Investigation of Novel Electrolytes for Use in Lithium-Ion Batteries and Direct Methanol Fuel Cells

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Investigation of Novel Electrolytes for Use in Lithium-Ion Batteries and Direct Methanol Fuel Cells

by

Kartik Pilar

A dissertation submitted to the Graduate Faculty in Physics in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The City University of New York

2018
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This manuscript has been read and accepted for the Graduate Faculty in Physics in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

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ABSTRACT

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Advisor: Steve Greenbaum

Energy storage and conversion plays a critical role in the efficient use of available energy and is crucial for the utilization of renewable energy sources. To achieve maximum efficiency of renewable energy sources, improvements to energy storage materials must be developed. In this work, novel electrolytes for secondary batteries and fuel cells have been studied using nuclear magnetic resonance and high pressure x-ray scattering techniques to form a better understanding of dynamic and structural properties of these materials. Ionic liquids have been studied due to their potential as a safer alternative to organic solvent-based electrolytes in lithium-ion batteries and composite sulfonated polyetheretherketone (sPEEK) membranes have been investigated for their potential use as a proton exchange membrane electrolyte in direct methanol fuel cells. The characterization of these novel electrolytes is a step towards the development of the next generation of improved energy storage and energy conversion devices.
For ajja and ajji.
Acknowledgements

I would like to express my deepest gratitude to my doctoral advisor, Prof. Steve Greenbaum. It is through your tutelage that I have become the scientist that I am today. Your expertise and patience have been invaluable to me through these past years. You have pushed me and encouraged me to go further than I previously thought possible, and for that I am honored and grateful.

I want to give a very special thanks to Dr. Phill Stallworth and Dr. Mallory Gobet. I have relied on both of you countless times to help me with every technical issue I have faced. You have given me guidance through any questions and issues I have experienced through my doctoral research. I cannot fathom making it through graduate school without your help.

I want to thank Prof. Sophia Suarez of Brooklyn College and Prof. Mehdi Zeghal of University of Paris-South for inviting me into their labs and mentoring me through this experience.

Additionally, I would like to thank my colleagues in the NMR lab, Prof. Armando Rua, Dr. Lisa Cirrincione, Dr. Marc Berman, Dr. Tetiana Nosach, Dr. Jing Peng, Domenec Paterno, Daniel Morales, Shen Lai, Stephen Munoz, Sunita Humagain, Nishani Jayakody, Christopher Mallia, Rachel Hecht, Bart Rosenzweig, and last but not least, Lorenzo Carbone. You have not only been my colleagues, but friends as well. Thank you for making my time in and out of the laboratory more enjoyable.

Finally, I would like to thank my family, amma, baba, and Kaushik. Without your love and support, I would be nowhere.
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Chapter 1. Batteries and Fuel Cells

1.1 Introduction

According to the United States Department of Energy, world-wide energy consumption by the year 2050 is projected to increase by more than 40% over 2015 consumption levels.\(^1\) As of 2014, approximately 81% of the world’s energy supply originated from fossil fuel sources.\(^2\) Currently, there is an international movement to shift from fossil fuel based sources towards more environmentally friendly renewable energy sources. The latter, which include solar, hydroelectric, and wind, are all intermittent sources of energy. However, these can be most efficiently utilized by incorporating within the technology improved energy storage and conversion devices. Technological advances along these lines must include improvements to batteries and fuel cells. Current battery research includes the development of environmentally friendly and lower cost Na-ion batteries, increased energy density Li-air batteries, as well as safer Li-ion batteries utilizing ionic liquid electrolytes.\(^3\)–\(^8\) Meanwhile, work on fuel cells include lowering operating temperatures, improved proton exchange membrane performance, and lowering cost.\(^9\)–\(^13\)

Increasing the proportion of energy produced from renewable energy sources is a vital step towards curbing the effects of global climate change.

Besides the environmental benefits, improvements to such technologies can provide significant enhancement to consumer products. Next generation secondary batteries with greater energy density and safety characteristics could be used to replace standard Li-ion and alkaline batteries in consumer electronics, including everything from cell phones, laptop computers, and electric cars. Fuel cells currently have many military applications, including to recharge handheld electronics and to as power sources for unmanned drones, as well as civilian applications, such as in vehicles to replace combustion engines.
The research discussed within this work will cover the characterization of ionic liquids as well as sulfonated polyetheretherketone (sPEEK)-based proton exchange membranes (PEMs). Ionic liquids show promise for use in next-generation Li-ion batteries via their reduced volatility compared to conventional organic solvent-based electrolytes. sPEEK membranes can be used as an electrolyte in direct methanol fuel cells (DMFCs), for use in electric vehicles, potentially as a replacement for combustion engines.

1.2 Lithium-Ion Batteries

Batteries can be thought of as energy storage devices, however the reality is that they convert stored chemical energy into useable electrical energy. Of particular interest in this work are secondary lithium-ion batteries, which can be discharged and charged as needed. John Goodenough is credited with having invented the modern day Li-ion battery in 1980. These batteries are most popular as they provide power to most consumer electronic devices, such as cell phones, tablets, laptops, hoverboards, etc. Compared to alternative battery designs, such as lead-acid and nickel-metal hydride (NiMH), Li-ion batteries exhibit especially high volumetric and gravimetric energy densities. In this way Li-ion batteries have progressively dominated commercial applications. Li-ion batteries consist of three basic components: two electrodes, an anode and cathode, and an electrolyte. A schematic of a Li-ion battery is shown in figure 1.1.
Currently, most Li-ion batteries utilize a Li_{1-x}MO_2 (M = Co, Mn, or Ni) cathode, a Li_xC_6 anode, and an organic solvent electrolyte, such as a mixture of ethylene carbonate ([CH_2O]_2CO) and dimethyl carbonate (OC[OCH_3]_2) with a lithium-based salt, commonly lithium hexafluorophosphate (LiPF_6). Lithium ions move between the anode and cathode through the electrolyte during charging and discharging. During discharging, the anode oxidizes during Li^+ extraction and the cathode reduces during Li^+ insertion (ie. Co(IV) + e^- → Co(III)). This process is reversed during charging. The redox lithium-ion battery chemistry is described by the following relations.

\[
\text{Anode: } Li_aC \leftrightarrow C + aLi^+ + ae^- \]
The right-pointing arrows indicate discharging while the left-pointing arrows indicate battery charging scenarios.

There exists significant room for improvement in lithium-ion battery chemistry. Notably, typical organic solvent electrolytes tend to exhibit high volatility and flammability, leading to safety concerns. Along these lines, this thesis investigates certain ionic liquid (IL)-based electrolytes that show some promise for safer batteries. There is a large effort towards investigating ionic liquid based electrolytes based on their desirable thermal stability. Additionally, by varying cation and anion combinations, ILs can be “tailored” to achieve desired properties. The ionic liquids studied here belong to a subset known as room temperature ionic liquids (RTILs), which remain in the liquid phase at and below room temperature. Chapters 3 and 5 of this thesis will discuss how changes to anion symmetry and cation alkyl chain length in these RTILs effect properties, such as ionic-coordination structures as well as ion dynamics.

1.3 Direct Methanol Fuel Cells

Due to a number of disadvantages with batteries in certain applications, including weight, charging times, etc., fuel cells offer an alternative for larger-scale energy needs. Unlike batteries, which are energy storage devices, fuel cells are purely energy conversion devices, where an externally stored hydrocarbon fuel is fed directly into the fuel cell and converted into electrical energy and CO₂ and H₂O waste. One of the fundamental designs is the hydrogen fuel cell, part of the subset of proton-exchange membrane (PEM) fuel cells, which utilizes compressed hydrogen gas as a fuel source. Although, this device is attractive by its simplicity, theoretical power output and zero carbon footprint, unfortunately, the necessity of using a compressed hydrogen gas storage
and distribution infrastructure is extremely challenging from a safety perspective. On the other hand, an extensive hydrocarbon fuel distribution infrastructure is already in place for liquid (gasoline, propane, diesel, etc.) fuels. This practical matter provides the impetus for investigating the use of hydrocarbon fuels in fuel cells.

Direct methanol fuel cell (DMFC) designs are perhaps the most promising candidates since they consume a simple hydrocarbon fuel, while utilizing current fuel infrastructures with a smaller carbon footprint. DMFCs utilize methanol (CH$_3$OH) as a fuel, which unlike hydrogen, remains in the liquid phase up to 65°C. Methanol has a volumetric energy density approximately five times larger than compressed hydrogen gas. Additionally, although compressed hydrogen gas has a significantly larger gravimetric energy density compared to methanol or even gasoline, the heavy compressed gas storage units required for hydrogen can undermine its advantages.$^{19}$

Much like batteries, DMFCs consist of three basic components: an anode, a cathode, and an electrolyte. A schematic of a DMFC can be seen in figure 1.2. Methanol fuel enters the fuel cell at the anode. A platinum catalyst at the anode aids in the breakdown of methanol into carbon dioxide (CO$_2$), which is released as waste, and the active fuel component, molecular hydrogen (H$_2$). That hydrogen is then ionized to become H$^+$ and free electrons (e$^-$). H$^+$ ions can then travel through a proton exchange membrane (PEM) electrolyte, while the electrons power a load. Oxygen, obtained from the atmosphere, then combines with electrons and H$^+$ at the cathode to form H$_2$O, which is released as waste.
Figure 1.2. Schematic of a direct methanol fuel cell.

There are a number of issues that pose limitations to the commercial viability of DMFCs. The most notable include the methanol crossover problem and high cost. Methanol crossover occurs when methanol fuel, instead of being oxidized at the anode, diffuses through the PEM to the cathodic side of the fuel cell. Not only does this lead to decreased efficiency, it “poisons” the cathode and ultimately results in the operational failure of the fuel cell.

Nafion, manufactured by E. I. du Pont de Nemours and Company, is currently the most widely used PEM electrolyte in fuel cells; however, it suffers from high methanol permeability. Previous studies have shown that the addition of nanoparticles embedded in Nafion can improve
fuel cell performance, including reducing methanol permeability.\textsuperscript{10,21,22} Chapter 4 of this thesis will investigate composite sulfonated polyetheretherketone (sPEEK) polymer membranes with embedded nanoparticles as an alternative to Nafion. Pristine sPEEK membranes possess narrower and less-connected diffusion channels compared to Nafion, which promise to reduce methanol crossover.\textsuperscript{23} Composite sPEEK membranes with organically-functionalized nanoparticles could lead to further enhancement of DMFC performance. Additionally, as Nafion can become prohibitively expensive, the use of sPEEK membranes can help achieve cost reduction for DMFCs.

1.4 References


18. Armand, M., Endres, F., MacFarlane, D. R., Ohno, H. & Scrosati, B. Ionic-liquid materials


20. Han, J. & Liu, H. Real time measurements of methanol crossover in a DMFC. *J. Power Sources* 164, 166–173 (2007).


Chapter 2. Experimental Techniques

2.1 Nuclear Magnetic Resonance

2.1.1. Principles

Nuclear magnetic resonance (NMR) is a spectroscopic technique that can be used to probe magnetic, and in certain cases electronic, environments about nuclei in matter. Protons and neutrons possess intrinsic angular momentum, known as spin \( I \), and correspondingly magnetic moments; specifically, \( I = \frac{1}{2} \) for protons and neutrons. More complex atomic nuclei, being composed of various numbers of protons and neutrons, also possess nuclear spin dependent upon the nuclear isotope. For example, \(^1\text{H}, ^{19}\text{F}, \text{and} ^{13}\text{C}\) have \( I = \frac{1}{2} \), \(^2\text{H}, ^6\text{Li}, \text{and} ^{14}\text{N}\) have \( I = \frac{1}{2} \), \(^7\text{Li}\) and \(^{11}\text{B}\) have \( I = \frac{3}{2} \), etc. Some nuclei, such as \(^{12}\text{C}\) and \(^{16}\text{O}\), have \( I = 0 \), in which case they cannot interact with external magnetic fields and are not observable via NMR.

The nuclear magnetic moment, \( \mu \), and the spin angular momentum, \( I \), are related by:

\[
\mu = \gamma I. \tag{2.1}
\]

Here, \( \gamma \) is known as the gyromagnetic ratio, which is a specific constant for each nuclear isotope. In the presence of an external magnetic field, \( B_0 \), a nuclear spin will precess about \( B_0 \), as shown in figure 2.1. The rate of this precession is given by:

\[
\omega_0 = \gamma B_0. \tag{2.2}
\]

Here, \( \omega_0 \) is the rate of precession of the nuclear spin about the magnetic field and is known as the Larmor frequency. In NMR, generally the direction of the external magnetic field is taken as the z-direction.
Figure 2.1. Spin precession around an external magnetic field, $B_0$.

The potential energy of the precessing magnetic moment is given by:

$$E = -\mu \cdot B_0. \quad \text{[Equation 2.3]}$$

which can also be written as:

$$E = -\gamma l_z B_0. \quad \text{[Equation 2.4]}$$

Therefore, the energy of the spins is dependent upon the $z$-component of the spin vector, $l_z$, for which the quantization rule is:

$$l_z = m\hbar, \quad \text{[Equation 2.5]}$$

where $m$ can be $m = -I, -I + 1, ..., I - 1, I$. Here, $I$ is the angular momentum quantum number associated with the nuclear spin. By equation 2.4, there are $2I + 1$ possible values for $l_z$, and therefore $2I + 1$ possible energy levels.

By combining equations 2.4 and 2.5, the energy of a nuclear spin in the presence of a magnetic field is:

$$E = -\mu_z B_0 = -\gamma m\hbar B_0. \quad \text{[Equation 2.6]}$$
Here, $\mu_z$ is the $z$-component of the magnetic moment. The energy difference between two consecutive energy levels then becomes:

$$\Delta E = \gamma B_0 = \hbar \omega_0 = \hbar \nu_0.$$  \[Equation 2.7\]

When no external magnetic field exists, there will be no difference between the magnetic energy levels and all possible spin states are degenerate. When a magnetic field is applied, the $2I+1$ states will have different energies. The energy difference between adjacent levels is proportional to the strength of the magnetic field, as depicted in figure 2.2. This is known as the Zeeman effect, or Zeeman splitting. A nuclear magnetic moment can be raised from a lower energy level to the next higher energy level by absorbing an amount of energy equivalent to $E$. Magnetic relaxation from the higher to a lower energy level can occur if the nuclear spin loses an amount of energy equivalent to $E$ to its surroundings.

![Diagram depicting the Zeeman splitting of nuclear quantum states in a magnetic field.](image)

**Figure 2.2.** Diagram depicting the Zeeman splitting of nuclear quantum states in a magnetic field.

When utilizing NMR techniques for condensed matter applications, an ensemble of interacting spins must be considered. For purposes of simplicity, the net magnetization of an
ensemble of nuclear spins with \( \ell = \frac{1}{2} \), shall be analyzed. The ratio of the populations between \( m = \frac{1}{2} \) and \( m = -\frac{1}{2} \) nuclei, referred to as spin up and spin down, respectively, at equilibrium in a magnetic field \( B_0 \) is given by:

\[
\frac{N_\beta}{N_\alpha} = e^{-\Delta E / k_B T}. \tag{Equation 2.8}
\]

Here, \( N_\alpha \) and \( N_\beta \) are the number of nuclei in the lower and higher energy level, respectively, \( k_B \) is the Boltzmann constant, \( \Delta E \) is given by equation 2.7, and \( T \) is the spin temperature, in Kelvin. Under most conditions, the population difference between the two energy states is small relative to \( k_B T \). For example, for a population of \( 10^6 \) \( ^1\text{H} \) nuclei in an 11.7 T magnetic field at room temperature, \( N_\alpha - N_\beta \approx 40 \). Because of this difference at equilibrium, there is a net magnetization, \( M_0 \), oriented in the same direction as \( B_0 \), as depicted in figure 2.3. This net magnetization is the vector summation of nuclear magnetic moments in the ensemble.

**Figure 2.3.** Net magnetization resulting from the summation of all the spin induced magnetic moments in the system.
NMR experiments are typically designed to yield spectra or relaxation profiles. Analysis of the fundamental magnetic interactions that this data provides allows for a structural and/or dynamical interpretation of the system under investigation. Many modern NMR studies employ pulsed radio-frequency (RF) fields in order to drive the nuclear magnetization away from equilibrium, or to transfer magnetization between nuclei, to demagnetize or decouple, to create partial or full saturation conditions, etc. The RF pulse is an oscillating magnetic field, near \( v_0 \), often referred to as \( B_1 \), and oriented orthogonally to \( B_0 \). The frequency of \( B_1 \) is approximately equivalent to the Larmor frequency of the nuclear spin. In most laboratory conditions, where \( B_0 \) is on the order of 25 T or less, the Larmor frequency is in the radio frequency range, on the order of 0 to 100 s of MHz. \( B_1 \) is created by pulsing a RF voltage across a solenoid inductor. This inductor encapsulates the sample and is oriented with its symmetry axis orthogonal to \( B_0 \), in the x-y plane. \( B_1 \) is usually applied for a short period of time, on the order of \( \mu \)s; however for saturation, magnetization transfer, and demagnetization, pulse durations can be on the order of 100 \( \mu \)s to 100 ms.

By applying \( B_1 \) with a frequency near the Larmor value for the nuclear spin, a resonance condition is reached. This leads to a rotation of the net magnetization vector of the entire spin population, \( M \), as in the rotating frame view shown in figure 2.4.
Figure 2.4. From the point of view of the precessing spins, the application of a RF $B_1$ field ($\pi/2$ pulse) rotates the net magnetization of the spin system away from the z-axis.

The angle of rotation of $M$ is equivalent to:

$$\theta = \gamma \tau B_1.$$  \[Equation 2.9\]

Here, the duration of the pulse is given by $\tau$. RF pulses are often referred to by the angle which they rotate $M$. For example, a $\pi/2$ pulse rotates $M$ into the x-y plane so its z-component is zero and a $\pi$ pulse rotates $M$ into the -z-axis.

Just after $B_1$ has acted, the spin system is no longer in thermal equilibrium with $B_0$. Correspondingly if left alone, the spin system ($M$) will, over time, return to its equilibrium state. This process, referred to as nuclear spin relaxation, can be broken down into two modes: 1) magnetization recovery along the z-axis, spin-lattice relaxation and 2) magnetization decoherence in the x-y plane, spin-spin relaxation. For simple magnetic dipolar relaxation, the relaxation modes can be adequately described using the Bloch relations.\(^1\) This Bloch picture shows that both spin-
lattice and spin-spin relaxation processes are exponential in nature. For example, if a $\pi/2$ pulse, oriented in the y-direction, is applied to a system of slightly magnetically interacting spins in equilibrium, the relaxation of $M$ can be described by:

$$M_x(t) = M_0 \cos(\omega_0 t) e^{-t/T_2}$$  \[Equation 2.10\]

$$M_y(t) = -M_0 \sin(\omega_0 t) e^{-t/T_2}$$  \[Equation 2.11\]

$$M_z = M_0 \left(1 - e^{-t/T_1}\right).$$  \[Equation 2.12\]

Here $T_1$ and $T_2$ are the characteristic times associated with spin-lattice and spin-spin relaxation, respectively. For this reason, spin-lattice relaxation can sometimes be referred to as $T_1$ relaxation and spin-spin relaxation can be referred to as $T_2$ relaxation.

It is through the precession of $M$ in the x-y plane, as described by equations 2.10 and 2.11, that a RF voltage can be induced within the solenoid inductor previously used to generate the $B_1$ field. This induced voltage created by $M$ as it precesses is called the free induction decay (FID). The FID can be Fourier transformed from the time domain into the frequency domain, resulting in a Lorentzian function centered about $\omega_0$ with a width which is inversely proportional to $T_2$. This frequency domain spectrum is the NMR spectrum which can be used to obtain information about structural and dynamic properties of the sample.

To assess structural and dynamic information from a given system, it becomes crucial to understand the interactions between nuclei and their surrounding environment. There are several types of NMR interactions, which are usually treated as perturbations to the Zeeman interaction. Therefore, the Hamiltonian for a NMR spin can be expressed as:

$$H = H_Z + H_{DD} + H_{CS} + H_Q.$$  \[Equation 2.13\]

Here, $H_Z$ is the Zeeman interaction described previously, $H_D$ is the dipole-dipole interaction, $H_{CS}$ is the chemical shift coupling, and $H_Q$ is the quadrupolar interaction.
Figure 2.5. Two nuclear magnetic dipole moments separated by a distance $r_{AB}$.

2.1.1.a. Dipole-Dipole Interaction

The magnetic dipole-dipole interaction is a through-space magnetic interaction between two magnetic moments. Each magnetic moment creates a magnetic field in the space surrounding it. Any other nuclear spin within its vicinity can interact with this magnetic field. The classical mutual energy of interaction between two magnetic moments, $A$ and $B$ shown in figure 2.5, is given by:

$$ E = \frac{\mu_0}{4\pi} \frac{\mu_A \mu_B}{r_{AB}^3} - \frac{3(\mu_A r_{AB})(\mu_B r_{AB})}{r_{AB}^5}. $$

[Equation 2.14]

Here, $\mu_0$ is the permeability constant and $r_{AB}$ is the internuclear vector pointing from $A$ to $B$.

Using the spin operators $I_A$ and $I_B$, the Hamiltonian for the magnetic dipole-dipole interaction becomes:
\[ H_{DD} = b_{AB}[(l_A \cdot e_{AB})(l_B \cdot e_{AB}) - l_A \cdot l_B]. \]  \[ \text{[Equation 2.15]} \]

where \( e_{AB} \) is the unit vector pointing in the direction between the positions of the two magnetic moments and \( b_{AB} \) is the coupling constant given by:

\[ b_{AB} = -\mu_0^2 \gamma_A \gamma_B \hbar / 4 \pi r_{AB}^3. \]  \[ \text{[Equation 2.16]} \]

For a system of nuclear spins, the total Hamiltonian is given as the sum over all pairs of magnetic moments, as:

\[ H_{DD} = \sum_B \sum_A^B -1 H_{AB}. \]  \[ \text{[Equation 2.17]} \]

In solids and liquids, the effect of the dipole-dipole interaction is a homogeneous broadening of the NMR lineshape, which can be very well represented analytically by a Voigt function.

In solids, dipolar broadening can lead to line widths large enough to obscure vital lineshape information. To alleviate this, a method known as magic-angle spinning (MAS) is utilized. To understand MAS, it is helpful to express the dipolar Hamiltonian in terms of its angular dependence:

\[ H_{DD} = \sum_B \sum_A^B -1 b_{AB} (3 \cos^2 \theta_{AB} - \frac{1}{3})(3l_A \cdot l_B - l_A \cdot l_B). \]  \[ \text{[Equation 2.18]} \]

From this, it is clear that contributions to the interaction are identically zero, \( 3 \cos^2 \theta_{AB} - \frac{1}{3} = 0 \), for the “magic angle” of \( \theta_{AB} = 54.74^\circ \). However, to truly remove the effects of the dipolar broadening, all \( r_{AB} \) must be oriented at this magic angle. To achieve this, the sample is rotated rapidly about an axis which is oriented 54.74° from \( B_0 \). This effectively averages all \( r_{AB} \) to the magic-angle orientation, as long as the rotation rate is greater than the static linewidth, at minimum.

**2.1.1.b. Quadrupolar Interaction**

Nuclei which possess spin with \( I > \frac{1}{2} \) have non-spherical charge distributions and therefore have electric quadrupole moments. In solids, where electric field gradients can be large, the magnetic energy levels of quadrupolar nuclei can be significantly perturbed. The quadrupolar
interaction is a coupling between the electric quadrupole moment of the nucleus with its surrounding electric field gradient, created primarily by the electron charge distribution. The electric field gradient, $V$, is a tensor quantity and can be represented as:

$$V = \begin{pmatrix} V_{XX} & V_{XY} & V_{XZ} \\ V_{YX} & V_{YY} & V_{YZ} \\ V_{ZX} & V_{ZY} & V_{ZZ} \end{pmatrix}. \quad [\text{Equation 2.19}]$$

and is therefore orientationally dependent. The nuclear quadrupole Hamiltonian can be expressed as:

$$H_Q(\theta) = \frac{eQ}{2I(2I-1)} \mathbf{I} \cdot \mathbf{V} \cdot \mathbf{I}. \quad [\text{Equation 2.20}]$$

Here, $e$ is the charge of an electron and $Q$ is the quadrupole moment of the nucleus.

The quadrupolar interaction is often significantly stronger than the dipole-dipole, chemical shift, and J coupling interactions. It can lead to significant line broadening caused by short $T_2$ relaxation times as well as short $T_1$ relaxation times.

2.1.1.c. Chemical Shift Interactions

There are various magnetic “shift” interactions, all of which scale with the field strength. They are differentiated by the particular mechanism that creates the interaction field. Chemical shifts refer to those “shift” interactions between nuclear magnetic moments and magnetic fields created by surrounding electronic currents (as in molecules) and through-space magnetic susceptibilities (as in solid-state studies of non-paramagnetic crystals and glasses). The local magnetic field around a nuclear magnetic moment can be described as the sum of two parts; the external field, $B_0$, and the local field produce by induced electronic currents, $B_{\text{induced}}$. As the local fields are induced by $B_0$, they increase with the size of $B_0$. The induced field can add or subtract from $B_0$. The total field around a nuclear magnetic moment can be expressed as:

$$B_{\text{total}} = B_0 + B_{\text{induced}}. \quad [\text{Equation 2.21}]$$
The induced magnetic field alters the nuclear spin precession frequency and the chemical shift refers to the frequency difference of a nuclear resonance relative to a reference. The resonant frequency of a nuclear spin can be expressed as:

\[ \omega_{total} = \gamma B_{total} = \gamma B_0 + \gamma B_{induced} = \omega_0 + \omega_{shift}. \]  

[Equation 2.22]

The normalized frequency expression for the chemical shift is:

\[ \delta = \left( \frac{\omega_{total} - \omega_{ref}}{\omega_{ref}} \right), \]  

[Equation 2.23]

where the numerator has units of Hz and the denominator units of MHz. Due to this, the “unit” for chemical shift is part-per-million or ppm.

2.1.2. Spin-Lattice Relaxation Measurements

An inversion recovery pulse sequence is utilized in this thesis to measure spin-lattice relaxation. This sequence, depicted in figure 2.6, consists of a \( \pi \) pulse, followed by a delay, \( \tau \), followed by a \( \pi/2 \) pulse, after which a FID can be acquired.

![Figure 2.6. Diagram of a standard inversion recovery pulse sequence.](image-url)
The first $\pi$ pulse rotates $M$ from the positive to the negative z-axis. During the delay, $\tau$, $M(\tau)$ recovers, depending on $\tau$, via spin-lattice relaxation towards the equilibrium value $M_0$ along the z-axis. The second pulse rotates $M(\tau)$ into the x-y plane, after which the FID can be acquired.

In this pulse sequence, the intensity of $M(\tau)$ is proportional to the signal intensity in the resulting NMR spectrum and is measured as $\tau$ is varied. The signal intensity can then be fit, with respect to $\tau$, according to equation 2.12. In this way, $T_1$, the characteristic time of spin-lattice relaxation, can be obtained. The goal is to gain knowledge of the spin-lattice relaxation mechanism. For $I = \frac{1}{2}$ systems, typically the largest contribution to $T_1$ relaxation comes from dipole-dipole interactions. Due to the fact that dipole-dipole interactions are inversely proportional to cube of the dipole-dipole distance, $T_1$ times are highly dependent on intramolecular motions and therefore can be used as a probe for tumbling or rotational motions.

2.1.3. Self-Diffusion Measurements

In the absence of a driving force, the motions of molecules within a system result from random thermal motions. This phenomenon is often referred to as Brownian motion. When no chemical potential gradient is present, the process is referred to as self-diffusion. NMR is a powerful tool for measuring self-diffusion, due to its isotope selectivity and non-destructive nature. Typically, diffusion NMR measurements are made by utilizing a modified echo pulse sequence.
A simple echo pulse sequence is shown in figure 2.7. In an echo pulse sequence, the intensity of the NMR signal, or echo, is dependent upon spin-spin relaxation. During the $\tau$ delays, the spins evolve via $T_2$ relaxation, thereby decreasing the intensity of the magnetization vector. From equations 2.10 and 2.11, the intensity of the echo is given by:

$$S_0 = M_0 e^{-2\tau/T_2}.$$  \[\text{Equation 2.24}\]

Here, $S_0$ is the intensity of the echo only considering attenuation due to $T_2$ relaxation. To measure self-diffusion coefficients, $D$, magnetic field gradients can be applied in the $z$-direction, so they are superimposed upon $B_0$. This leads to further attenuation of the echo intensity described by:

$$S(t_e) = S_0 \langle e^{i\phi(t_e)} \rangle.$$  \[\text{Equation 2.25}\]

Here, $S$ is the echo intensity, $t_e$ is the time at which the echo occurs, and $\langle e^{i\phi(t_e)} \rangle$ accounts for the spin dephasing which occurs as a result of inhomogeneous $T_2$ processes due to the magnetic field gradient.

The bracketed term in equation 2.25, describing the spin dephasing due to the magnetic field gradient, is the sum of all spin phase contributions and can be expressed as:
\[ \langle e^{i\phi(t_e)} \rangle = \exp(i\langle \Phi(t_e) \rangle) - \frac{1}{2} (\langle \Phi^2(t_e) \rangle - \langle \Phi(t_e) \rangle^2) + \cdots. \]  
\[ \text{[Equation 2.26]} \]

For free diffusion, with no driving force, \( \Phi(t_e) \) has a normal distribution and therefore averages to 0. Due to this, equation 2.25 reduces to the first order to:

\[ S(t_e) = S_0 \exp^{-1/2\langle \Phi^2(t_e) \rangle}. \]
\[ \text{[Equation 2.27]} \]

The spin phases are dependent on \( \gamma \), the magnetic field gradient, \( g \), and the position of the spin along the \( z \)-axis, \( z \). Then, \( \langle \Phi^2(t_e) \rangle \) becomes:

\[ \Phi(t_e) = -\gamma \int_0^{t_e} g(t') z(t') dt'. \]
\[ \text{[Equation 2.28]} \]

This integral can be expanded as:

\[ \Phi(t_e) = -\int_0^{t_e} G(t) v(t) dt, \]
\[ \text{[Equation 2.29]} \]

where \( v(t) \) is the velocity of the nuclei, \( G(t_e) = 0 \), and

\[ G(t) = \gamma \int_0^t g(t') dt'. \]
\[ \text{[Equation 2.30]} \]

Using this, the second term of equation 2.27 becomes:

\[ \langle \Phi(t_1) \cdot \Phi(t_2) \rangle = \int_0^{t_e} \int_0^{t_e} G(t_1) G(t_2) \langle v(t_1) \cdot v(t_2) \rangle dt_1 dt_2. \]
\[ \text{[Equation 2.31]} \]

For simple diffusion:

\[ \langle r(t_1) \cdot r(t_2) \rangle = 2D \delta(t_2 - t_1) t_1, \]
\[ \text{[Equation 2.32]} \]

therefore:

\[ \langle v(t_1) \cdot v(t_2) \rangle = 2D \delta(t_2 - t_1). \]
\[ \text{[Equation 2.33]} \]

Combining equations 2.25, 2.27, 2.31, and 2.33, the general equation for echo intensity as a function of the applied magnetic field gradient, \( G(t_l) \), becomes:

\[ S(t_e) = M_0 \exp \left( \frac{-2t_e}{T_2} \right) \exp \left( -D \int_0^{t_e} G^2(t_1) dt_1 \right). \]
\[ \text{[Equation 2.34]} \]
The pulsed field gradient (PFG) spin echo (SE) NMR pulse sequence utilized to measure self-diffusion coefficients in this thesis is depicted in figure 2.8. For this pulse sequence, equation 2.34 becomes:

\[
S(2\tau) = M_0 \exp \left( -\frac{2\tau}{T_2} \right) \exp \left( -D(yg\delta)^2(\Delta - \delta/3) \right). \quad \text{[Equation 2.35]}
\]

Here, \( \tau \) is the delay time between RF pulses, \( g \) is the magnetic field gradient strength, \( \delta \) is the duration of the magnetic field gradient pulses, and \( \Delta \) is the time between the gradient pulses, also known as the diffusion time. Usually, a measurement will be made by varying \( g \) and measuring the effect on echo intensity. The subsequent data can be fit to equation 2.35 to obtain \( D \).

Figure 2.8. Diagram of a PFGSE pulse sequence. Green pulses indicate magnetic field gradient pulses.

The PFGSE pulse sequence is dominated by \( T_2 \) relaxation of the spins. However, in systems with slow molecular tumbling, \( T_2 \ll T_1 \). For such systems, it becomes beneficial to utilize a PFG
stimulated echo (PFG STE) pulse sequence, see figure 2.9. This pulse sequence minimizes the duration the magnetization is stored in the x-y plane, where relaxation is dominated by $T_2$. After the first gradient pulse, a $\pi/2$ pulse to rotate the magnetization into the z-axis where spin relaxation is dependent upon slower $T_1$ relaxation processes. Finally, a third $\pi/2$ pulse is applied to rotate the spins into the x-y plane prior to the second, decoding, gradient pulse.

The use of pulsed field gradients during diffusion NMR experiments create eddy currents which can negatively affect NMR signal reception. The use of bipolar pulsed field gradients has been shown to minimize these effects which are produced by the repetition of strong pulsed field gradients. Longitudinal eddy current delays (LEDs) can be utilized prior to FID acquisition to further minimize the effects of eddy currents. Additionally, when conducting variable temperature diffusion NMR measurements, temperature gradients across the sample can create convection flow, which must be accounted for through the use of pulse sequences which utilize convection compensation methods.

Figure 2.9. Diagram for a PFG STE pulse sequence utilizing bipolar pulsed field gradients and a longitudinal eddy current delay.
2.1.4. High Pressure NMR

From thermodynamics, it is understood that varying the temperature of a system, at ambient pressure, will cause changes in the thermal energy as well as the volume of the system. In order to better understand the molecular dynamics of a system, it becomes necessary to probe these effects separately. Although, temperature dependent NMR studies are commonplace, this provides motivation for less common variable pressure NMR studies.

By applying pressure to various systems, intermolecular distances are compressed and intermolecular interactions are increased. In this thesis, analysis of the activation volume, $V$, is utilized to quantify the effect of pressure on dynamic properties of a system. The activation volume is defined as:

$$\Delta V = -k_BT \left[ \frac{\partial \ln(A)}{\partial P} \right]_T.$$

[Equation 2.36]

Here, $T$ is the temperature of the system, $P$ is the pressure applied to the system, and $A$ is the dynamic process being probed, either the self-diffusion coefficient, $D$, or the relaxation rate, $R_1 = \frac{1}{T_1}$. The activation volume is the minimum amount of localized free volume required for a dynamic process to occur.

For high pressure NMR measurements, a custom-made Cu-Be probe is utilized. The probe is connected to a manual hydraulic pump which can pressurize the sample within the probe utilizing Fluorinert (3M Company) as a pressurizing fluid. Fluorinert is $^1$H free, therefore it does not contribute background signal when conducting $^1$H NMR measurements. Samples were hermetically sealed in polyethylene bags rather than standard NMR tubes to allow for the transfer of pressure to the sample system.\(^4\)

Due to the nature of the Cu-Be probe, PFG NMR becomes impossible as the changing magnetic fields would induce strong eddy currents in the NMR probe. Therefore, with high
pressure diffusion measurements, a static-field gradient (SFG) is utilized. This involves lowering the NMR probe to a position below the homogeneous portion of the superconducting NMR magnet, into the naturally occurring magnetic field gradient, hence this technique is often referred to as fringe-field NMR. The strength of the fringe-field gradient is calibrated to determine the gradient strength, $g$, using a reference sample with a known self-diffusion coefficient, usually $^1$H diffusion in H$_2$O. Since the gradient strength cannot be varied as it is for PFG NMR, the delay time $\tau$ is varied. The echo intensities can thereby be measured with respect to $\tau$, and analyzed according to:

$$S(\tau) = M_0 \exp \left( -\frac{2\tau}{T_2} \right) \exp (-D(\gamma g)^2 \tau^3).$$

[Equation 2.37]

This expression can be linearized, in the event that $T_2$ is unknown, to extract the self-diffusion coefficient, $D$.

### 2.2. X-Ray Scattering

#### 2.2.1. Principles

In most solid and liquid systems, neighboring atoms are typically separated by distances on the order of a few Å. In order to resolve physical characteristics within this length scale spectroscopically, electromagnetic waves must have a wavelengths smaller than the distances being probed. For this reason, x-rays, from 0.1 Å to 100 nm, allow for the characterization of nanoscale structure via their scattering interactions with matter.

Typically, for x-ray scattering experiments two types of x-ray sources are encountered: 1) conventional x-ray tubes and 2) synchrotron radiation. Conventional x-ray tubes have been employed in the experiments described in this thesis. X-ray tube sources commonly utilize either copper or molybdenum anodes, each capable of creating radiation with characteristic wavelengths of $\lambda = 1.54$ Å and $\lambda = 0.71$ Å, respectively. The x-ray beam is then passed through a
monochromator to isolate only the desired wavelength, depending upon the anode source used, after which the beam is collimated before reaching the sample.

When the x-ray radiation passes through the sample, it is scattered elastically with its wavelength unchanged. X-ray scattering occurs via interactions with the electron clouds of atoms. For a single scattering process, the amplitude, $A_j$, of the scattered photon can be described by:

$$A_j = b_j e^{-2\pi i (k_0 - k_f) \cdot r_j / \lambda}.$$  \[Equation 2.38\]

Here, $b_j$ is the scattering cross section, $k_0$ is the wavenumber of the incident photon, $k_f$ is the wavenumber of the scattered photon, and $r$ is the vector pointing to the position of the scattering center. For ensembles of atoms, the scattering amplitudes from all atoms must be summed as:

$$A(k) = \sum_j b_j e^{-2\pi i (k_0 - k_f) \cdot r_j / \lambda},$$  \[Equation 2.39\]

or using $Q = k_f - k_0$, where $Q$ is referred to as the scattering vector:

$$A(Q) = \sum_j b_j e^{-2\pi i Q \cdot r_j / \lambda}.$$  \[Equation 2.40\]

The scattering intensity can then be given by the product of the scattering amplitude and its complex conjugate:

$$I(Q) = |A|^2 = \sum_j \sum_k b_j b_k e^{Q \cdot r_{jk}}.$$  \[Equation 2.41\]

Here, $r_{jk}$ is the distance vector pointing from the $j^{th}$ scattering center to the $k^{th}$ scattering center, and $b_j$ and $b_k$ are the atomic scattering cross sections. Because photons are scattering off of the electrons bound to atoms, the atomic scattering densities are dependent upon the number of electrons in an atom.

A basic x-ray scattering experiment is depicted in figure 2.10. After transmission through the sample, the scattered photons are detected at the image plate, which is placed a distance $d$ from the sample. The image plate will detect photons of the appropriate x-ray wavelength over a period.
of exposure time. For an isotropic solution, the scattered photons will create concentric rings along the image plate, as according to equation 2.41. The number of photons detected is integrated radially to obtain an intensity as a function of the scattering radius. Twice the scattering angle, $2\theta$, can be determined as:

$$2\theta = \tan(r/d),$$  \hspace{1cm} \textbf{[Equation 2.42]}

where $r$ is the scattering radius and $d$ is the distance between the sample and the image plate. Once the scattering angle has been found, the scattering vector, $Q$, can be calculated as:

$$Q = 2\pi \sin 2\theta / \lambda.$$  \hspace{1cm} \textbf{[Equation 2.43]}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{schematic_xray_scattering.png}
\caption{Schematic of an x-ray scattering experiment.}
\end{figure}

From equation 2.41, photons will exhibit scattering vectors which follow the condition:

$$Q = 2\pi/r_{jk}.$$  \hspace{1cm} \textbf{[Equation 2.44]}

Because the intermolecular distances, $r_{jk}$, are not well defined in a liquid as in a solid, sharp scattering peaks will not be observed. However, x-ray scattering of liquids can still probe
characteristic distances, nanoscale aggregation, and ordering in liquids. This technique can be especially useful to probe ion aggregation in ionic liquids, allowing for the measurement of the size of aggregates as well as the relative density of various aggregates.5–8

2.2.2. High Pressure X-ray Scattering

High pressure x-ray scattering experiments are taken utilizing a diamond anvil cell (DAC) system, shown in figure 2.11. In this system, a Cu-Be gasket approximately 1 mm thick, with a hole whose diameter is approximately 3 mm, is placed between two diamond anvils. The sample is placed within the gasket hole along with a ruby chip. Pressure is applied to the outer surface of the diamond anvils. By Bernoulli’s principle, small amounts of pressure, on the order of kPa, supplied by a pressurized Ar gas source on the outer surface of the diamond anvils can translate to much greater internal pressure on the sample and ruby chip, on the order of GPa. The internal pressure of the DAC can be calibrated by measuring the spectral shift of the $R_I$ fluorescence line of the ruby chip.9
Figure 2.11. Schematic of a diamond anvil cell for use with high pressure x-ray scattering measurements.

Two major drawbacks exist with DAC x-ray scattering. The first, is a significantly reduced signal-to-noise ratio. Due to the thin sample width in the DAC, the signal-to-noise ratio becomes reduced and scattering from the atmosphere between the sample and the image plate contributes a significant amount of noise which cannot be averaged out effectively with increased exposure times. Ideally, the experimental setup would be contained within a vacuum chamber, thereby significantly reducing noise. Unfortunately, such a system was not available at the time of this work. Additionally, the internal pressure of the DAC can compress the Cu-Be gasket as the pressure is increased. This will change the effect sample width, so comparing scattering intensities between different spectra becomes less reliable.
2.3 References


4. Farrington, J. A. Variable Pressure and Temperature NMR Studies of Fuel Cell Polymer Electrolyte Membranes. (Graduate Center, City University of New York, 2010).


Chapter 3. Effects of Anion Asymmetry in N-Methoxyethyl-N-Methyl-Pyrrolidinium Based Ionic Liquid Solutions

This project was done in collaboration with Dr. Stefano Passerini of Karlsruhe Institute for Technology and his colleagues in Germany. The NMR portion of this work was conducted at Hunter College. This work has been accepted for publication in ChemSusChem (DOI: 10.1002/cssc.201702288).

3.1 Introduction

Ionic liquids (ILs) are molten salts which are defined as salts that remain in the liquid phase at temperatures below 100°C. This family of materials possess many characteristics which hold vast capabilities for their potential use as electrolytes, including non-flammability, low vapor pressure, thermal and electrical stability, and relatively high ionic conductivity.1 Several studies have investigated the use of ionic liquids as electrolytes in secondary lithium-ion batteries2–7 as well as supercapacitors.8–10 However, one of the major drawbacks limiting the forward progress of the use of ionic liquid based electrolytes is their high viscosities compared to more standard organic solvent electrolytes, which results in lower ionic conductivities.

Ionic liquids containing pyrrolidinium (Pyr) based cations and bis(trifluoromethanesulfonyl)imide (TFSI) anions are a highly studied family of ionic liquids.10–17 However, the introduction of a relatively new, asymmetrical anion, fluorosulfonyl-(trifluoromethanesulfonyl)imide (FTFSI), seems to show promise of improvements compared to the TFSI anion, which possesses a higher degree of symmetry, including lower viscosity and higher conductivity.18 In this chapter, solutions of N-methoxyethyl-N-methyl-pyrrolidinium bis(trifluoromethanesulfonyl)imide (Pyr12O1-TFSI) with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and N-methoxyethyl-N-methyl-pyrrolidinium
fluorosulfonyl-(trifluoromethanesulfonyl)imide (Pyr_{1201}-FTFSI) with lithium fluorosulfonyl-(trifluoromethanesulfonyl)imide (LiFTFSI) salt have been studied using diffusion NMR, Raman spectroscopy, and density functional theory (DFT). Together, these techniques allow the study of ion aggregation and coordination, caused by the high charge density of Li^+, as well as ion diffusion mechanisms.

### 3.2 Sample Preparation

The synthesis of Pyr_{1201}-TFSI is described by Ferri et al.\textsuperscript{19} The preparation of Pyr_{1201}-FTFSI was performed using a two-step process, as described in previous literature.\textsuperscript{18,20,21} N-methylpyrrolidine (>99%, Fluka), potassium fluorosulfonyl-(trifluoromethanesulfonyl)imide (Provisco CS Ltd), and ethylacetate (analytical reagent grade, Fluka) were used as received. 2-bromoethyl methyl ether (>95%, TCI Japan) was distilled at 35°C and 2 kPa prior to use.

Pyr_{1201}-Br was prepared by alkylation of N-methylpyrrolidine in ethylacetate at 35°C. Pyr_{1201}-FTFSI were obtained by metathesis in aqueous solution. The product was then purified using alumina and charcoal.\textsuperscript{21,22} The resultant ionic liquid was dried for two days on a turbomolecular pump, to below 10^{-7} mbar. The water content of these ionic liquids was measured, by Karl-Fischer titration, to be below 5 ppm. The LiFTFSI salt (Provisco CS) was also dried for two days on a turbomolecular pump, to below 10^{-7} mbar. Solutions were made by mixing appropriate amounts of ionic liquid and salt and stirring at room temperature until the salt was completely dissolved. All samples were prepared in a dry room, with a dew point less than -50°C. The resulting solutions were dried again for 24 hours on an oil pump and then 24 hours on a turbomolecular pump. The water content of the mixtures was measured, by Karl-Fischer titration, to be less than 5 ppm. Structural diagrams are depicted in figure 3.1.
Figure 3.1. Structural diagrams of the Pyr$_{12}O_1$ cation and TFSI and FTFSI anions. Diagrams follow CPK coloring conventions, in which C is grey, N is blue, S is yellow, O is red, and F is green.

3.3 NMR Measurements

Ionic liquid solutions with lithium salt were studied using multinuclear diffusion NMR. Diffusion measurements were made on $^1$H, $^7$Li, and $^{19}$F nuclei at 25°C and 50°C. A pulsed-field gradient (PFG) stimulated echo pulse sequence was utilized for all measurements, with at least 16 values of the gradient strength and constant delay times. Due to the elemental composition of the ions, $^1$H measurements probed Pyr$_{12}O_1^+$ diffusion, $^{19}$F measurements probed TFSI$^-$ and FTFSI$^-$ diffusion in their respective samples, while $^7$Li measurements probed Li$^+$ diffusion.

Measurements were conducted on a Varian Direct Drive 300 MHz NMR spectrometer with a 7.15 T, wide-bore magnet and a Doty DSI-1034 gradient probe, capable of pulsed-field gradient strengths of 1380 G/cm. For these measurements, resonances occurred at 300 MHz, 283 MHz, and
117 MHz for $^1$H, $^{19}$F, and $^7$Li, respectively. All resulting diffusion attenuation curves were found to be single-component in nature. Reported diffusion measurements have an uncertainty of 5%.

Self-diffusion results for Py$_{12}O_{1}$-FTFSI and Py$_{12}O_{1}$-TFSI at 25°C are reported in figures 3.2 and 3.3. These figures show that diffusion coefficients for all ions decreased with increasing lithium salt concentration. The Stokes-Einstein relationship:

$$D = \frac{k T}{\pi r n}$$

where $D$ is the rate of diffusion, $k$ is Boltzmann’s constant, $T$ is the absolute temperature, $c$ is a constant between 4 and 6, $r$ is the hydrodynamic radius, and $n$ is viscosity of the fluid, cannot be literally applied to these solutions due to their ionic nature. However, the relationship between salt concentration and the rate of diffusion is primarily an effect of the increased viscosity associated with increased salt concentration solutions.\textsuperscript{16}
Figure 3.2. Graph showing self-diffusion coefficients for Pyr$_{12}$O$_1$-FTFSI solutions with LiFTFSI at varying concentrations at 25°C.
Figure 3.3. Graph showing self-diffusion coefficients for Pyr$_{12}$O$_1$-TFSI solutions with LiTFSI at varying concentrations at 25°C.

At low salt concentrations, 40 mol% and lower, the results depict Pyr$_{12}$O$_1$ cations diffusing at faster rates than the TFSI or FTFSI anions, which, in turn, diffused faster than Li cations. At first, the slow rate of Li$^+$ diffusion might seem counterintuitive due to its small size. However, molecular dynamics studies demonstrate that in several similar ionic liquids containing
pyrroloidinium-based cations with (trifluoromethanesulfonyl)-(nonfluorobutanesulfonyl)imide (IM$_{14}$), bis(pentafluoromethanesulfonyl)imide (BETI), or bis(trifluoromethanesulfonyl)imide (TFSI) anions with lithium salts, Li[A$_2$]$^{-1}$ complexes form, where A is the anionic species.$^{23,24}$ It would be reasonable to assume these complexes also exist in the FTFSI$^{-}$ based electrolytes. In these complexes, Li$^+$ coordinates with four oxygen atoms on two anions. Due to the high charge density of Li$^+$, anions readily coordinate with Li$^+$ compared to Pyr$_{1201}$$^+$. This formation of Li[A$_2$]$^{-}$ complexes can lead to the low diffusion rates of Li$^+$ found in these solutions. At higher salt concentrations in the Pyr$_{1201}$-FTFSI solutions, this trend breaks. It would be expected that the increased viscosity of the greater lithium salt concentration samples would have a stronger effect on diffusion rates of larger ions, in this case the lithium-anion aggregates. However, at 60 mol% LiFTFSI concentration, all ions exhibit similar diffusion rates. This will be discussed in detail later, within this chapter.
Figure 3.4. Graph showing self-diffusion coefficients for Pyr$_{12}$O$_1$-FTFSI solutions with LiFTFSI at varying concentrations at 50°C.
Figure 3.5. Graph showing self-diffusion coefficients for Pyr$_{1201}$-TFSI solutions with LiTFSI at varying concentrations at 50°C.

Results for 50°C measurements can be seen in figures 3.4 and 3.5. Again, although the Stokes-Einstein relationship (equation 3.1) cannot literally be applied to these solutions, the increase in temperature has led to significant increases in the ion diffusion rates. Furthermore, at
higher lithium salt concentrations in the Pyr$_{12}$O$_1$-FTFSI samples, pyrrolidinium cations diffuse faster than other ions. This is a deviation from the trend seen at 25°C.

At 50°C, it was also shown that in Pyr$_{12}$O$_1$-TFSI solutions, Li cations diffused at a faster rate than TFSI anions even at low concentrations. This effect was not seen with the Pyr$_{12}$O$_1$-FTFSI solutions. This might indicate that, although temperature reduces lithium-anion coordination within these ionic liquids, the asymmetric nature of the FTFSI anion aids coordination and can partially counteract the effects of increased temperature.

Furthermore, lithium transference numbers can be calculated from diffusion measurements by

\[
 t^{Li} = \frac{(D_{Li}X_{salt})}{(D_{Pyr}X_{IL} + D_{Li}X_{salt} + D_{anion})},
\]

[Equation 3.2]

where \(D_{Li}\), \(D_{Pyr}\), \(D_{anion}\) are the diffusion coefficients of lithium, pyrrolidinium, and the anion, respectively, \(X_{salt}\) and \(X_{IL}\) are the molar ratios of lithium salt and ionic liquid, respectively, and \(t^{Li}\) is the lithium transference number. Results of these calculations are shown in figures 3.6 and 3.7.
Figure 3.6. Graph showing calculated lithium transference numbers of ionic liquid solutions at 25°C.
Figure 3.7. Graph showing calculated lithium transference numbers of ionic liquid solutions at
50°C.

At 50°C and low salt concentrations, solutions containing TFSI anions exhibited higher transference numbers than seen in solutions with FTFSI anions. This is a direct result of the increased lithium-anion coordination associated with FTFSI anions described previously. With any lithium salt concentration at 25°C, FTFSI solutions showed higher lithium transference
numbers than solutions with TFSI anions. As expected, lithium transference numbers increase with lithium salt concentration.

### 3.4 Raman Spectroscopy and Density Functional Theory Studies

Raman spectroscopy measurements were made using a RAM II FT-Raman module of a Bruker Vertex70v FT-IR spectrometer, utilizing a laser wavelength of 1064 nm. Spectra were recorded using between 500 and 2000 scans with a resolution of 2 cm\(^{-1}\). Spectral fitting was completed using a multipeak fitting package in IGOR PRO 6.3.2.1 using a Voigt function with a fixed Lorentzian:Gaussian ratio of 1:1.

Similar to TFSI and FSI anions,\(^{31-34}\) the Raman spectrum of the FTFSI anion depicts the characteristic imide expansion-contraction mode in the spectral region between 700 and 780 cm\(^{-1}\), shown in figure 3.8. This vibrational mode is sensitive to both anion conformation and coordination with Li\(^+\). For uncoordinated FTFSI\(^-\) in the pure ionic liquid, the expansion-contraction mode is assigned to the peak centered at 728 cm\(^{-1}\).\(^{35}\) A second peak is observed in the pure ionic liquid, centered at 761 cm\(^{-1}\), which has been assigned to the mixed mode comprised of the symmetric CF\(_3\) deformation and the S-F stretching motions and is relatively insensitive to both conformation and coordination.
Figure 3.8. Raman spectra for Py$_{12}$O$_{12}$FTFSI mixtures with LiFTFSI. The spectra are shifted vertically for clarity. Scattering intensities are presented in arbitrary units.

As LiFTFSI concentration is increased, the intensity of the peak centered at 761 cm$^{-1}$ decreases. Additionally, a feature appears at 746 cm$^{-1}$ beginning as a shoulder which then grows in intensity. At the highest Li salt concentration, 65 mol%, the overall peak center exists at 751 cm$^{-1}$. These vibrational modes were deconvoluted into a series of Voigt functions, shown in figure 3.9.
Figure 3.9. Deconvolution fits of the Raman spectra for Pyr12O1-FTFSI ionic liquid mixtures with LiFTFSI. The blue line is the fitted curve while the red line is the experimental Raman data. The black peaks correspond to uncoordinated FTFSI, while the green and purple peaks correspond to Li$^+$ coordinated FTFSI. Grey peaks correspond to other Pyr12O1$^+$ and FTFSI$^-$ modes.

Using the method previously described by Umebayashi et al., the average number of anions coordinating with Li$^+$, $n$, was calculated by fitting to

$$\frac{I_f}{c_{Li}} = I_f \left( \frac{c_{FTFSI}}{c_{Li}} \sim n \right).$$  \[Equation 3.3\]

Here, $I_f$ is the intensity of the free anion peak, $c_{Li}$ is the Li$^+$ concentration, $I_f$ is the molar scattering coefficient, and $c_{FTFSI}$ is the total concentration of FTFSI$^-$ in all three conformers. The plot for equation 3.3 is shown in figure 3.10, for which a calculated value of $n$ was found to be 1.2. This value is significantly lower than for TFSI-based electrolytes, for which $n \approx 2$.\textsuperscript{23,24}
DFT calculations were performed to further explain the low average FTFSI\(^{-}\) to Li\(^{+}\) coordination number. \([\text{Li}_x\text{FTFSI}_y]^{x-y}\) complexes were created using the optimized \(\text{syn, gauche, and anti FTFSI}\) conformations, which were previously reported,\(^{35}\) in Avogadro 1.1.0, an open-source molecular builder and visualization tool.\(^{36}\) Structural geometries were optimized and vibrational frequencies were calculated using a 6-31G(d,p) basis set with a B3LYP DFT functional,\(^{37–39}\) chosen so the geometries and vibrational frequencies would be directly comparable to previously published data.\(^{35}\) All calculations were made using Gaussian 09 RevD.01.\(^{40}\) Vibrational mode assignments were made by animating each mode in Avogadro.

Each anion can coordinate a maximum of two oxygen atoms with any lithium cation. As \(n\) was found to be 1.2 and there is a reasonable expectation of Li\(^{+}\) being, at least, 4-coordinate while...
in solution, there must be some anions which are not accounted for in the calculation of $n$ through Raman data.

Complexes larger than Li[FTFSI$_2$]$^-$ were modeled and optimized structures are shown in figure 3.11. Larger complexes, including those which contained a single Li$^+$, were shown to contain, in addition to bidentate-coordinated anions, monodentate contact ion pairs. The calculated vibrational frequency of the FTFSI$^-$ expansion-contraction mode of the monodentate contact ion pairs was found to be comparable to uncoordinated FTFSI$^-$, a trend previously noted in TFSI-based ionic liquids in which TFSI$^-$ is coordinated to either Li$^+$ or Mg$^{2+}$. Due to this, it is likely that the peaks previously attributed to the uncoordinated anions in the Raman spectra can be partially attributed to anions which are coordinated in a monodentate geometry. This justifies the low calculated value for $n$. 

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Figure 3.11. Optimized structures for $[\text{Li}_x\text{FTFSI}_y]^{x-y}$ from DFT calculations. Pink spheres represent Li.
Figure 3.12. Coordination structures of single FTFSI anions. Note that these are simplifications, so Li$^+$ is not represented as 4-coordinate. These structures were extracted from optimized structures shown in figure 3.11.

The frequencies of the expansion-contraction mode for the various coordination structures follow the trend: $\nu(\text{aggregate}_2, \text{aggregate}_3) > \nu(\text{bidentate}) > \nu(\text{aggregate}_1, \text{monodentate, free})$. Peaks within the expansion-contraction mode of the FTFSI anion can be attributed accordingly. The peak centered at 751 cm$^{-1}$, which appears in solutions containing 30 mol% LiFTFSI and greater, can be associated with agg$_2$ or agg$_3$ anions and the peak centered at 746 cm$^{-1}$ can be associated with bidentate-coordinated anions. The two low-frequency peaks centered at 732 and 724 cm$^{-1}$ can contain contributions from the uncoordinated and monodentate-coordinated anions, as well as agg$_1$ anions if they are present in these mixtures. As the low-frequency peaks are broad and overlapping, it is not possible to extract the various contributions from each anion structure.
The agg₂ and agg₃ peak only appears in solutions with greater lithium salt concentrations. Solutions with less than 30 mol% lithium salt primarily contain smaller complexes, with only one Li⁺. Due to this, the Li⁺ diffusion measured via NMR can mostly be attributed to the vehicular mechanism, for solutions with lithium salt concentrations below 30 mol%. The larger difference between the Raman shift of bidentate-coordinated anions to the uncoordinated anions in FTFSI⁻ compared to TFSI⁻ suggests a strong interaction between the anion and Li⁺ in these complexes, which would favor the vehicular diffusion mechanism.

Above 30 mol% LiFTFSI concentrations, larger lithium-anion complexes tend to form which increase the viscosity of the system, thereby reducing the diffusion coefficients of all ionic species. This effect, although still present, seems to have a decreased impact on Li⁺ diffusion compared to other ionic species. This effect suggests a significant contribution to lithium diffusion via a structural diffusion mechanism, in which anions are exchanged in the first solvation shell of Li⁺. This structural diffusion mechanism has been previously described by molecular dynamics simulations of FSI⁻ based ionic liquids.⁴³,⁴⁴ This mechanism can be thought of as a “hopping” mechanism, with Li ions hopping between coordination sites within a large [LiₓFTFSIᵧ]ₓ−ᵧ network. The rise of structural diffusion of Li⁺ at salt concentrations above 40 mol% accounts for the crossover between Li⁺ and FTFSI⁻ diffusion rates as seen in figures 3.2 and 3.4. Through the aid of structural diffusion mechanisms, Li⁺ even becomes the fastest diffusion species at 25°C with 60 mol% LiFTFSI, as other ionic species are hindered by the increased viscosity of the solution.

3.5 Conclusions

By allowing for higher lithium salt concentrations than TFSI⁻ based ionic liquids,⁴⁵ FTFSI⁻ based ionic liquids can achieve much larger lithium transference numbers than previously measured in ionic liquids. This is further enhanced by the structural diffusion mechanism of Li⁺ at
high LiTFSI concentrations, allowing Li\textsuperscript{+} to partially overcome the high viscosity of the ionic liquid and lithium salt solution.

This is an important step for ionic liquid based electrolytes, as lithium transference numbers approaching one are preferred for use in lithium-ion batteries as they can reduce electric field gradients within the electrolyte. To a certain extent, increased cation transference numbers can outweigh losses in conductivity in electrolytes due to higher viscosities.\textsuperscript{47}

3.6 References


8. Arbizzani, C. \textit{et al.} Safe, high-energy supercapacitors based on solvent-free ionic liquid


45. Matsumoto, H. et al. Low Melting and Electrochemically Stable Ionic Liquids Based on


Chapter 4. Studies on Sulfonated Polyetheretherketone (sPEEK) Membranes for Use in Direct Methanol Fuel Cells (DMFCs)

This project was done in collaboration with Dr. Isabella Nicotera of University of Calabria and colleagues in Italy, as well as Dr. Sophia Suarez of Brooklyn College. The high pressure NMR portion of this work was conducted by the author at Brooklyn College. This work was published in Journal of Solid State Electrochemistry (DOI: 10.1007/s10008-016-3167-x).

4.1 Introduction

Currently, Nafion, manufactured by E. I. du Pont de Nemours and Company, is the most widely used proton exchange membrane (PEM) in proton exchange membrane fuel cells (PEMFCs). Its use in hydrogen fuel cells is widely accepted, however it faces issues when utilized in direct methanol fuel cells (DMFCs). The largest barrier to viable DMFCs for commercial use is the permeation of raw methanol fuel from the anode, through the PEM, to the cathodic side of the fuel cell. This not only decreases the energy efficiency due to wasted fuel, but can lead to operational failure of the fuel cell. One strategy investigated to improve PEM performance has been the addition of embedded inorganic fillers. Previous studies have shown that composite Nafion membranes with organically modified titanium oxide nanoparticles show better mechanical properties, reduced methanol crossover, and higher power density than pristine Nafion in DMFCs.1–6

In this chapter, a cheaper alternative to Nafion is probed in an attempt to further reduce methanol permeability of the PEM. Aromatic main chain polymers have been significantly studied for this purpose.7–10 Specifically, sulfonated polyetheretherketone (sPEEK) membranes with a propylsulfonic-modified titanium oxide nanoparticle filler will be studied. The structure of these membranes contain narrower channels, which could help inhibit methanol crossover in DMFCs.11
Although previous work has studied the proton conductivity of these organic-inorganic composites, the effect of the microstructure of these membranes has received little attention.

In this study, several analytical techniques were used to characterize sPEEK membranes in their pure form, with titanium oxide nanofiller, and with organically modified titania nanofiller. High pressure NMR measurements were made at Brooklyn College, and preparation of the membranes and other characterization techniques were done by collaborators at the University of Calabria, University of Verona, University of Basilicata, and the University of Rome “Tor Vergata”, including variable temperature NMR, transmission electron microscopy (TEM), Raman spectroscopy, dynamic mechanical analysis (DMA), acid-base titration, electrochemical impedance spectroscopy (EIS), and tests on functional membrane electrode assemblies (MEA).

4.2 Sample Preparation

Polyetheretherketone (PEEK, 132 repeat units/mole) was purchased in its powder form from Victrex. All other raw materials were purchased from Sigma-Aldrich. Titanium oxide (\(\text{TiO}_2\)) nanoparticles were created by the rapid hydrolysis of an alcoholic solution of titanium alkoxide.\(^{12}\) Propylsulfonic-functionalized titania nanoparticles (\(\text{TiO}_2\)-\(\text{C}_3\text{H}_7\text{SO}_3\text{H}\)) was prepared by a two-step pathway. First, mercaptopropyl moieties were introduced onto titania surface, then thiol groups were oxidized into sulfonic acid groups to obtain propylsulfonic-functionalized titania.\(^2\) The functional groups were found to be 2 wt.% through CHNS/O elemental analysis and neutron activation analysis (NAA).

Sulfonation of the PEEK membranes was done through a reaction with sulfuric acid (\(\text{H}_2\text{SO}_4, 96\%\)) for 55 hours at 25°C.\(^{13}\) The degree of sulfonation (DS) of the resulting product was evaluated using \(^1\text{H}\) NMR and by titration and found to be \(DS = 0.5\).
Composite membranes were prepared containing 10 wt.% TiO$_2$ or TiO$_2$-RSO$_3$H via solution casting. 250 mg of sPEEK was dissolved in approximately 20 mL of dimethylacetamide (DMAc). This solution would be added to a solution of the necessary filler, also in solution with DMAc. The resulting solution was stirred at 80°C, to the point that after the solvent was evaporated, 5 mL of the solution remained. The product was then placed in a Petri dish and maintained at 80°C overnight. Pure sPEEK membranes were prepared in a similar manner. Membranes with a thickness of approximately 100 µm were selected. Before characterization experiments, all membranes were treated with 0.5 M H$_2$SO$_4$ solution and distilled H$_2$O.$^{13}$

4.3 NMR Measurements

Variable temperature NMR measurements were made on fully hydrated membranes. Membranes were either hydrated with pure water or a 2 M aqueous methanol solution. The confinement of the solution molecules within the sPEEK membranes induces a significant broadening of their $^1$H NMR signal. Consequently, in the case of aqueous methanol solutions, the spectral resolution prevents the distinction between the peaks of water and methanol. Methanol solutions were thus deuterated (D$_2$O/CH$_3$OD or H$_2$O/CD$_3$OD) to selectively observe either methanol or water, respectively. Membranes were dried in an oven, then hydrated by soaking in baths of either water or methanol solution overnight. Samples were then removed from the bath and blotted dry with a clean absorber (Kimwipe) to remove excess moisture on the surface of the membrane. The solvent uptake was determined by measuring the mass of the dried sPEEK membrane and the mass of the fully hydrated membrane and by applying:

$$\text{wt. \%} = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}} \times 100.$$  \hspace{1cm} [Equation 4.1]

Here, $m_{\text{dry}}$ is the mass of the membrane before hydration, $m_{\text{wet}}$ is the mass of the membrane fully hydrated, and wt.\% is the water uptake of the hydrated membrane. The water uptake level of each
membrane is shown in table 4.1. It was observed that the addition of the nanoparticles significantly reduces the membranes’ ability to adsorb water. This is most likely due to the higher rigidity of the composite membranes. The presence of fillers, especially with sulfonic acid groups, enhances cross-linking of polymer chains, thereby increasing the rigidity of the membrane.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Water Uptake (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>sPEEK</td>
<td>50</td>
</tr>
<tr>
<td>sPEEK/TiO$_2$</td>
<td>42</td>
</tr>
<tr>
<td>sPEEK/TiO$_2$-RSO$_3$H</td>
<td>37</td>
</tr>
</tbody>
</table>

Table 4.1 Water uptakes as calculated using equation 4.1 for fully hydrated sPEEK membranes.

Variable temperature diffusion and spin-lattice relaxation measurements were made using Bruker AVANCE 300MHz wide bore NMR spectrometer with a z-gradient diffusion probe (30 G/cm/A). Hydrated samples were placed in 5mm NMR tubes. For diffusion measurements, a pulsed-field gradient (PFG) stimulated-echo pulse sequence was utilized, and an inversion-recovery pulse sequence was used for spin-lattice relaxation ($T_1$) measurements. Measurements were made between 20 and 130°C.

Diffusion results are presented in figure 4.1 for membranes fully hydrated with pure H$_2$O. Significant increases in the diffusion coefficient, $D$, between 20 and 100°C were measured. This trend is rather intuitive as increased thermal energy should increase the motion of the water within the membrane. However, a significant drop in the diffusion coefficient above 100°C was observed. This is attributed to the evaporation of water from the membranes. Previous studies have shown a correlation between increased water uptakes in polymer electrolytes and faster diffusion.\textsuperscript{14–16} Interestingly, for the sPEEK membrane with titanium oxide nanofiller, water diffusion increased
when compared to the pure sPEEK membrane. It seems that the addition of nanofiller counteracts the effects of lower water uptake and induces higher rates of diffusion.

Figure 4.1. PFG-NMR diffusion coefficients for $\text{H}_2\text{O}$ in fully hydrated membranes as a function of temperature.

This effect was not observed with the organically modified nanoparticles. sPEEK membranes with TiO$_2$-RSO$_3$H nanofiller presented a lower rate of water diffusion. This could be due to the strong interactions between the sPEEK polymer chains and the sulfonic groups of the nanofiller. These interactions would result in a reduction of the nanofiller’s hydrophilic active area. This theory is corroborated by the reduced water uptake.
$T_1$ measurements probe more localized motions, including rotational motion, at time scales equivalent to the reciprocal of the NMR frequency $(\frac{1}{300 \text{ MHz}} \approx 3.3 \text{ ns})$. When the tumbling correlation time, $\tau_c$, which is temperature dependent, is equivalent to the timescales being probed, a minimum of $T_1$ with respect to temperature is reached. This is indicative of the temperature at which the energy from the excited spin states can be most efficiently transferred to the tumbling motion of the molecules.

Figure 4.2 depicts characteristic $T_1$ times for membranes fully hydrated with pure water. The temperature range observed for these studies was greater than the temperature corresponding to the $T_1$ minimum, indicated by increasing characteristic $T_1$ times with increasing temperatures. Within this domain, larger $T_1$ values are indicative of faster tumbling rates.
Figure 4.2. Characteristic spin-lattice relaxation times for $^1$H in fully hydrated membranes as a function of temperature.

The composite membranes, with nanoadditives, almost always exhibited shorter T$_1$ times through the observed temperature range, compared to the pure sPEEK membranes. This is indicative of strong interactions between the water and the nanoparticles, especially with the sulfonic groups. These low T$_1$ values for the composite membranes indicate more restricted motions of water molecules.

The membranes hydrated with selectively deuterated 2 M methanol solutions were also studied. This procedure simulates conditions of a hydrated membrane functioning in a working DMFC. Methanol and water diffusion were measured for each of the membranes, and the results
can be seen in figures 4.3-4.5. It was observed that, below 80°C, water and methanol diffused at similar rates in the pure sPEEK membranes. However, at higher temperatures, the rate of water diffusion decreased significantly more rapidly than methanol diffusion. However, composite membranes saw significant reductions in methanol diffusion rates while simultaneously observing faster water diffusion across the entire temperature range observed. It can be seen that the addition of nanoparticles seems to block methanol diffusion through the membrane.

**Figure 4.3.** Diffusion coefficients for methanol and water in pure sPEEK membranes fully hydrated with 2 M selectively deuterated methanol solutions.
Figure 4.4. Diffusion coefficients for methanol and water in sPEEK membranes with TiO$_2$ nanoparticles hydrated with 2 M selectively deuterated methanol solutions.
It can be hypothesized from this data that the interactions between the sulfonic groups on the titania nanoparticles and the polymer chains cause high reticulation of the diffusion channels. This would reduce the size of the channels, thereby decreasing porosity of the membranes, while simultaneously increasing the tortuosity of the channels. Such a change would imply a similar hindrance to water diffusion as well. To counteract this affect, $^1$H diffusion observed for H$_2$O can be aided by the Grotthuss mechanism of proton diffusion. Additionally, due to the larger molecular size of methanol compared to water, methanol would experience greater sterical hindrance than water within the membranes.
The tortuosity and porosity of membranes can be examined quantitatively via the scaling equation:

\[ D = \frac{\varepsilon}{\tau} D_0^{17-19}. \]  

[Equation 4.2]

Here, \( D \) is the diffusion coefficient of water within the membranes while hydrated with 2 M methanol solutions, \( D_0 \) is the diffusion coefficient of pure water within the membranes, \( \varepsilon \) is a parameter to describe the porosity of the membranes (less than or equal to 1), and \( \tau \) is a parameter to describe the tortuosity of the diffusion channels (greater than or equal to 1). Therefore, the \( \varepsilon/\tau \) ratio can be used to describe the diffusion channels within the three membranes. \( \varepsilon/\tau = 1 \) describes a medium through which perfectly straight diffusion paths exist. Diffusion data at 20°C was used to calculate porosity and tortuosity ratios, as seen in table 4.2.

**Table 4.2.** Porosity/tortuosity ratios were calculated using water diffusion data at 20°C for sPEEK membranes.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>( \varepsilon/\tau )</th>
</tr>
</thead>
<tbody>
<tr>
<td>sPEEK</td>
<td>0.17</td>
</tr>
<tr>
<td>sPEEK/TiO₂</td>
<td>0.20</td>
</tr>
<tr>
<td>sPEEK/TiO₂-RSO₃H</td>
<td>0.14</td>
</tr>
</tbody>
</table>

These values corroborate our description of these ionomer systems. The higher value found for the non-functionalized titania nanoparticle composite membrane can be indicative of a higher porosity. Whereas the reduced value of the porosity/tortuosity ratio for the organically functionalized nanoparticle composite membrane corresponds to the enhanced reticulations of the polymers as well as the decrease in the size of diffusion channels. This supports a lower porosity and a greater tortuosity of the membranes.
Additionally, methanol $^1$H $T_1$ times for all membranes were measured. Results are shown in figure 4.6. Composite membranes exhibited decreased $T_1$ times, across the entire observed temperature range. This corroborates results from $^1$H water $T_1$ measurements. Again, these results are indicative of reduced mobility of methanol at a localized level.

![Figure 4.6.](image)

**Figure 4.6.** Spin-lattice relaxation times for $^1$H in methanol for membranes fully hydrated with 2 M selectively deuterated methanol solutions.

High pressure NMR measurements were made on an Oxford 300 MHz magnet utilizing a Varian INOVA spectrometer and a custom-made CuBe high pressure probe. Pressure was applied using a Harwood Engineering manual hydraulic pump and Fluorinert FC-3283 as a pressurizing
fluid, to reach pressures of up to 200 MPa. Again, membranes were hydrated with selectively
deuterated 2 M solutions to observe methanol and water diffusion independently. Samples were
hermetically sealed in polyethylene bags to prevent contact with the pressurizing fluid while still
allowing the application of pressure. Trials were run with an empty polyethylene bag and
Fluorinert pressurizing to verify insignificant $^1$H background signal is produced.

For all samples, as expected, the diffusion coefficient decreases with increasing pressure,
as seen in figures 4.7-4.10. Activation volumes were calculated according to equation 2.25 and are
presented in table 4.3. It is shown that the nanofiller increased the activation volume for methanol
diffusion and decreased the activation volume associated with water diffusion. This trend is true
at both 30°C and 55°C. This indicates that the presence of nanoparticles, especially the organically
functionalized nanoparticles, significantly hinders the methanol crossover and favors water
diffusion through the membrane.
Figure 4.7. Diffusion coefficient for $\text{H}_2\text{O}$ in membranes fully hydrated with selectively deuterated 2 M methanol solutions at 30°C.
Figure 4.8. Diffusion coefficient for H₂O in membranes fully hydrated with selectively deuterated 2 M methanol solutions at 55°C.
Figure 4.9. Diffusion coefficient for methanol in membranes fully hydrated with selectively deuterated 2 M methanol solutions at 30°C.
Figure 4.10. Diffusion coefficient for methanol in membranes fully hydrated with selectively deuterated 2 M methanol solutions at 55°C.

Table 4.3. Activation volumes calculated for water and methanol diffusion in samples fully hydrated with 2 M selectively deuterated methanol solutions.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Activation Volume (cm³/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H₂O/CD₂OD (2 M)</td>
</tr>
<tr>
<td></td>
<td>303 K</td>
</tr>
<tr>
<td>sPEEK</td>
<td>16.5</td>
</tr>
<tr>
<td>sPEEK/TiO₂</td>
<td>11.6</td>
</tr>
<tr>
<td>sPEEK/TiO₂-RSO₃H</td>
<td>10.4</td>
</tr>
</tbody>
</table>
4.4 Dynamic Mechanical Analysis and Electrochemical Studies

Dynamic mechanical analysis (DMA) measurements were made using a Metravib DMA/25 equipped with a shear jaw for use with films. Results were obtained by applying a dynamic strain of amplitude $10^{-3}$ at 1 Hz between temperatures of 25°C and 250°C. The temperature was adjusted at a rate of 2°C/min. Measurements of storage modulus ($E'$) and loss factor ($\tan \delta$) were made during both heating and cooling scans.

Figure 4.11 shows that the pure sPEEK membranes and the membrane with TiO$_2$ nanoparticles have similar storage moduli at low temperatures. However, above 50°C the storage modulus of the membrane with the titania nanofiller increases at a rate higher than the pure sPEEK membranes as a function of temperature, and remains higher over the rest of the probed temperature range. The sPEEK membranes with the organically functionalized nanoparticles display a higher storage modulus than either of the other membranes across the entire temperature range. These results demonstrate that the nanoparticles improve the mechanical properties of the membrane by increasing the stiffness of the final composite. This beneficial effect is likely due to the stronger intermolecular interactions between the polymeric chains. Upon the cooling cycle, the original room temperature storage modulus was recovered.

Figure 4.12 depicts an alpha transition for all membranes within the observed temperature range. Pure sPEEK membranes showed a glass transition at 228°C. The composite membranes showed a shift of this transition towards higher temperatures with a reduction in the loss tangent values, from 1.6 to 0.7. This is most likely due to the higher stiffness of the composite membranes with respect to the pure sPEEK membranes.
Figure 4.11. Storage modulus as a function of temperature for pristine and composite sPEEK membranes measured via DMA.
Ion exchange capacity (IEC) was measured by acid-base titration. Membranes of known dry mass were equilibrated in 1.0 M NaCl aqueous solution for 24 hours to replace H\(^+\) with Na\(^+\). The solution was titrated with 0.1 M NaOH using phenolphthalein as an indicator. IEC values, in units of meq/g were calculated by:

\[
IEC = \frac{V_{NaOH} \times C_{NaOH}}{m_{dry}}.
\]

Figure 4.12. Loss factor (tan \(\delta\)) as a function of temperature for all membranes showing single alpha transitions.
Here, $V_{NaOH}$ is the added titrant volume at the equivalent point in mL, $C_{NaOH}$ is the molar concentration of the titrant, and $m_{dry}$ is the dry mass of the sample in g. Additionally, the number of water molecules per sulphonic acid group was estimated by:

$$A = \frac{n_{H2O}}{n_{SO3H}} = \frac{10 \times WU\%}{18 \times IEC} \quad \text{[Equation 4.4]}$$

Results are reported in table 4.4.

A decrease in the IEC with the composite membranes as well as a decrease in the hydration number was calculated. This can be explained by hydrogen bonding between SO$_3$H groups of the sPEEK and Si-OH and SO$_3$H groups of TiO$_2$-RSO$_3$H, which segregates the protogenic groups, reducing the amount of ion exchange functionalities.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>IEC (meq/g)</th>
<th>Λ</th>
</tr>
</thead>
<tbody>
<tr>
<td>sPEEK</td>
<td>1.73</td>
<td>16</td>
</tr>
<tr>
<td>sPEEK/TiO$_2$</td>
<td>1.53</td>
<td>15</td>
</tr>
<tr>
<td>sPEEK/TiO$_2$-RSO$_3$H</td>
<td>1.44</td>
<td>14</td>
</tr>
</tbody>
</table>

Proton conductivity was measured via electrochemical impedance spectroscopy (EIS) using a VMP3 BioLogic Science Instruments multichannel potentiostat. Membranes were placed between E-Tek ELAT HT 140E-W gas diffusion electrodes with a platinum loading of 5 mg/cm$^2$. The conductivity was measured as a function of temperature, between 20°C and 110°C, at 100% relative humidity at 25 mV.

As seen in figure 4.13, the membrane with titania nanofiller saw a significant decrease in conductivity across the entire observed temperature range. This is likely due to the non-conductive nature of titania. Although the composite membrane with organically modified filler exhibited lower IEC values and reduced water self-diffusion coefficients, it retains similar conductivities to
the pristine sPEEK membranes: up to 0.04 mS/cm at 100°C. This can be explained by an increase in the Grotthuss mechanism of $^1$H diffusion of water. While the vehicular diffusion mechanism is hindered by the increased tortuosity and narrowing of the diffusion channels with the organically modified nanofiller, interactions with the functional group on the nanofiller aids the Grotthuss diffusion mechanism, thereby raising the conductivity of the organically functionalized composite membrane.

![Figure 4.13. EIS measurements of conductivity for pristine and composite membranes at 100% relative humidity.](image)

Performances were tested in membrane electrode assemblies (MEAs) for both power as well as methanol permeation. MEAs were formed by hot-pressing electrodes onto a membrane for 5 min at 120°C. MEAs were placed in a single cell, purchased from Fuel Cell Technologies, Inc.,
with an active area of 5 cm². A home-built test station was used to feed the cathode with humidified oxygen and the anode with a 2 M methanol solution. The feed supply of methanol was monitored by a FEM 1.10 TT.18 S diaphragm metering pump by KNF, with a flow rate of 2 mL/min. The oxygen supply was controlled by a MKS PR4000 mass-flow controller with a flow rate of 150 sccm and the humidifier temperature was set to ensure 100% relative humidity of the gas. Polarization and power density curves were obtained at both 70°C and 90°C using a VMP3 BioLogic Science Instruments multichannel potentiostat. Methanol permeation was measured by linear sweep voltammetry, measuring the steady-state limiting current density at the cathode due to the oxidation of methanol permeating from the anode side. During these measurements, the anode was fed with a 2 M methanol solution and the cathode was fed with humified N₂. Limiting current density was measured applying a voltage from 0.0 to 1.3 V with a scan rate of 2 mV/s.

As seen in figures 4.14 and 4.15, the composite membranes exhibited enhanced performances in the MEA tests. This agrees with NMR diffusion measurements as higher water mobility and the increased contribution of the Grotthuss mechanism of proton conductivity enable lower resistance and therefore a higher current density in a DMFC. The composite membrane with the organically modified nanofiller obtained the best performance in a MEA, operating with a maximum power density of 40 mW/cm² and current density of 200 mA/cm² at 90°C. Additionally, figure 4.16 clearly shows the beneficial effect of the nanofiller on preventing methanol permeation in the MEA.
Figure 4.14. DMFC polarization and power density curves at 70°C for the MEAs equipped with each membrane.
Figure 4.15. DMFC polarization and power density curves at 90°C for the MEAs equipped with each membrane.
4.5 Conclusions

The use of composite sPEEK membranes with an organically functionalized titanium oxide nanofiller as a proton exchange membrane has shown significant increases to DMFC performance. Composite membranes were able to achieve increases in power density of over 45% at 70°C and 30% at 90°C in MEAs compared to pristine sPEEK PEMs. Simultaneously, methanol crossover was significantly reduced in a functioning cell.

NMR results indicate that these results are due to effects of the composite membranes narrowing and increasing the tortuosity of diffusion channels which can inhibit vehicular diffusion. These effects would be more pronounced on the vehicular diffusion of methanol rather than water,
due to its increased molecular size. Additionally, interactions between the organically functionalized nanoparticles and water enhance Grotthuss diffusion mechanisms of water, thereby retaining conductivity despite the changes to the diffusional paths. Further work is required to bring DMFCs to a point of commercial viability, however this work shows progress towards that goal.

### 4.6 References


Chapter 5. Structural Investigation of N-Alkyl-N-Methyl-Pyrrolidinium Ionic Liquids and Their Solutions with Li-Salt Under High Pressure

This project was done in collaboration with Dr. Stefano Passerini of Karlsruhe Institute of Technology and Dr. Mehdi Zeghal of University of Paris-South and their colleagues in Germany and France. The x-ray scattering work was conducted by the author during a graduate research fellowship at the University of Paris-South. This work has been accepted for publication in Journal of Chemical Physics.

5.1 Introduction

Previous studies, using both computational and experimental techniques, on ionic liquids containing cations with medium to long alkyl chains have shown a tendency for cations to form aggregates.\textsuperscript{1–3} However, only limited data exists for these ionic liquids or their aggregates under high pressures. In this study, a set of N-alkyl-N-methyl-pyrrolidinium (PyriA\textsuperscript{+}) based ionic liquids with a bis(trifluoromethanesulfonyl)imide (TFSI\textsuperscript{−}) anion has been investigated. Of interest is the effect of adding LiTFSI salt, which, while necessary for lithium battery applications, also introduces a degree of complexity in the ionic liquid structure, forming lithium-anion complexes due to the high charge density of Li\textsuperscript{+}.\textsuperscript{4,5}

5.2 Sample Preparation

Ionic liquids were synthesized according to previously published procedures.\textsuperscript{6} Pyri\textsubscript{A}X, with X = I or Br and A = 3, 6, or 9, was synthesized by reacting N-methylpyrrolidine (Pyri) with the appropriate haloalkyl (XA) in ethyl acetate. Pyri\textsubscript{A}X, being insoluble in ethyl acetate, was rinsed multiple times with ethyl acetate to remove impurities and excess reagents. The desired final ionic
liquids were synthesized by reacting $\text{Py}_{1A}X$ with LiTFSI in aqueous solution, which led to the formation of hydrophobic $\text{Py}_{1A}\text{TFSI}$ as well as hydrophilic LiX. The aqueous phase was subsequently removed.

$\text{Py}_{1A}\text{TFSI}$ were washed multiple times with deionized water to remove water soluble salt impurities. Ionic liquids were purified with activated carbon and acidic alumina, during which ethyl acetate was added to reduce viscosity of the mixture. Liquid portions were separated via vacuum filtering and were then placed in an evaporator at 85°C under vacuum to remove the solvent. Ionic liquids were finally dried at 60°C under vacuum for 2 hours then at 120°C for at least 20 hours. Structural diagrams for the ionic liquids are depicted in figure 5.1.

**Figure 5.1.** Structural diagrams for $\text{Py}_{1A}$ cations and the TFSI anion. Diagrams follow CPK coloring conventions, in which C is grey, N is blue, S is yellow, O is red, and F is green.
Ionic liquids were studied in both their pure form as well as with 30 mol% LiTFSI salt. Lithium salt was dried under vacuum for 2 days prior to use. Mixtures were created by mixing appropriate proportions of ionic liquid and lithium salt for at least 10 hours. Ionic liquids, lithium salt, and their mixtures were stored and handled in an inert Argon glovebox.

5.3 High Pressure X-Ray Scattering

A collimated molybdenum x-ray source ($\lambda = 0.7107$ Å) was utilized with a MAR345 image plate to make x-ray scattering measurements. The image plate was placed at a distance of 412 mm from the diamond anvil cell, which contained the sample. The acquisition time for each scattering measurement was 1200 s. It was found that when the acquisition time was increased to greater than 1200 s, an increase in the signal-to-noise ratio was not observed. This effect is due to the small sample thickness inherent in the diamond anvil cell design in combination with the scattering of the x-rays from atmospheric molecules between the sample and image plate.

The internal pressure of the diamond anvil cell was determined using the spectral shift of the $R_1$ fluorescence line of several rubies placed in the cell. Using this method, the uncertainty in the pressure calibration was ±0.1 GPa. Measurements were made between ambient pressure and 9.2 GPa; however, not all samples could be probed up to 9.2 GPa due to small variations in the gasket size and thickness within the diamond anvil cell. Each sample was measured to, at least, 5.5 GPa. All scattering patterns are presented with background signal subtracted out. Due to variation in the sample depth with variable pressure, calibration into absolute units was not possible. For this reason, all scattering patterns are presented in arbitrary intensity units.

Figure 5.2 shows that for pure Pyr$_{19}$-TFSI three scattering peaks are observed. A peak is located at $Q \approx 0.4$ Å$^{-1}$, which has been associated with medium to long alkyl chain lengths on the cation. This peak is usually seen as indicative of cation aggregation and will be referred to as
the “prepeak” or first scattering peak. Another peak is located at $Q \approx 0.8 \text{ Å}^{-1}$, which has been associated with the distance between like-charges. This peak shall be referred to as the second peak. The largest peak, located at $Q \approx 1.4 \text{ Å}^{-1}$, has been assigned to several inter- and intramolecular contributions, predominantly from cation polar head-anion correlations. This largest peak shall be referred to as the third scattering peak.

![Graph showing high pressure x-ray scattering results for Pyr$_{19}$-TFSI.](image-url)

**Figure 5.2.** High pressure x-ray scattering results for Pyr$_{19}$-TFSI.
Figures 5.3-5.6 show that for ionic liquids with $A = 3, 6$ no prepeak is observed. This is in disagreement with previously reported ambient pressure x-ray scattering data for Pyr$_{16}$-TFSI, in which a prepeak was found.$^3$ This is due to the broad nature of the prepeak previously reported and the low signal-to-noise ratio associated with high pressure x-ray scattering. In addition to high pressure measurements taken using a diamond anvil cell, ambient pressure x-ray scattering measurements for all samples were taken utilizing a similar setup; however, samples were placed in 5 mm capillary tubes. Results from the ambient pressure measurements, which are not depicted, found a prepeak for Pyr$_{16}$-TFSI scattering measurements, and were entirely consistent with previously published results.$^3$
Figure 5.3. High pressure x-ray scattering results for Pyr$_{13}$-TFSI.
Figure 5.4. High pressure x-ray scattering results for Pyr$_{13}$-TFSI with 30 mol% LiTFSI.
Figure 5.5. High pressure x-ray scattering results for Pyr$_{16}$-TFSI.
Figure 5.6. High pressure x-ray scattering results for Pyr\(_{16}\)-TFSI with 30 mol\% LiTFSI.

Previous studies on imidazolium-based ionic liquids have shown ionic liquids with hexafluorophosphate (PF\(_6^-\)) anions to crystallize more easily than those with tetrafluoroborate (BF\(_4^-\)) anions when subjected to high pressure. 1-Butyl-3-methylimidazolium (BMIM)-PF\(_6\) was shown to crystallize at ~0.1 GPa, while BMIM-BF\(_4\) has shown no evidence of crystallization up to
1.4 GPa.\textsuperscript{15–19} This demonstrates a strong relationship between the ionic liquid anion and phase behavior as a function of pressure.

No evidence for crystallization was found in Pyr\textsubscript{1}\textsubscript{A}-TFSI or its mixtures with lithium salt across the probed pressure range. Due to the similarities between imidazolium and pyrrolidinium-based cations, it is likely that the different scattering patterns are due to effects of the anion. Furthermore, it is probable that the much larger size, greater charge delocalization, and higher conformational flexibility of the TFSI\textsuperscript{-} compared to BF\textsubscript{4}\textsuperscript{-} or PF\textsubscript{6}\textsuperscript{-} prevent the crystallization of the ionic liquids at pressures below 9 GPa. This is supported by Raman studies, which found no crystallization of N,N-diethyl-N-methyl-N-(2-methoxyethyl)ammonium bis(trifluoromethanesulfonyl)imide (DEME-TFSI) at pressures up to 5.5 GPa.\textsuperscript{20}

A strong correlation is observed between the addition of LiTFSI and the decrease in intensity of the second scattering peak, associated with charge ordering. Previous studies have shown that ionic liquid mixtures with LiTFSI can form stable coordinations between Li cations and two TFSI anions, one in the cis and one in the trans conformer, effectively forming a single larger anion with a charge of -1.\textsuperscript{4,5,21} The difference in the size of free TFSI anions compared to Li[TFSI]\textsubscript{2}\textsuperscript{-} complexes can lead to a noticeable decrease in intensity of the second diffraction peak. Also, due to the larger size of the Li[TFSI]\textsubscript{2}\textsuperscript{-} complex, the second and third scattering peaks shift to smaller Q values.\textsuperscript{3} This latter effect is most noticeable in Pyr\textsubscript{13}-TFSI and its mixture with LiTFSI, as seen in figure 5.7. In ionic liquids with an observable prepeak, these effects cause a convolution between the prepeak and the second scattering peak, which has been previously reported.\textsuperscript{3} Due to this, along with the lower signal-to-noise ratio, second scattering peaks were indiscernible in ionic liquid and lithium salt mixtures with cation alkyl chain lengths of 6 or 9 carbons.
Figure 5.7. Positions are shown for the second scattering peak for (a) Pyr13-TFSI, (b) Pyr16-TFSI, and (c) Pyr19-TFSI, as well as their mixtures with lithium salt. Vertical error bars which are not seen lie within the printed data point.

With increased pressure, a shift in the position for third scattering peak to larger Q values is observed for all samples, as shown in figure 5.8. This is indicative of compression of the distances between cation rings and anions.
Figure 5.8. Positions are shown for the third scattering peak for (a) Pyr13-TFSI, (b) Pyr16-TFSI, and (c) Pyr19-TFSI, as well as their mixtures with lithium salt. Vertical error bars which are not seen lie within the printed data point.

Interestingly, the second peak, associated with distances between like-charges, also shifts to larger Q values with the application of pressure for samples containing lithium salt, but no
noticeable change is observed for the second peak in the pure ionic liquids. In the pure ionic liquids, the Coulombic interactions could prevent the compression of distances between similarly charged ions.

Previous high pressure studies on ionic liquids utilizing TFSI anions have shown how pressure can limit conformational changes of TFSI$^-$ between cis and trans conformers, favoring the smaller cis conformer with increasing pressure.\textsuperscript{22–24} These findings suggest that the application of pressure can inhibit coordination between Li$^+$ and TFSI$^-$, preventing the formation of Li[TFSI]$^2-$ complexes. The reduced size of the TFSI anion compared to the Li[TFSI]$^2$ anionic complex allows for closer characteristic distance between like-charges in the ionic liquid and salt mixtures with the application of pressure.

The shift of scattering peak positions, when observed, is most significant below 2 GPa. Raman and IR spectroscopy studies of similar ionic liquids have demonstrated the existence of a glassy state at similar pressures.\textsuperscript{22,23} This incompressibility beyond 2 GPa could be indicative of such a transition into a glassy state.

Molecular dynamics simulations in which 1-octyl-3-methylimidazolium tetrafluoroborate (OMIM-BF$_4$) exhibited cation aggregation with the octyl chain being characterized by a high fraction of the trans conformation have been reported.\textsuperscript{25} With increased pressure, a decrease in the simulated prepeak intensity was attributed to an increased fraction of the gauche conformation along the octyl chain.\textsuperscript{25} Diagrams of the trans and gauche conformers can be seen in figure 5.9. These conformational changes decrease the instance of cation aggregation, through a reduction in the chain-chain interaction volume. Similar results can be seen in figure 5.1 and figure 5.10 for Pyr$_{19}$-TFSI in both its pure form as well as with 30 mol\% LiTFSI, where increased pressure
decreases the size of the prepeak associated with cation aggregation. These results are consistent with previous experimental literature on OMIM-BF$_4$.$^{26}$

**Figure 5.9.** Diagrams of the *trans* and *gauche* conformers.
Figure 5.10. High pressure x-ray scattering results at selected pressures for Pyr19-TFSI with 30 mol% LiTFSI.

5.4 Conclusions

Ionic liquid and lithium salt mixtures have shown significant nanoscale structural complexity. These results depict a structure which appears to break down upon the application of pressure. Cation aggregation has been shown to decrease significantly, along with a breakdown of
lithium-anion complexes. Both structural changes might be attributed to hindrance of conformational changes between \textit{cis} and \textit{trans} conformers of TFSI\textsuperscript{−} under the application of pressure. Molecular dynamics studies on these ionic liquid and lithium salt mixtures under the application of pressure could provide further insight into these structural changes and could further the interpretation of x-ray scattering results.

5.5 References

7. Mao, H. K., Bell, P. M., Shaner, J. W. & Steinberg, D. J. Specific volume measurements of Cu, Mo, Pd, and Ag and calibration of the ruby R1 fluorescence pressure gauge from 0.06 to 1 Mbar. \textit{J. Appl. Phys.} 49, 3276–3283 (1978).
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24. Suarez, S. N. *et al.* Do TFSA Anions Slither? Pressure Exposes the Role of TFSA
