indicates an increasing fraction (structural disorder) of sp²-bonded carbon atoms with the increasing nitrogen content.⁴ The lower the value of I_D/I_G , the smaller the sp² clustering in the examined t*a*-C:(N)_x films.²⁵ Numerical results are presented in Table 6.2. The results are consistent with those obtained by XPS analysis, supporting the hypothesis that there is increasing sp² hybridization in t*a*-C films with increasing N incorporation.

Electrode	I_D/I_G	FWHM(G band) (cm ⁻¹)	G-band position (cm ⁻¹)
ta-C	0.53 ± 0.02	210.0 ± 1.3	1557.5 ± 0.8
ta-C:N 10sccm	0.76 ± 0.02	202.3 ± 1.7	1555.6 ± 0.8
ta-C:N 30sccm	0.87 ± 0.04	197.2 ± 3.0	1549.1 ± 1.1
ta-C:N 50sccm	0.87 ± 0.05	197.4 ± 4.2	1550.1 ± 1.8

Table 6.2. Raman spectral parameters for t*a*-C and t*a*-C:(N)_x electrodes.

Data are reported as average \pm standard deviation (n = 10 000).

Another significant Raman spectral feature, reflective of the *ta*-C:(N)_x thin-film electrode microstructure, is the width of the G band. Based on the work of Schwan et al.²⁶, four factors affectthe G peak width: i) the size of the sp²-bonded carbon clusters, ii) the cluster distribution, iii) the stress in the film and iv) the chemical environment. As the stress of the film is an of importance contribution to the line broadening, the stress cannot be ruled out. The data for Young's modulus (Table 6.3) represents the stress of the examined electrodes revealed significant differences in the values. Sakata et al.²⁷ reported a linear relationship between both parameters; the width of the G band linearly increase with stress. Nearly the same dependence has been found for the electrodes used in this investigation (Figure 6.7 A); the G linewidth increase with increasing stress. The decreased residual stress of the electrodes with an increased N content is ascribed to the nitrogen incorporation and the resulting sp² hybridized carbon bonding. The sp² bonded reduces the residual stress as the C=N bond is shorter in length (1.29 Å) as compared to the C-C (1.54 Å) and C=C (1.34 Å) bond lengths.² In other words, the G-band width decreases with increasing N content, indicating an increased fraction of sp² bonded carbon (Figure 6.7B). ^{1,24}



Figure 6.7. The variation of G-band width with the stress (A) and the nitrogen flow rate (B) for t*a*-C:(N)_x thin film electrodes ($n = 10\ 000$).

The G-band position is the last Raman parameter commonly used for the characterization of the (nitrogenated) tetrahedral amorphous carbon films. As Table 6.2 documents, the G-band position is shifted to the lower wavenumbers with increasing N content. Such behavior is consistent with increasing sp²-bonded carbon content and an increasing number and/or size of the sp² clusters.

Lastly, the Raman spectra of the *ta*-C:N films reveals a peak at 512 cm^{-1} . This is the firstorder phonon mode for the Si substrate. The presence of the Si band is an indicator of the optical transparency to visible light, as well as the film thickness. With increasing N₂ gas flow (*i.e.*, increasing N content in the films), the films become less transparent (increasing adsorption coefficient of the film).^{28,29} The film thicknesses were fairly constant at 200-300 nm as determined by contact profilometry.

Property	ta-C	ta-C:N (10 sccm)	ta-C:N (30 sccm)	ta-C:N (50 sccm)
Thickness (nm)	245	226	211	213
Contact Angle (water)	$64 \pm 1^{\circ}$	$66 \pm 3^{\circ}$	$59\pm2^{\circ}$	$60 \pm 2^{\circ}$
Young's Modulus (GPa)	428	395	303	239
Density (g cm ⁻³)	2.73	2.66	2.47	2.32

Table 6.3. Physical properties of t*a*-C and t*a*-C(:N)_x electrodes.

Atomic Force Microscopy

Contact-mode AFM images $(1\mu m \times 1\mu m)$ of the t*a*-C:N thin-film electrodes are presented in Figure 6.8. Images were recorded from at least at five locations on each film to determine the surface roughness and to assess the film coverage over the substrate. All films uniformly covered the entire substrate. All films have a nodular morphology. With the increasing N content, there is increased surface roughness. The nominal surface roughness (measured over a 1 μm^2 area) of these films is 6 ± 3 (t*a*-C), 9 ± 4 (t*a*-C:N 10 sccm N₂), 12 ± 4 (t*a*-C:N 30 sccm N₂) and 15 ± 4 nm (t*a*-C:N 50 sccm N₂). The nodules increase in number density with increasing N content. The roughness of the films is possibly affected by the N incorporation in the film or nitrogen normal bonding ^{25,30}, and an increased number of sp²-bonded carbon domains.³¹ According to



Figure 6.8. AFM images of t*a*-C and t*a*-C:(N)_x thin-film electrodes deposited with (A) 50, (B) 30, (C) 10 and (D) 0 sccm of N₂. Images were recorded in the contact mode.

Lifshitz et al.,³² increasing surface roughness as an indicator of greater sp² hybridization. During the ta-C(:N)_x film growth process, the carbon microparticles from the solid graphite source detach and get implanted into the depositing film. This also likely leads to the nodular morphology as the incorporation changes the angle of incidence by altering C ions. Finally, the lower density of the sp²-bonded carbon consequently causes a concentrated increase of volume, resulting in a creation of 'nodules' on the electrode surface.^{1,33}

Static Contact Angle Measurements

The wettability of the different t*a*-C:N thin-film electrode surfaces was evaluated using static contact angle measurements with ultrapure water. Figure 6.9 shows photographs of the water droplet on the different t*a*-C:N films as received. The nominal contact angles measured at different locations in each film were $64 \pm 1^{\circ}$ (t*a*-C), $66 \pm 3^{\circ}$ (t*a*-C:N 10 sccm N₂), $59 \pm 2^{\circ}$ (t*a*-C:N 30 sccm



Figure 6.9. Photographs of the water droplet on t*a*-C and t*a*-C:(N)_x thin films deposited with (A) 0, (B) 10, (C) 30 and (D) 50 sccm of N₂. Water drop volume = 1μ L.

 N_2) and $60 \pm 2^\circ$ (ta-C:N 50 sccm N_2). These comparable values indicate all the surfaces are slightly hydrophilic. This is to be expected given the amorphous carbon layer on the ta-C:N film surface and the polar surface carbon-oxygen functionalities present (12-15 at. %). The contact angles show no trend with the N_2 content in the films, suggesting that the water wettability is independent on the nitrogen content. Generally, there are several factors that affect the surface wettability of carbon electrodes. These factors are surface roughness, surface passivation, the presence of sp² and sp³-bonded carbon at the surface, and a presence of surface carbon-oxygen functional groups. ^{2,34}

6.2.1.2. Electrochemical Properties of ta-C(N)_x Thin Films

Background Current Profiles

Background cyclic voltammetric *i*-*E* curves for t*a*-C and t*a*-C:N_x electrodes with various nitrogen levels (0, 10, 30 and 50 sccm N_2) in 1 M KCl are presented in Figure 6.10. The curves do



Figure 6.10. Background cyclic voltammetric *i-E* curves for a t*a*-C electrode (black) and t*a*-C:N electrodes deposited with 10 sccm (red), 30 sccm (green) and 50 sccm N₂ (blue) in 1 M KCl. Scan rate = 0.1 V s^{-1} . Geometric area = 0.2 cm^2 .

not change in shape with cycle number. All curves are featureless within the investigated potential window. Obtained data suggest that the level of incorporated nitrogen has a minor effect on the background current magnitude. Tested electrodes exhibit an expected behavior; the background current is increasing with the increasing nitrogen content. For example, at 0.2 V, the anodic current for ta-C (0 sccm N₂) electrode is 0.96 μ A, while the current for the 50 sccm ta-C:N electrode is 1.35 μ A. A

more significant trend of increasing background current with increasing incorporated N has previously been reported.¹ The electrode capacitance, C_{dl} , can be calculated from the equation, $c_{dl} = \frac{I}{vA}$. A summary of calculated values for the film is presented in Table 6.4. For comparison, previously measured data for GC and BDD electrodes are included.

Table 6.4. Calculated capacitance values for ta-C and ta-C:N thin-films deposited with various N₂ gas flows (10, 30 and 50 sccm). GC and BDD electrode data included for comparison. (n=3 electrodes each)

Electrode	Capacitance, µF cm ⁻²
BDD	9.1 ± 0.6
ta-C	46.4 ± 1.8
ta-C:N 10sccm	51.3 ± 1.6
ta-C:N 30sccm	53.1 ± 1.9
ta-C:N 50sccm	59.8 ± 1.3
GC	71.1 ± 3.2

All electrodes exhibit background current that increases linearly with the scan rate, indicative of a capacitive process. For example, the anodic current measured at 0.2 V increased linearly with the scan rate for all electrodes with linear regression correlation coefficients of 0.9998 for t*a*-C (0 sccm N₂), 0.9996 (10 sccm N₂, 0.9997 (30 sccm N₂), and 0.9996 (50 sccm N₂) (data not shown). It is supposed that the background current is primarily capacitive in nature as no

significant faradaic surface reactions are expected in the examined potential range. If there is any faradaic current passing due to surface redox processes, for example, the voltammetrically-determined electrode capacitance will be higher than the true value. Based on the high values of 40-70 μ F cm⁻², it is likely that the current measured at 0.2 V is not solely capacitive. A typical capacitance for a smooth metallic electrode is 25-30 μ F cm⁻².

Capacitance–Potential Profiles $(C_{dl}-E)$

The double layer capacitance of the different t*a*-C and t*a*-C:N electrodes is influenced by the density of electronic states, that is the excess charge carrier density at different potentials. The carrier concentration in the film affects the number of charge carriers available. The excess surface charge on the t*a*-C:N films (point of zero charge is unknown) is counterbalanced by an equivalent amount of excess charge on the side of the interface. Therefore, these experiments provide information regarding the electronic properties of the material.

Capacitance values were also determined using an 10 mV sine wave at frequency 40 Hz and calculated from the equation,

$$Z_{im} = \frac{1}{2}\pi f C_{dl}$$
(6.1)

where Z_{im} is the imaginary part of the impedance $(\frac{Vs}{c})$, *f* is used frequency (s⁻¹), and C_{dl} is the double layer capacitance (*Fcm*⁻²)

Figure 6.11 presents C_{dl} -E profiles of the ta-C and ta-C:N electrodes in 1 M KCl. The capacitance at all potentials increases with increasing N incorporation. The 50 sccm ta-C:N electrode exhibits the largest capacitance of the four, ranging from 20 to 30 µF cm⁻². On the other hand, the lowest capacitance in the range from 9 to 12 µF cm⁻² was obtained for the ta-C electrode. Increasing N incorporation leads to an increased carrier concentration in the film and this contributes to the increasing c_{dl} . For comparison, the C_{dl} for boron-doped diamond in this electrolyte ranges from 5-11 µF cm⁻² over the potential range, while GC ranges from 35 to 72 µF cm⁻².



Figure 6.11. Capacitance vs. potential profiles for ta-C (\blacksquare), 10 sccm ta-C:N (\bullet), 30 sccm ta-C:N (\bullet), and 50 sccm ta-C:N (\blacktriangledown) in 1 M KCl over the potential range from -1 to 1 V. Data are normalized to the geometric area = 0.2 cm².

Electrochemical Activity in Inner- and Outer-Sphere Redox Couples in Aqueous Electrolyte Solutions

The activity of the t*a*-C(:N)_x thin-film electrodes was investigated using multiple soluble redox systems. Cyclic voltammetric *i*–*E* curves for 0.1 mM Fe(CN)₆^{-3/-4} + 1 M KCl, at increasing scan rate from 0.1 to 0.5 V s⁻¹, are shown in Figure 6.12 (A – D). Well-defined oxidation and



Figure 6.12. Cyclic voltammetric *i*-*E* curves for a (**A**) t*a*-C, (**B**) 10 sccm t*a*-C:N, (**C**) 30 sccm t*a*-C:N, and (**D**) 50 sccm t*a*-C:N (**D**) films in 0.1 mM $\text{Fe}(\text{CN})_6^{3-/4-} + 1$ M KCl at increasing scan rate from 0.1 to 0.5 V s⁻¹. Geometric area = 0.2 cm².

reduction peaks are seen for all four films. At these scan rates, ΔE_p varies from 74 ± 4 mV to 109 ± 12 mV for all the films, consistent with quasi-reversible electrode kinetics. The oxidation peak current for each electrode increases linearly with the square root of the scan rate (R² > 0.9992), indicating the current is limited by semi-infinite linear diffusion of the analyte to the electrode. A direct comparison of electrode performance is documented in Figure 6.13 and Table 6.5. The results indicate a more reversible behavior (decreasing values of ΔE_p) with increasing nitrogen content. ΔE_p decrease from 109 to 83 mV for Fe(CN)₆^{-3/4}. Calculated heterogeneous electron-transfer rate constants increase for films with increasing N content with values of (0.49 ± 0.02) × 10⁻², (0.64 ± 0.20) × 10⁻², (2.58 ± 0.25) × 10⁻² and (1.49 ± 0.22) × 10⁻² cm s⁻¹, respectively, for 0, 10, 30, and 50 sccm of N₂. The reason for faster kinetics on film with higher sp² content might be an increasing density of active sites with an increasing nitrogen content.³⁵



Figure 6.13. Comparison of cyclic voltammetric *i*-*E* curves recorded at all used electrodes in 0.1 mM Fe(CN)₆^{3-/4-} in 1 M KCl, measured at ta-C:N_x thin-film electrodes prepared with different N content. Scan rate = 0.1 V s⁻¹. Geometric area = 0.2 cm².

Analyte	Electrode	<i>i</i> p ^{ox} (µA)	$\Delta E_{p} (mV)$	D_{ox} , 10^{-5} (cm ² s ⁻¹)	<i>k⁰_{app}</i> , 10 ⁻² (cm s ⁻¹)
Fe(CN)6 ^{3-/4-}	ta-C	7.08 ± 0.39	109 ± 12	1.07 ± 0.20	0.49 ± 0.02
	ta-C:N 10sccm	7.34 ± 0.36	102 ± 8	1.04 ± 0.27	0.64 ± 0.20
	ta-C:N 30sccm	7.58 ± 0.60	74 ± 4	1.54 ± 0.50	2.58 ± 0.58
	ta-C:N 50sccm	8.06 ± 0.08	83 ± 3	1.66 ± 0.07	1.49 ± 0.22
Ru(NH3) 6 ^{2+/3+}	ta-C	8.41 ± 0.15	56 ± 1	2.53 ± 0.05	N/A
	ta-C:N 10sccm	8.10 ± 0.12	56 ± 1	2.46 ± 0.10	N/A
	ta-C:N 30sccm	7.79 ± 0.34	56 ± 1	2.17 ± 0.15	N/A
	ta-C:N 50sccm	8.23 ± 0.16	57 ± 1	2.31 ± 0.15	N/A
Ferrocene	ta-C	5.65 ± 0.45	56 ± 1	1.93 ± 0.17	N/A
	ta-C:N 10sccm	5.60 ± 0.29	56 ± 2	2.21 ± 0.26	N/A
	ta-C:N 30sccm	5.55 ± 0.48	56 ± 1	2.01 ± 0.40	N/A
	ta-C:N 50sccm	5.65 ± 0.11	58 ± 1	1.34 ± 0.17	N/A
FCA	ta-C	6.93 ± 0.34	59 ± 1	1.30 ± 0.05	N/A
	ta-C:N 10sccm	6.20 ± 0.13	61 ± 1	1.25 ± 0.30	N/A
	ta-C:N 30sccm	7.20 ± 0.23	61 ± 1	1.16 ± 0.09	N/A
	ta-C:N 50sccm	6.75 ± 0.40	63 ± 1	1.26 ± 0.16	N/A
FeMeOH	ta-C	8.49 ± 0.12	56 ± 1	2.57 ± 0.09	N/A
	ta-C:N 10sccm	8.57 ± 0.29	56 ± 2	2.63 ± 0.20	N/A
	ta-C:N 30sccm	8.82 ± 0.08	56 ± 1	2.69 ± 0.15	N/A
	ta-C:N 50sccm	8.72 ± 0.20	56 ± 1	2.60 ± 0.31	N/A

Table 6.5. Summary of cyclic voltammetric data for $Fe(CN)_6^{-3/-4}$, $Ru(NH_3)_6^{+3/+2}$, Ferrocene, FCA, and FeMeOH in1M KCl measured at ta-C:(N)_x electrodes (n=3).

All redox analyte concentrations were 0.1 mM. Scan rate = 0.1 V s^{-1} . Geometric area = 0.2 cm^2 .

^a The apparent heterogeneous electron-transfer rate constants were determined from the $\Delta E_p - v$ method described by Nicholson.³⁶ Values reported are mean \pm SD based on curves recorded at 0.1 - 0.5 V s⁻¹, where quasi reversible behavior was observed. The RSD of calculated k^{0}_{app} was in range of 2 to 6 %.

N/A - Peak splitting is out of the peak splitting interval defined by Nicholson; k^{0}_{app} cannot be calculated.

Table 6.5 shows a summary of the cyclic voltammetric data. The Ru(NH₃) $_{6}^{+3/+2}$ redox system is classified as an outer-sphere or surface insensitive one on most electrodes. The reaction involves simple electron transfer on most electrodes including diamond^{10,11} and sp² carbon. ^{12,37} Compare to examined Fe(CN) $_{6}^{-3/-4}$, k^{0}_{app} for Ru(NH₃) $_{6}^{+3/+2}$ is relatively insensitive to the carbon electrode microstructure surface, surface chemistry and adsorbed monolayers on sp² carbon electrodes. k^{0}_{app} is mainly influenced by the electrical properties (*i.e.*, carrier concentration, and mobility) of the electrode.

A comparison of cyclic voltammetric i-E curves for Ru(NH₃) $_{6}^{+3/+2}$ in 1 M KCl at the different ta-C(N)_x thin-film electrodes is shown in Figure 6.14. The redox system was reversibly behaved at all four films. This means the ΔE_p was 59 mV and independent of the scan rate. For all four films, the values i_p^{ox}/i_p^{red} ratios were near to 1, and the i_p^{ox} versus the square root of scan rate was linear, indicating a diffusion-controlled reaction rate. The k^{θ}_{app} could not be determined at these scan rates by the Nicholson method because of the reversibility. These voltammetric results



Figure 6.14. Comparison of cyclic voltammetric *i*-*E* curves for $Ru(NH_3)_6^{+3/+2}$ in 1 M KCl at the different ta-C(N)_x thin film electrodes. Scan rate = 0.1 V s⁻¹. Geometric area = 0.2 cm².

indicated that all four ta- $C(N)_x$ thin-films possess a high density of electronic states that leads to high rates of electron transfer.

Furthermore, the data presented in Table 6.5 data shows the apparent electron-transfer rate constants for ferrocene and several derivatives, ferrocene carboxylic acid, and ferrocene methanol, in 1 M KCl. These redox systems were selected due to their ability to undergo heterogeneous electron transfer in RTILs. All three redox systems exhibit reversible electrochemical behavior at these scan rates with ΔE_p values ranging from 56 ± 1 to 63 ± 1 mV. Therefore, similar to the Ru(NH₃)₆^{+3/+2}, the rate constant cannot be calculated. As the cyclic voltammetric response was similar for these redox systems at all the *ta*-C:N electrodes only the *ta*-C:N 30 sccm electrodes were used for the studies reported in the following text.

Electrochemical Behavior of Ferrocene Derivatives in Room Temperature Ionic Liquids

Representative cyclic voltammetric *i*-*E* curves of ferrocene in [BMIM][OTF], [BMIM][BF₄], and [BMIM][PF₆] recorded at *ta*-C:N (30 sccm) thin-film electrode at increasing scan rate from 0.1 to 0.5 V s⁻¹ are shown in Figure 6.15 A-D. Several points deserve to be highlighted. At first, well-defined oxidation and reduction peaks for all three RTILs are observed, but the ΔE_p values and peak current magnitudes at a given scan rate are different in the three RTILs.



Figure 6.15. Cyclic voltammetric *i*-*E* curves for 1 mM ferrocene in [BMIM][OTF] (**A**), [BMIM][BF₄] (**B**), and [BMIM][PF₆] (**C**), measured using a 30 sccm ta-C:N thin-film electrode. Scan rates = 0.1 to 0.5 V s⁻¹. Geometric area = 0.2 cm².

Second, the peak currents were unchanged over twenty cycles, indicating stability of the oxidized form of ferrocene in the investigated time frame, as well as no other chemical reaction coupled with the electron transfer of ferrocene. Third, the $i_p{}^{ox}$ values increase linearly with a square root of scan rate indicating that currents are limited by diffusion of ferrocene towards the electrode. The ΔE_p values increase and peak current decrease with increasing viscosity of the RTILs (Figure 6.16). The ΔE_p values are 133 ± 6 ([BMIM][OTF], $\eta = 90$ mPa s), 142 ± 4 ([BMIM][BF4], $\eta = 112$ mPa s), and 188 ± 3 mV ([BMIM][PF6], $\eta = 201$ mPa s) at all the electrodes. The diffusion coefficients were calculated from the $i_p{}^{ox}$ vs $v{}^{1/2}$ plot slopes according to the Randles-Sevcik equation. The calculated values are on the order of 10⁻⁷ cm² s⁻¹ in all three RTILs which is two order of magnitude lower than the values in aqueous electrolyte (10⁻⁵ cm² s⁻¹). This is due to the greater viscosity of the RTILs.



Figure 6.16. Cyclic voltammetric *i*-*E* curves for 1 mM ferrocene in [BMIM][OTF] (black), [BMIM][BF₄] (red), and [BMIM][PF₆] (blue). Measured at a t*a*-C:N (30 sccm of N₂) thin-film electrode. Scan rate = 0.1 V s^{-1} . Geometric area = 0.2 cm^2 .

Analyte	Electrolyte	ΔE_p (mV)	<i>Viscosity,</i> mPa s	Dox , 10 ⁻⁷ (*10 ⁻⁵) (cm ² s ⁻¹)	<i>k_{app}</i> , 10 ⁻⁴ (cm s ⁻¹) ^a
FCA	KCl	61 ± 1	1	$1.16\pm0.09*$	N/A
	[BMIM][OTF]	145 ± 4	90 ³⁸	1.37 ± 0.04	2.86 ± 0.20
	[BMIM][BF4]	163 ± 4	112 ³⁹	0.99 ± 0.02	1.92 ± 0.23
	[BMIM][PF6]	164 ± 4	201 ³⁹	0.98 ± 0.02	1.90 ± 0.21
FeMeOH	KCl	56 ± 1	1	$2.69\pm0.15*$	N/A
	[BMIM][OTF]	115 ± 4	90	1.33 ± 0.03	4.55 ± 0.30
	[BMIM][BF4]	141 ± 4	112	1.02 ± 0.13	2.60 ± 0.29
	[BMIM][PF6]	159 ± 1	201	1.13 ± 0.09	1.95 ± 0.02
Ferrocene	KCl	56 ± 1	1	$2.01\pm0.40*$	N/A
	[BMIM][OTF]	133 ± 6	90	2.81 ± 0.93	4.88 ± 1.24
	[BMIM][BF4]	142 ± 4	112	1.30 ± 0.33	2.89 ± 0.79
	[BMIM][PF6]	188 ± 3	201	0.44 ± 0.04	0.69 ± 0.01

Table 6.6. Summary of cyclic voltammetric data for FCA, FeMeOH and ferrocene in KCl, [BMIM][OTF], [BMIM][BF₄], and [BMIM][PF₆] measured at *ta*-C:N 30 sccm electrodes (n=3).

Redox analyte concentrations were 0.1 mM in KCl and 1mM in RTILs. Scan rate = 0.1 V s⁻¹. Geometric area = 0.2 cm^2 .

^a The apparent heterogeneous electron-transfer rate constants were determined from the ΔE_p - υ method described by Nicholson.³⁶

N/A - Peak splitting is out of the peak splitting interval defined by Nicholson; k^{0}_{app} cannot be calculated.

The k^{0}_{app} for ferrocene decreases with increasing viscosity of the RTIL. Calculated values are 0.69 (± 0.01) × 10⁻⁴ [BMIM][PF₆], 2.89 (± 0.79) × 10⁻⁴ [BMIM][BF₄], and 4.88 (± 1.24) × 10⁻⁴ cm s⁻¹ [BMIM][OTF].The viscosity of the electrolyte solution affects the rate constant by reducing the frequency of attempts the reactant makes to surmount the activation barrier and convert to the product, the so-called nuclear frequency factor, v_n . Based on the transition state theory, the k^0_{app} can be expressed as follows:

$$k^{0} = K_{p}\kappa_{el}\nu_{n}exp\left(-\frac{\Delta G^{*}}{RT}\right)$$
(6.2)

where K_p is the precursor equilibrium constant, κ_{el} is the electronic transmission coefficient, ν_n is the nuclear frequency factor, ΔG^* is the Gibbs free energy for electron transfer, R is the gas constant, and T is the absolute temperature.⁴⁰ As the equation indicates, the rate constant is in a direct relationship with a nuclear frequency factor, ν_n . The ν_n describes the effective frequency of passing through the transition state. The dynamics of such as process are in indirect correlation with the electrolyte viscosity, $1/\eta$. Even though we were not able to calculate the k^{0}_{app} for the ferrocene derivates, the previously published research by our group has reported a k^{0}_{app} of 5.5 (± 1.2) × 10⁻² cm s⁻¹ for ferrocene in aqueous solutions. Consequently, the k^{0}_{app} values for ferrocene in RTILs used in this investigation are approximately 100 times higher compared to the aqueous solution, that is in a perfect agreement with its viscosity (Table 6.6).

Besides ferrocene, ferrocene carboxylic acid and ferrocene methanol were also studied. The cyclic voltammetric *i*-*E* curves of FCA and FeMeOH in [BMIM][OTF] are presented in Figure 6.17. Similarly to ferrocene, the electron-transfer kinetics of FCA and FeMeOH are quasireversible at these low scan rates and strongly dependent on the RTIL viscosity. For both redox couples, the redox reaction is diffusion controlled, as the i_p^{ox} increases linearly with an increasing square root of scan rate. The calculated diffusion coefficients for FCA and FeMeOH in [BMIM][OTF] are 1.37 (± 0.04) and 1.33 (± 0.03) × 10⁻⁷ cm² s⁻¹, which is approximately 100 × lower compared to values in aqueous electrolyte solutions. As was the case of ferrocene, the diffusion coefficients for these two redox systems are influenced by the viscosity of the RTIL (1 mPa s for KCl versus 90 mPa s for [BMIM][OTF]). The heterogeneous electron-transfer rate constants of FCA and FeMeOH in [BMIM][OTF] are 2.86 (\pm 0.20) and 4.55 (\pm 0.30) × 10⁻⁴ cm s⁻¹. An almost identical conclusion was conceded for all investigated redox species: the electron transfer rate is affected by the RTILs and its viscosity, with a highest rate for the least viscous [BMIM][OTF], and the smallest rate value for the most viscous [BMIM][PF₆].



Figure 6.17. Cyclic voltammetric *i*-*E* curves of 1 mM FCA (**A**) and FeMeOH (**B**) in [BMIM][OTF] measured at a 30 sccm t*a*-C:N thin-film electrode at increasing scan rate from 0.1 to 0.5 V s⁻¹. Geometric area = 0.2 cm^2 .

6.2.2 Surface Modification by RF Oxygen Plasma Treatment

The t*a*-C:N films consisted of some native surface carbon-oxygen functional groups. Preliminary research was conducted to learn how changing the surface chemistry of these electrodes affects heterogeneous electron-transfer reactions in RTILs. The surfaces were chemically modified in an RF oxygen plasma. The plasma modification was performed using a commercial plasma cleaner(PCD-32G, Harrick Scientific). The oxygen pressure in the chamber was maintained to 300 mtorr during the treatment for a 15 min period. The plasma power was 18 W.

The plasma-treated ta-C(:N)_x electrode surfaces were characterized by Raman spectroscopy, scanning electron microscopy, atomic force microscopy, and static water contact angle measurements. The SEM micrographs and AFM images revealed no detectable morphological changes in the film after treatment. For example, there was no detectable roughening, surface etching or film detachment after the plasma treatment. The Raman spectroscopic and contact angle measurements, however, revealed changes in the microstructure and surface chemistry after treatment. These changes are described below.

Raman Spectroscopy

Raman maps $(100 \times 100 \ \mu\text{m})$ the G-band position evaluated from spectra measured at different points across the *ta*-C:N 30 sccm film surface are shown below Figure 6.18A and B show data for a film before and after the 15 min O₂ plasma treatment. The G-band position, as well as the I_D/I_G intensity ratio, affected by the plasma treatment. The O₂ plasma treatment causes a slight shift in the G-band line from 1549.7 ± 1.2 to 1542.4 ± 0.5 cm⁻¹, while the I_D/I_G intensity ratio decreases from 0.89 ± 0.04 to 0.76 ± 0.01 . These trends suggest that the O₂ plasma treatment leads to an increasing ratio of the sp³ to sp²-bonded carbon in the film. This can be understood by considering that the gasification rate of sp²-bonded carbon by atomic oxygen produced in the plasma in greater than the gasification rate of the sp³-bonded carbon. Therefore, more of the sp²-bonded carbon is removed as CO or CO₂ driving the process. Summary data for the Raman characterization are presented in Table 6.2.



Figure 6.18. Raman spectra maps of the G-band peak position recorded over $100 \times 100 \,\mu\text{m}$ on the t*a*-C:N films (30 sccm N₂) (A) before and (B) after 15 min O₂ plasma treatment. Laser power = 4.5 W, $\lambda_{\text{exc}} = 532$ nm, integration time = 3 sec.

Electrode treatment	I_D/I_G	G band position (cm ⁻¹)
As grown	0.87 ± 0.04	1549.7 ± 1.2
Oxygen plasma modified	0.74 ± 0.01	1542.4 ± 0.5

Table 6.7. Raman spectral parameters for as grown and after oxygen plasma modified ta-C:N (30 sccm) electrodes (n = 10 000).

Static Contact Angle Measurement

The water wettability of the electrode surfaces was significantly affected by the O₂ plamsa treatment. The surface oxygenated t*a*-C:N electrodes exhibited significantly diminished values of contact angle; $48 \pm 2^{\circ}$ (t*a*-C), $44 \pm 1^{\circ}$ (t*a*-C:N 10 sccm), $38 \pm 1^{\circ}$ (t*a*-C:N 30 sccm) and $35 \pm 2^{\circ}$ (t*a*-C:N 50 sccm), compared to those recorded at "as received" t*a*-C(:N)_x (Figure 6.19). The values indicate the O₂ plasma treatment increased electrode surface hydrophilicity.⁷ The decreased



Figure 6.19. Static contact angle values for water on the t*a*-C and t*a*-C:(N)_x electrodes deposited with 0, 10, 30 and 50 sccm of N₂ before and after a 15 min O₂ plasma treatment. Data obtained on as grown (black squares) and O₂ plasma modified (red circles) electrodes are shown (n=3).

contact angle indicates strong attractive forces with the surface that cause the liquid to spread. The introduction of polar oxygen functional groups maybe responsible for these attraction dipoledipole forces. The surface tension of water decreases on the plasma-treated surfaces.⁴¹ The trend of decreasing water contact angle with increased N content suggests an influential role of the sp²- carbon sites. Therefore, as the N content and consequently the fraction of sp² bonded carbon in the film increase, the concentration of polar surface carbon-oxygen functional groups likely increase and the hydrophilicity increases.³⁴ It could also be that the types of carbon-oxygen functional groups.

Atomic Force Microscopy

As mentioned above, no morphological changes were observed by SEM or AFM after exposure to the O₂ plasma treatment. The AFM images of as grown and O₂-plasma modified *ta*-C:N (30 sccm) electrodes are shown in Figure 6.20. The roughness of the electrode surfaces was calculated over an area of $3 \times 3 \mu m$. A significant increase in the film roughness caused by the oxygen radicals etching the carbons in the film was expected.⁴² However, the film morphology remained relatively unchanged, with surface roughness values of 12 ± 4 and 16 ± 2 nm for the as grown and O₂-plasma modified films, respectively. Therefore, it is expected that the roughness of the film is controlled by the bonding fraction rather than the atoms bonded on the film surface.⁴³



Figure 6.20. AFM images of an (**A**) as grown and (**B**) O₂-plasma modified t*a*-C:N (30 sccm) electrode. The plasma treatment conditions were 300 mtorr O₂, 18 W, and 15 min.

Background Voltammetric Currents

Figure 6.21 shows background cyclic voltammetric *i-E* curves in 1 M KCl for an as-grown and O₂-plasma modified t*a*-C:N (30 sccm N₂) thin-film electrode at 0.1 V s⁻¹. Both curves are featureless in the investigated potential window, and the current magnitude did not change with cycle number. The current – scan rate dependence (not shown) was linear, indicating purely capacitive current. The background current in 1 M KCl decreased slightly after the O₂-plasma treatment. Accordingly, the double layer capacitance decreased from 53.1 ± 1.9 to 45.4 ± 1.2μ F cm⁻². The same decreasing trend in capacitance was observed for all the investigated O₂plasma treated t*a*-C(:N)_x thin-film electrodes (Table 6.8). A possible reason for this is the increase in the sp³/sp² carbon ratio at the surface that is caused by the gasification of some of the sp²-bonded carbon on the surface. It is well known that the background voltammetric current, as well as the



Figure 6.21. Background cyclic voltammetric *i-E* curves for t*a*-C:N thin film electrode (30 sccm N₂) as grown (black) and after oxygen plasma treatment (red curve) in 1 M KCl. Scan rate = 0.1 V s^{-1} . Geometric area = 0.2 cm^2 . The O₂ plasma treatment conditions: 300 mtorr O₂, 18 W, and 15 min.
double layer capacitance, is influenced by the microstructure of the carbon electrode material.⁴⁴ The sp²-bonded carbon contributes electronic states in the band gap. Loss of these states reduces the excess surface charge at different potentials leading to less counterbalancing charge on the solution side of the interface, *i.e.*, lower C_{dl} . The loss of the sp² carbon surface layer would also reduce any faradaic current associated with surface redox processes.

Table 6.8. Calculated capacitance (cyclic voltammetric current at 0.2 V) for t*a*-C and t*a*-C:N thin-film electrodes before and after O_2 plasma treatment. The films used were grown with 0, 10, 30 and 50 sccm N_2 added. (n = 3).

	As Grown	Oxygen Plasma Modified		
Electrode	Capacitance, µF cm ⁻²	Capacitance, µF cm ⁻²		
ta-C	46.4 ± 1.8	38.8 ± 2.7		
ta-C:N 10sccm	51.3 ± 1.6	43.0 ± 1.4		
ta-C:N 30sccm	53.1 ± 1.9	45.4 ± 1.2		
ta-C:N 50sccm	59.8 ± 1.3	47.2 ± 1.4		

Electrochemical Activity of Inner-Sphere and Outer-Sphere Redox Couples

Figure 6.22 A shows cyclic voltammetric *i-E* curves for Fe(CN)₆-3^{/-4} in 1 M KCl measured at an as grown (black) and O₂ plasma-treated (red) t*a*-C:N (30 sccm N₂) electrode. In both cases, the curves reveal well-defined redox waves. The oxygen-terminated surface is expected to inhibit the Fe(CN)₆-3^{/-4} electron-transfer kinetics, at least for BDD electrodes.⁸ Interestingly, a rather unexpected result was obtained and that is the plasma treatment increase the rate of electrontransfer based on a decreased nominal ΔE_p values from 102 ± 8 to 77 ± 1 mV, as compared with the as-deposited electrode. Thus, the electrode reaction kinetics become faster with k^0_{app} increasing from 0.64 (± 0.20) × 10⁻² cm s⁻¹ for the as-deposited to 2.04 (± 0.13) × 10⁻² cm s⁻¹ for the plasmatreated films. This represents a 3× increase in rate constant for this inner-sphere redox system. Table 6.9 reveals that faster electron-transfer kinetics were observed for all the t*a*-C(:N)_x films after O₂ plasma treatment for this redox system. Figure 6.22B shows cyclic voltammetric *i-E* curves for Ru(NH₃)₆^{3+/2+} in 1M KCl. Unlike Fe(CN)₆-^{3/-4}, the Ru(NH₃)₆^{3+/2+} redox reaction kinetics



Figure 6.22. Cyclic voltammetric *i-E* curves for (**A**) 0.1 mM $Fe(CN)6^{3-/4-}$ and (**B**) $Ru(NH_3)6^{3+/2+}$ both in 1 M KCl, at an as deposited (black) and O₂ plasma treated (red) t*a*-C:N thin-film electrode (30 sccm N₂). Plasma treatment conditions:300 mtorr,18 W and 15 min. Scan rate = 0.1 V s⁻¹. Geometric area = 0.2 cm².

are largely insensitive to the carbon electrode (HOPG, GC and BDD) microstructure, surface chemistry and surface cleanliness. The main factor affecting the kinetics is the electrode conductivity (*i.e.*, density of electronic states). The results reveal no difference in peak currents or ΔE_p after the O₂ plasma treatment. The same trend was observed for all the t*a*-C:N films with difference levels of incorporated N. Reversible behavior was seen for all of these films at scan rates up to 0.5 Vs⁻¹.

Table 6.9. Summary of cyclic voltammetric data for $Fe(CN)_6^{-3/-4}$ and $Ru(NH_3)_6^{+3/+2}$ in 1 M KCl measured at ta-C:(N)_x electrodes before (grey background) and after (white background) O₂ plasma modification (n = 3 electrodes of each type).

Analyte	Electrode	$i_{p}^{ox}(\mu A)$	$\Delta E_{p}\left(mV\right)$	D _{ox} , 10 ⁻⁵ (cm ² s ⁻¹)	k ^θ app, 10 ⁻² (cm s ⁻¹)
Fe(CN) ₆ ^{3-/4-}	ta-C	7.08 ± 0.39	109 ± 12	1.07 ± 0.20	0.49 ± 0.02
		6.85 ± 0.32	96 ± 7	1.07 ± 0.12	0.77 ± 0.33
	ta-C:N 10sccm	7.34 ± 0.36	102 ± 8	1.04 ± 0.27	0.64 ± 0.20
		7.52 ± 0.27	77 ± 1	1.56 ± 0.13	2.04 ± 0.13
	ta-C:N 30sccm	7.58 ± 0.60	74 ± 4	1.54 ± 0.50	1.91 ± 1.25
		7.74 ± 0.54	66 ± 1	1.95 ± 0.06	5.74 ± 0.38
	ta-C:N 50sccm	8.06 ± 0.08	83 ± 3	1.66 ± 0.07	1.49 ± 0.22
		7.40 ± 0.08	67 ± 1	1.70 ± 0.04	5.03 ± 0.71
$Ru(NH_3)_6^{2+/3+}$	ta-C	8.41 ± 0.15	56 ± 1	2.53 ± 0.05	N/A
		7.67 ± 0.06	56 ± 2	2.23 ± 0.21	N/A
	ta-C:N 10sccm	8.10 ± 0.12	56 ± 1	2.46 ± 0.10	N/A
		7.96 ± 0.21	56 ± 1	2.27 ± 0.09	N/A
	ta-C:N 30sccm	7.79 ± 0.34	56 ± 1	2.17 ± 0.15	N/A
		8.34 ± 0.23	55 ± 1	2.27 ± 0.09	N/A
	ta-C:N 50sccm	8.23 ± 0.16	57 ± 1	2.31 ± 0.15	N/A
		7.39 ± 0.18	57 ± 1	2.02 ± 0.10	N/A

Scan rate = 0.1 V s^{-1} . Geometric area = 0.2 cm^2 .

The apparent heterogeneous electron-transfer rate constants were determined from the ΔE_p -v method described by Nicholson.³⁶

N/A - Peak splitting is out of the peak splitting interval defined by Nicholson; k^{0}_{app} cannot be calculated.



Figure 6.23. The variation of heterogeneous electron-transfer rate constant for $Fe(CN)_6^{-3/-4}$ in 1 M KCl at ta-C(:N)_x thin-film electrodes deposited with different N₂ gas flow rates.

Figure 6.23 plots the normal rate constant, k^0_{app} , for Fe(CN)₆^{-3/-4} for the different t*a*-C:N films The rate constant increases with increasing N₂ flow (*i.e.*, increasing N content in the film and increasing fraction of sp²-bonded carbon) used during the electrode deposition. The exception is the result for the 50 sccm t*a*-C:N electrode where a slight decrease was observed. Rate constants are higher for the O₂ plasma -reated electrodes. Factors that could be contributing to the increased kinetics are i) introduction of more active sites for this surface-sensitive redox system and/or ii) potential electrode cleaning by the O₂ plasma treatment.

Investigation of redox system activity were also performed in RTILs. A comparison of data for a t*a*-C:N (30 sccm N₂) thin-film electrode before and after O₂ plasma treatment is shown in Figure 6.24. Data are presented for FeMeOH in KCl, [BMIM][OTF], [BMIM][BF₄], and

[BMIM][PF₆] (Fig. 6.24 A-D). For FeMeOH in KCl (Fig. 6.24 A), ΔE_p and peak currents were unchanged after plasma treatment. Fast electron-transfer was observed on both electrodes as the ΔE_p values were 56 ± 1 mV.

Figure 6.24 B shows curves for 1mM FeMeOH in [BMIM][OTF] before (black) and after (red) treatment. This result also confirms that there is no change in the electrical conductivity or electronic properties of the electrode after treatment. The ΔE_p value increased from 115 ± 4 mV to



Figure 6.24. Comparison of cyclic voltammetric *i-E* curves for 1mM FeMeOH in 1M KCl (**A**), [BMIM][OTF] (**B**), [BMIM][BF₄] (**C**), and [BMIM][PF₆] (**D**) recorded at a *ta*-C:N (30 sccm N₂) thin-film electrode before (black) and after (red) oxygen plasma modification. Scan rate = 0.1 V s^{-1} . Geometric area = 0.2 cm^2 .

153 ±9 mV, indicating more sluggish electron-transfer kinetics. The k^{0}_{app} decreased from 4.55 $(\pm 0.30) \times 10^{-4}$ to 1.99 $(\pm 0.44) \times 10^{-4}$ cm s⁻¹. Rate constant data are presented in Table 6.10. Interestingly, a different effect was observed for the same redox system in the other two RTILs, [BMIM][BF4] and [BMIM][PF6]. Slight decrease in the nominal ΔE_p and increase in the calculated k^{0}_{app} values were observed. The values for k^{0}_{app} increased from 2.60 (± 0.29) to 3.51 (± 0.85) × 10⁻⁴ cm s⁻¹ in for [BMIM][BF4] and from 1.95 (± 0.02) × 10⁻⁴ to 2.91 (± 1.13) × 10⁻⁴ cm s⁻¹ in [BMIM][PF6]. Statistical analysis revealed no difference in the values at p ≤ 0.05.

Table 6.10. Summary of cyclic voltammetric data for $Fe(CN)_6^{-3/-4}$ and $Ru(NH_3)_6^{+3/+2}$ in 1 M KCl and different RTILs measured at ta-C:(N)_x electrodes before (grey background) and after O₂ plasma (white background) treatment (n = 3 electrodes of each type).

		As Grown	After O ₂ Plasma Treatment
Analyte	Electrolyte	$k^{0}_{app,} 10^{-4} (\mathrm{cm \ s^{-1}})$	k^{0}_{app} , 10 ⁻⁴ (cm s ⁻¹)
FCA	KCl	N/A	N/A
	[BMIM][OTF]	2.86 ± 0.20	2.24 ± 0.31
	[BMIM][BF4]	1.92 ± 0.23	2.88 ± 0.03
	[BMIM][PF6]	1.90 ± 0.21	2.54 ± 0.63
FeMeOH	KCl	N/A	N/A
	[BMIM][OTF]	4.55 ± 0.30	1.99 ± 0.44
	[BMIM][BF4]	2.60 ± 0.29	3.51 ± 0.85
	[BMIM][PF6]	1.95 ± 0.02	2.91 ± 1.13
Ferrocene	KCl	N/A	N/A
	[BMIM][OTF]	4.88 ± 1.24	3.74 ± 0.39
	[BMIM][BF4]	2.89 ± 0.79	3.17 ± 0.44
	[BMIM][PF6]	0.69 ± 0.01	2.05 ± 0.72

Scan rate = 0.1 V s^{-1} . Geometric area = 0.2 cm^2 .

The apparent heterogeneous electron-transfer rate constants were determined from the ΔE_p -v method described by Nicholson.³⁶

N/A - Peak splitting is out of the peak splitting interval defined by Nicholson; k^{0}_{app} cannot be calculated.

Overall the results indicate a slight variation in the electrode activity for the different redox systems in the three RTILs after plasma treatment. The variation is seen in the values for k^{0}_{app} but statistically given the variabilities, there was no significant difference in k^{0}_{app} before and after treatment. This could be because of a low n value of 3. The exception was for ferrocene in [BMIM][PF₆]. The k^{0}_{app} increased from 0.69 (± 0.01) × 10⁻⁴ (as grown) to 2.05 (± 0.72) × 10⁻⁴ cm s⁻¹ (O₂ plasma treatment).

6.3. Conclusions

Tetrahedral amorphous carbon thin-film electrodes deposited with various N_2 flow rates of 0, 10, 30, and 50 sccm were characterized. The increasing N_2 flow rate leads to increasing N content and sp²-bonded carbon within the film, although the changes for these films were not as dramatic as have were reported previously.¹ The as grown and O_2 plasma-treated electrodes were characterized by Raman spectroscopy, AFM, XPS, static water contact angle measurements, and electrochemical methods using different redox systems in aqueous electrolytes and RTIL media.

XPS revealed that the N content in the near-surface region increased with N₂ flow rate during deposition. XPS also revealed that the near-surface microstructure of the t*a*-C:N_x films consists of a mixture of sp² and sp³-bonded carbon. The percentage of sp²-bonded carbon in the near-surface region and presumably in the bulk, increased with increasing N incorporation, ranging from 70.3 % for pure t*a*-C to 83.0 % for t*a*-C:N 30 sccm. It should be noted that the XPS date reflect the microstructure in the upper 10 nm of the films where an amorphous carbon layer is known to form. Therefore, these high fractions of sp² carbon maybe reflective of this layer and not the fraction within the films. The percentage of sp² carbon in these ta-C:N films is higher and do not vary as much as we have previously reported for another batch of films.¹ AFM results revealed that the roughness of the ta-C:N_x increases with the nitrogen incorporation.

As the N content in the films increases, the electrochemical behavior also changes. The voltammetric background current and the double layer capacitance increase increase with N content. The relatively rapid electron-transfer kinetics for $Fe(CN)_6^{-3/-4}$ increase with an increasing N content. The kinetics of outer-sphere redox system, $Ru(NH_3)_6^{+3/+2}$, were largely unchanged with the N content indicating that the electronic properties of the films are not significantly altered by the N incorporation.

The kinetics of electron transfer in RTILs were investigated using ferrocene, ferrocene methanol and ferrocene carboxylic acid. The diffusion coefficients and heterogeneous electron-transfer rate constants for these redox systems were ca. $100 \times 100 \times$

The oxygenated t*a*-C(:N)_x thin-film electrodes produced by RF plasma treatment showed enhanced electrode kinetics for Fe(CN)₆^{-3/-4} in aqueous electrolyte solutions, suggesting a possible increase in the density of active sites and or a cleaning effect by the oxygen plasma. For the outersphere redox system Ru(NH₃)₆^{+3/+2}, no changes in ΔE_p and k^0_{app} were observed on ta-C:N electrodes before and after plasma treatment. The electron-transfer kinetics for ferrocene and the ferrocene derivatives in the RTILs did not follow a clear trend at the plasma-modified electrodes. Future work will continue to investigate the effects of surface modification on heterogeneous electron-transfer kinetics at *ta*-C:N electrodes.

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CHAPTER 7. HPLC-ED ANALYSIS OF ESTROGENIC COMPOUNDS: A COMPARISON OF AN ANALYTICAL PERFORMANCE OF DIAMOND AND TETRAHEDRAL AMORPHOUS CARBON ELECTRODE PERFORMANCE

7.1. Introduction

High-pressure liquid chromatography with amperometric detection was used to quantify estrogenic compounds in water samples. The main goal was to compare the detection figures of merit for boron-doped diamond and nitrogen-incorporated tetrahedral amorphous carbon thinfilm electrodes. The target analytes were endocrine disrupting compounds (EDCs). Furthermore, EDCs in spiked tap, natural well and river water samples were quantified.

Different carbon electrodes have been utilized for electroanalytical measurements . These include glassy carbon, pyrolytic graphite, and polycrystalline diamond.¹ As glassy carbon electrodes have been in use for many years, significant research has been dedicated to its characterization.^{1–3} Nevertheless, due to its microstructure, glassy carbon is subject to a surface fouling and unwanted microstructural changes at very positive potentials that are often required to detect target pharmaceuticals and pollutants.^{4–9} In contrast, BDD electrodes exhibit excellent properties for electroanalytical measurements, such as wide potential window, low background current, microstructural stability at high potentials, low limits of detection, weak molecular adsorption, fouling resistance, and response reproducibility. As presented and discussed in previous chapters, the ta-C:N electrodes exhibit similar electrochemical properties as compared to those of BDD. These superb properties make both the BDD and ta-C:N electrode materials attractive candidates for electroanalytical measurements. Even though the ta-C:N electrodes have not yet been investigated extensively in electroanalysis, they are currently receiving an increasing scientific interest. Traditionally, electrochemical detectors are coupled with flowing techniques, such as flow injection analysis,^{9–11} high-pressure liquid chromatography,^{12,13} or capillary zone

electrophoresis.^{14,15} Such as detection schemes are attractive because they are inexpensive, field deployable and provide excellent detection figures of merit.

EDCs have garnered increasing attention within the scientific community in recent years because they are a class of organic pollutants that mimic the function of endogenous hormones.^{16,17} EDCs include estrogen and estrogen-like compounds with the three main naturally- occurring estrogens being estradiol, estriol, and estrone (Figure 7.1).^{18,19} Worldwide, steroidal estrogens pose a threat to human and aquatic health because of their increasing prevalence in soil, plants and water supplies.¹⁹ ECDs have a key role in the female reproductive system and secondary sex characteristic development.^{20,21} Moreover, it has been proven that ECDs have a regulatory role in several physiological processes during growth, for example in nervous system maturation,²² bone formation²³ or fat deposition.²⁴ Numerous studies have also shown that increased levels of urinary estrogen metabolites may lead to an increased risk of breast cancer,^{25–27} cognitive dysfunction²⁸ or coronary artery disease.²⁹ Research also shows that endocrine disruptors may pose the greatest risk during prenatal and early postnatal development when organ and neural systems are forming.

These estrogen metabolites, which are excreted by humans and animals, are not completely removed by conventional water purification systems. Therefore, they can enter natural bodies of water and soil through industrial and municipal effluent and agricultural runoff.^{16,17,19,30} Other endocrine disruptors may also be found in many everyday products including plastic bottles, metal



Figure 7.1. Chemical structures of steroidal estrogens: estradiol (A), estriol (B), and estrone (C).

food cans, detergents, flame retardants, food, toys, cosmetics, and pesticides. Currently, the estrogen metabolites are on the E.P.A.'s Contaminant Candidate List 3. As such, these are contaminants currently not subject to any primary drinking water regulation. This will likely change in the future as these contaminants become more prevalent, so there will be a need for inexpensive, rapid, and sensitive methods for the detection of estradiol, estriol, and estrone in various sample types (water, soil, biological fluids).

Several methods have been employed for the determination of estrogen metabolites in biological fluids and aqueous media, including high-performance liquid chromatography,^{31–34} liquid chromatography-mass spectrometry,³⁵ gas chromatography-mass spectrometry¹⁸ and flow injection analysis with amperometric detection.^{4,5} Brocenschi et al. were the first to report on the electrooxidation of estrone at BDD and t*a*-C:N thin-film electrodes.⁴ Estrone undergoes irreversible oxidation at ~0.9 V vs. Ag/AgCl in 0.5 mol L⁻¹ H₂SO₄ with little to no adsorption.⁴ The authors also reported on the quantification of estrogenic compounds by flow injection analysis with amperometric detection using a BDD thin-film electrode. A detection limit (S/N=3) of 0.1 µmolL⁻¹ was reported.⁵ Wang et al. employed HPLC–EC for the detection of estradiol metabolites in urine samples and obtained detection limits less than 1 ngmL⁻¹ for all compounds.³¹ Other groups have reported on the detection of estrogenic compounds on chemically functionalized BDD,³⁶ Ni-modified glassy carbon³⁷ and metal porphyrin-modified graphene oxide.³⁸ So far, there has not been a comparison of the detection figures of merit for estrogenic metabolites by HPLC–EC using BDD and t*a*-C:N thin-film electrodes.

7.2. Results and Discussion

Low background current and noise (standard deviation about the mean), and a quick stabilization time after potential application are key attributes of a desirable electrode material for HPLC–EC. Background currents for these BDD and t*a*-C:N electrodes in 10 mmol L⁻¹ phosphate buffer (pH 3)/acetonitrile (60:40 v/v%) were measured over a 30-min period at applied potentials from 0.8 to 1.5 V. This potential range is where the estrogenic compounds undergo oxidation.^{4,5} In this mixed mobile phase, stabilization times for both electrodes were in the 5–10 min range. This compared to 15–30 min, or longer, for freshly polished glassy carbon. Figure 7.2 shows (A) background current and (B) noise values as a function of potential for the BDD and *ta*-C:N electrodes in the mixed water-organic mobile phase. The background current plotted is the average value over the last 5 min of a 30-min period. The noise is the standard deviation of the 5-min current data. Both electrodes displayed increasing background current with potential, however, there was no significant difference in the values for the two at potentials from 0.8 to 1.3 V.



Figure 7.2. Plots of the (**A**) mean background current and (**B**) noise for *ta*-C:N and BDD thin-film electrodes as function of the applied potential from 0.8 to 1.5 V. Measurements were made in the mobile phase 10 mmol L⁻¹ phosphate buffer (pH 3)/acetonitrile (60:40 v/v%). Flow rate = 2 mL min⁻¹.

Differences were observed above 1.3 V with the current being slightly greater for BDD. The noise at all potentials was lower for the *ta*-C:N electrode. Past work revealed that the background current and noise are generally slightly lower for BDD as compared to *ta*-C:N electrodes.^{6–9} The reason for the opposite behavior observed herein is unclear but maybe be related to the fact that this particular *ta*-C:N film may have had a lower fraction of electrochemically active area than past *ta*-C:N electrodes used.^{6–9} The physiochemical and electronic properties of *ta*-C:N films tend to be more variable than BDD films. Importantly, the background current and noise for both of these novel carbon electrodes are 5–10× lower than the values for glassy carbon. Analytical advantages of BDD and *ta*-C:N electrodes are their superb microstructural stability and oxidation resistance that lead to low and stable (minimal drift) background currents and allow them to be used at high positive detection potentials.

In order to determine the optimum detection potential for estriol, estradiol and estrone, hydrodynamic voltammograms were recorded at both electrodes over a potential range from 1.0 to 1.5 V in 0.5 V increments. This potential range was determined from prior voltammetric and FIA–EC results.^{4,5} Figure 7.3 shows the resulting curves recorded using (A) *ta*-C:N and (B) BDD electrodes. A well-defined limiting current region is not seen for any of the analytes at either electrode because the oxidation current for the reaction occurs at potentials near the onset for solvent discharge (*i.e.*, water electrolysis) for both electrodes, the optimum detection potential for the analysis appears to be close to 1.4 V in this mixed mobile phase. The slightly higher current recorded for BDD is most likely due to a difference in the channel height of the thin-layer gasket used in the flow cell. This variation results from differences in how tightly the two pieces of the flow cell are connected (*i.e.*, how compressed the neoprene gasket is). It should be noted that more sigmoidally-shaped hydrodynamic voltammograms were observed for these analytes at different



Figure 7.3. Hydrodynamic voltammograms for 20 μ L of 100 μ mol L⁻¹ estriol, estrone and estradiol in 10 mmol L⁻¹ phosphate buffer (pH 3)/acetonitrile (60:40 v/v%) recorded at (**A**) *ta*-C:N and (**B**) BDD thin-film electrodes. Flow rate = 2 mL min⁻¹.

BDD and t*a*-C:N electrodes ^{4,5} It is presumed that the differences in curve shapes are due to slight variations in the boron-doping level, surface chemistry and, in the case of t*a*-C:N, the nitrogen content. Increased film conductivity, for example, will shift the onset current for the estrogenic compound oxidation to less positive potentials ($E_{1/2}$ ~1.2–1.3 V).

In cases where a well-defined hydrodynamic curve is not observed, a better measure of the optimum detection potential can be gained from plots of the signal-to-background ($I_{tot}-I_{bkg}/I_{bkg}$) ratio (S/B) versus the applied potential. Such plots are presented in Figure 7.4 for both electrodes. The optimum detection potential for all three electrodes is between 1.35 and 1.50 for t*a*-C:N and 1.40 to 1.50 V for BDD. The lower background current for the t*a*-C:N electrode leads to a greater S/B ratio. Based on these data, a detection potential of 1.40 V was selected for all three estrogenic compounds in the HPLC–EC analysis described below. The larger current observed for estriol is due to a greater number of electrons transferred per molecule in the oxidation reaction (2 vs.1).⁵

The onset potential for measurable oxidation current for the estrogen compounds in this mixed mobile phase is 1.2 V for BDD and slightly less positive for t*a*-C:N.

Reversed-phase HPLC separation of all three estrogenic compounds was achieved within a total run time of 8 min using conditions slightly modified from those reported by Brocenschi et al.⁵ In the present work, the mobile phase was 10 mM phosphate buffer (pH 3)/acetonitrile (60:40% v/v), and the flow rate was 2 ml min⁻¹. Retention times of 1.54, 4.90 and 6.32 min were reproducibly observed for estriol (E1), estradiol (E2), and estrone (E3), respectively, as shown in Figure 7.5. The results were confirmed using HPLC with UV detection.



Figure 7.4. Plots of the signal-to-background ratio vs. potential for all three estrogenic compounds at (**A**) t*a*-C:N and (**B**) BDD electrodes. Values are shown for 20 μ L injections of 100 μ mol L⁻¹ estriol, estrone and estradiol in 10 mmol L⁻¹ phosphate buffer (pH 3)/acetonitrile (60:40 v/v%). Flow rate = 2 mL min⁻¹.



Figure 7.5. Reversed-phase HPLC chromatogram for 20 μ L of 100 μ mol L⁻¹ of estriol, estradiol and estrone in 10 mmol L⁻¹ phosphate buffer (pH 3)/acetonitrile (60:40%, v/v) recorded at *ta*-C:N thin-film electrode. Detection potential = 1.4 V. Flow rate = 2 ml min⁻¹.

The response reproducibility (retention time and peak height) was investigated by performing 30 injections of 100 μ mol L⁻¹ estriol, estradiol and estrone in 10 mmol L⁻¹ phosphate buffer (pH 3)/acetonitrile (60:40 v/v%) at t*a*-C:N and BDD thin-film electrodes. Figure 7.6 shows chromatograms for 10 consecutive injections. Table 6-1 presents quantitative data for the peak height (signal) and retention time reproducibility over 30 injections.

Analyte	Electrode	Signal reproducibility (%RSD)	Retention time reproducibility (%RSD)
Estriol	BDD	8.13	3.91
	ta-C:N	6.18	1.55
Estradiol	BDD	5.04	1.66
	ta-C:N	7.85	1.18
Estrone	BDD	5.29	1.57
	ta-C:N	8.60	1.18

Table 7.1. Short term response reproducibility over 30 consecutive injections of the estrogen metabolite solution recorded at *ta*-C:N and BDD thin-film electrode.

Both electrodes exhibited response reproducibility with values in the 5–8% RSD range. These values were determined from 30 injections over an operational time of 4 h. These values, recorded in an aqueous/organic electrolyte, are slightly higher than previously reported reproducibility data for these analytes at BDD and t*a*-C:N electrodes in FIA–EC using an aqueous electrolyte carrier solution,^{7–9} Importantly, there was excellent response stability over time with no evidence of fouling at an analyte concentration of 100 μ molL⁻¹ and a positive potential of 1.40 V. There was also no evidence of any electrode microstructural alteration as background currents remained low and stable over time. This stable behavior is typical of BDD and t*a*-C:N thin-film electrodes, in contrast to the fouling and structural degradation that occurs at sp² electrode



Figure 7.6. Ten repeated injections of 100 μ mol L⁻¹ estriol, estradiol and estrone in 10 μ mol L⁻¹ phosphate buffer (pH 3)/acetonitrile (60:40 v/v%) recorded at (A) t*a*-C:N and (B) BDD thin-film electrodes. Flow rate = 2 mL min⁻¹. Detection potential = 1.4 V.

materials at extremely positive potentials.⁷ Excellent retention time reproducibility was observed for both used electrodes, with RSD values lower than 4%.

Calibration curves were constructed using external standards ranging in concentration from 100 to 0.2 μ mol L⁻¹ for estriol, and 100 to 0.4 μ mol L⁻¹ for estradiol and estrone. Response curves for both (A) t*a*-C:N and (B) BDD electrodes are presented in Figure 7.7. Replicate measurements were made at each concentration. An excellent linearity over three orders of magnitude in concentration was observed for both electrodes. The linear regression correlation coefficients were greater than 0.995.

A summary of multiple detection figures of merit for both electrodes is presented in Table 6-2. The slopes of the response curves are statistically similar for both t*a*-C:N and BDD indicating equivalent sensitivity for both. The minimum concentrations detected (S/N=3) with BDD were 0.16 μ molL⁻¹ (46 ppb), 0.27 μ molL⁻¹ (73 ppb) and 0.35 μ molL⁻¹ (95 ppb) for estriol, estradiol and



Figure 7.7. Logarithmic calibration curves for 20 μ L injections of estriol, estrone and estradiol in 10 mmol L⁻¹ phosphate buffer (pH 3)/Acetonitrile (60/40 v/v%). Injected concentrations from 0.2 to 100 μ mol L⁻¹, recorded at (A) *ta*-C:N and (B) BDD thin film electrodes. Flow rate = 2 mL min⁻¹.

Analyte	Flootrado	Range of linearity	Slope	D ²	*Limit of detection	
	Liectioue	(µmol L ⁻¹)	(mA mol ⁻¹ L)	K-	$(\mu mol \ L^{-1}) \ (S/N = 3)$	
Estriol	BDD	0.2-100	9.6 ± 0.1	0.9979	0.16 ± 0.01	
	ta-C:N	0.2-100	11.2 ± 0.7	0.9960	0.20 ± 0.03	
Estradiol	BDD	0.4-100	9.9 ± 0.4	0.9992	0.27 ± 0.01	
	ta-C:N	0.4-100	10.5 ± 0.2	0.9967	0.29 ± 0.01	
Estrone	BDD	0.4-100	9.1 ± 0.3	0.9971	0.35 ± 0.03	
	ta-C:N	0.4-100	10.4 ± 0.2	0.9952	0.34 ± 0.02	

Table 7.2. Summary of the analytical detection figures of merit for the estrogenic compounds at *ta*-C:N and BDD thin-film electrodes.

Data are reported as mean \pm standard deviation (n = 3 different electrodes of each type).

estrone, respectively. Similar detection limits were found for t*a*-C:N electrode: 0.20 μ molL⁻¹ (58 ppb) 0.29 μ molL⁻¹ (79 ppb) and 0.34 μ molL⁻¹ (95 ppb) for estriol, estradiol and estrone, respectively. These results indicate that the t*a*-C:N electrode exhibits performance comparable with that of BDD, suggesting the use of this sp²/sp³ carbon material is a reliable option for the detection of organic molecules, such as the estrogenic compounds.

The HPLC–EC method was used to analyze three water samples for estrogenic compounds: river water, well water and local tap water. None of the estrogenic compounds were detected in any of the three as received samples. No preconcentration step was used, such as solid phase extraction, which may have produced detectable signals. Therefore, either the compounds were not present at all or they were present at concentrations below detection limits. The method was then applied (blind analysis by the student) to these three real samples after spiking with the estrogenic compounds, each at a concentration of 7 μ mol L⁻¹ (189–200 ppb). Recovery studies were carried out and the results are shown in Table 6-1-3. In general, high recovery values were obtained using both electrodes for all three estrogenic compounds. The highest recoveries from 91

Table 7.3. Recovery studies of estriol, estradiol and estrone in three different water samples using HPLC–EC with BDD and a t*a*-C:N.

Concentration added (µmol L ⁻¹) 7							
		River water		Well water		Tap water	
Analyte	Electrode	Cdetected	Recovery	Cdetected	Recovery	Cdetected	Recovery
		(µmol L ⁻¹)	(%)	$(\mu mol L^{-1})$	(%)	(µmol L ⁻¹)	(%)
Estriol	BDD	6.68 ± 0.08	95	6.46 ± 0.30	92	7.10 ± 0.65	101
	ta-C:N	7.33 ± 0.11	105	7.08 ± 0.06	101	7.18 ± 0.21	103
Estradiol	BDD	6.10 ± 0.41	87	6.16 ± 0.18	88	7.02 ± 019	100
	ta-C:N	6.38 ± 0.01	91	6.10 ± 0.13	87	6.89 ± 0.13	100
Estrone	BDD	6.03 ± 0.06	86	6.55 ± 0.15	94	6.34 ± 0.13	91
	ta-C:N	6.21 ± 0.01	89	6.40 ± 0.02	91	6.74 ± 0.16	96

to 103% for the three estrogenic compounds were obtained for the tap water. Slightly lower recoveries from 87 to 101% were seen for the well water. Overall, these results indicate that these estrogenic compounds can be detected using these two novel electrodes without loss in the complex matrices of well and river water.

To place these detection figures of merit in some context, comparisons were made with figures of merit reported in the literature for other HPLC–EC methods. The linear dynamic range is wider but the limit of detection of our method is slightly higher than results for one HPLC–EC method reported in the literature for estrone, estradiol and estriol (0.6–8.0 ppb, LOD = 0.19 ppb).³⁹ Glassy carbon was the electrode used for detection. Our detection figures of merit are superior to another HPLC–EC method reported on using glassy carbon modified with carbon nanotubes (estradiol, 1–100 μ M, LOD = 92 ppb).⁴⁰ HPLC–EC methods using solid-phase microextraction produced lower limits of detection for these estrogenic compounds in waste and river water than our method (0.01–0.07 ppb).^{41,42}

7.3. Conclusions

In this study, the analytical performance of BDD and t*a*-C:N electrodes was compared for the determination of three estrogen metabolites (estradiol, estriol, and estrone) by HPLC–EC. Analysis of the compounds in standard solutions, and as received tap water, river water and well water was demonstrated. The results indicate that both *ta*-C:N and BDD are excellent electrodes for detecting these compounds, which require high potentials for oxidation. The electrodes exhibit low background current and noise, have fast stabilization times, require no conventional pretreatment for activation, and afford high stability, high sensitivity, wide linear dynamic range, and relatively low limits of detection. Together with HPLC–EC, *ta*-C:N and BDD electrodes are useful electrodes for the rapid analysis of estrogen metabolites.

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CHAPTER 8. CONCLUSIONS AND FUTURE DIRECTIONS

The goal of this research was to gain a better understanding of how the microstructure and other physical and chemical properties of carbon electrodes (glassy carbon, boron-doped diamond, and nitrogen incorporated tetrahedral amorphous carbon) affect background voltammetric current, capacitance, and heterogeneous electron-transfer kinetics for different systems in aqueous electrolytes and room temperature ionic liquids. A focus was placed on studying ta-C:N_x electrodes due to the fact that it is a relative new type of carbon electrodes that has not been extensively studied. The electrode material possesses many electrochemical characteristics of the famous boron doped materials, such as low background current and noise, microstructural and chemical stability, fast electron transfer kinetics for some redox molecules, weak molecular adsorption, and no conventional surface pretreatment requirement. Equal priority to the ta-C:N was the usage of RTILs as an electrolyte. Room temperature ionic liquids have garnered increasing attention within the electrochemical community world, but their full usage is currently limited because of an incomplete understanding of the double layer organization and its effect on the electron transfer processes.

The basic structural and electrochemical properties of all three carbon electrodes (GC, BDD, and t*a*-C:N) with a focus on t*a*-C:N electrode were investigated in Chapter 3. The background current profile, voltammetric response of multiple redox systems, and heterogeneous electron-transfer rate constants for these redox systems were studied. The obtained results revealed that the background current for the t*a*-C:N electrode falls between that of BDD and GC. k^o values for all the redox analytes at t*a*-C:N were comparable to the values at BDD and GC. The ta-C:N supports relatively rapid electron transfer for a wide range of redox system with formal potentials from ca. 0.9 to -1.0 V vs. Ag/AgCl.

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Room temperature ionic liquids were introduced in Chapter 4. At first, the presence of the most common impurity, water, has been discussed. As RTILs are solvent (water) free medium, their unique properties are significantly affected by its presence. The physical and electrochemical properties (such as viscosity and dielectric constant, hence the voltammetric background current, diffusion coefficient of redox analytes and electron-transfer kinetics) as drastically altered by this contamination. In this chapter, a new effective method for water removal, so called 'sweeping', was introduced and compared with the conventional vacuum drying method. It has been found that the sweeping purification method was superior to the conventional vacuum drying; the process was both water removal and time efficient. Additionally, basic electrochemical properties of t*a*-C:N electrode in contact with RTILs were presented. The electrode exhibited a low and stable background current with a working potential window up to 6 V. Both the background current and the electron transfer kinetics were found to be drastically affected by the water impurity.

The electrochemical behavior of *ta*-C:N electrode in RTILs was fully investigated in Chapter 5. The heterogeneous electron transfer rate constant for ferrocene carboxylic acid in two ionic liquids [BMIM][BF4], [EMIM][BF4] was measured. For comparison of *ta*-C:N electrochemical behavior, the BDD and GC electrodes were used. Even though the FCA is traditionally viewed as a surface insensitive redox system, it has been found that both the electrode microstructure and the RTIL's physical properties have a significant effect on its electron transfer kinetics. Furthermore, the diffusion coefficients and heterogeneous electron transfer rate constants were investigated as a function of temperature. Both studied factors increase with increasing temperature as an effect of decreasing viscosity. Finally, it has been found that the fastest electron transfer kinetics of FCA in both RTILs carries out on the BDD electrode, followed by the *ta*-C:N and GC electrode.

The work described in Chapter 6 investigated the effect of nitrogen incorporation into the ta-C electrodes and its effect on structural, physicochemical and electrochemical properties. Furthermore, the effect of oxygen plasma modification on these properties has been discussed. It has been confirmed that the ta-C(:N)_x consists of sp² and sp³ bonded carbon. The nitrogen incorporation significantly affected the structural and electrochemical properties of the studied ta- $C(:N)_x$ films. The XPS and Raman analysis revealed an increasing sp² content for films deposited with a higher nitrogen flow rate. Also, the increased nitrogen content affects the roughness of the film as the surface become more irregular. The increasing double layer capacitance and the electron transfer kinetics for surface sensitive redox species in aqueous solutions have been observed with the increasing nitrogen content. The kinetics of the electron transfer in RTILs was found to be significantly influenced by the nature of the used RTILs. As the viscosity of the RTILs is about 100×1000 lower compare to the aqueous electrolytes, the diffusion coefficients and rate constants decreased by a factor of ~100. The surface oxygen plasma modification revealed an unexpected behavior; the electron transfer of surface sensitive redox couple was enhanced in the aqueous solution, while there was no significant effect observed in RTILs. The XPS and Raman analysis confirmed and increasing sp³ bonded carbon concentration for the oxygen-terminated films, while no significant surface etching was detected by the AFM.

In the last chapter, the analytical performance of t*a*-C:N electrodes in comparison with BDD electrodes has been studied. The point of interest was focused on the most commonly used analytical technique, high-pressure liquid chromatography. The estrogenic compounds, estrogen, estradiol, and estrone have been chosen as target compounds, due to their relatively problematic electrochemical detection. The detection requires high detection potential, in our case specifically 1.4 V, that can cause a microstructural degradation, commonly seen at sp² carbon electrodes.

Moreover, the analytes tend to adsorb on such as surface, causing the electrode fouling. The *ta*-C:N electrode however exhibit excellent electroanalytical properties, comparable to those of BDD electrode, as both electrodes performed low background current and noise, microstructural stability, and almost identical sensitivity and limits of detection for all three estrogenic compounds.

Little information is available on the surface chemistry of the t*a*-C(:N)_x films after the oxygen plasma modification (Chapter 6). Future thoughtful studies using XPS and Raman analysis may reveal more information on the functional groups presented on the film surface. The effect of the oxygen surface termination could be studied using a suitable redox system sensitive to carbon-oxygen functionalities. The future work could also be focused on other types of surface modification, such as hydrogen termination. Moreover, the molecular functionalization using the electroreduction of aryl diazonium reagents could be investigated. Such as electrode surface functionality that can be incorporated.

Finally, the problematic behavior of charged redox systems (*e.g.*, Fe(CN)₆^{3-/4-}) in RTILs should be studied. During the investigations, it has been found that the electrode activity is problematic because of either poor solubility in RTILs and or electrochemical inactivity presumably due to large activation barriers. The understanding of this issue would be another key step toward understanding the fundamental processes on electrode – electrolyte interface in RTILs.