The Synthesis and Characterization of Ionic Liquids for Alkali-Metal Batteries

and a Novel Electrolyte for Non-Humidified Fuel Cells

by

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of the Requirements for the Degree
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ABSTRACT

This thesis focused on physicochemical and electrochemical projects directed towards two electrolyte types: 1) class of ionic liquids serving as electrolytes in the catholyte for alkali-metal ion conduction in batteries and 2) gel membrane for proton conduction in fuel cells; where overall aims were encouraged by the U.S. Department of Energy.

Large-scale, sodium-ion batteries are seen as global solutions to providing undisrupted electricity from sustainable, but power-fluctuating, energy production in the near future. Foreseen ideal advantages are lower cost without sacrifice of desired high-energy densities relative to present lithium-ion and lead-acid battery systems. Na/NiCl₂ (ZEBRA) and Na/S battery chemistries, suffer from high operation temperature (>300ºC) and safety concerns following major fires consequent of fuel mixing after cell-separator rupturing. Initial interest was utilizing low-melting organic ionic liquid, [EMI⁺][AlCl₄⁻], with well-known molten salt, NaAlCl₄, to create a low-to-moderate operating temperature version of ZEBRA batteries; which have been subject of prior sodium battery research spanning decades. Isothermal conductivities of these electrolytes revealed a fundamental kinetic problem arisen from “alkali cation-trapping effect” yet relived by heat-ramping >140ºC.

Battery testing based on [EMI⁺][FeCl₄⁻] with NaAlCl₄ functioned exceptional (range 150-180ºC) at an impressive energy efficiency >96%. Newly prepared inorganic ionic liquid, [PBr₄⁺][Al₂Br₇⁻]:NaAl₂Br₇, melted at 94ºC. NaAl₂Br₇ exhibited super-ionic conductivity $10^{-1.75}$ Scm⁻¹ at 62ºC ensued by solid-state rotator phase
transition. Also improved thermal stability when tested to 265°C and less expensive chemical synthesis. \([\text{PBr}_4]^+\text{[Al}_2\text{Br}_7^-]\) demonstrated remarkable, ionic decoupling in the liquid-state due to incomplete bromide-ion transfer depicted in NMR measurements.

Fuel cells are electrochemical devices generating electrical energy reacting hydrogen/oxygen gases producing water vapor. Principle advantage is high-energy efficiency of up to 70% in contrast to an internal combustion engine <40%. Nafion-based fuel cells are prone to carbon monoxide catalytic poisoning and polymer membrane degradation unless heavily hydrated under cell-pressurization. This novel “SiPOH” solid-electrolytic gel (originally liquid-state) operated in the fuel cell at 121°C yielding current and power densities high as 731mAcm\(^{-2}\) and 345mWcm\(^{-2}\), respectively. Enhanced proton conduction significantly increased \(\text{H}_2\) fuel efficiency to 89.7% utilizing only 3.1mlmin\(^{-1}\) under dry, unpressurized testing conditions. All these energy devices aforementioned evidently have future promise; therefore in early developmental stages.
This thesis is dedicated to my dearest loved ones, closest friends & the neighborhood.

“As an undergraduate you must first learn how to learn (humorously chuckled), then as a doctoral student you learn how to answer questions (stared intently), and finally as a post-doctorate you learn how to ask questions.”

– Kenneth Seddon

“Strange is our situation here on Earth. Each of us comes for a short visit, not knowing why, yet sometimes seeming to divine a purpose.”

– Albert Einstein

“I find out what the world needs. Then I go ahead and try to invent it.”

– Thomas Edison
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I truly appreciate the invaluable research training, justifiably an apprenticeship, under Austen with his 60+ years as a physical chemist; has been an incredible journey in a duration of 6+ years of · scientific methodology · ionic liquids expertise · electrochemical device knowledge · to say the upmost very least. I am honored to have Ana and Don as members along with the chair, on my committee. I would like to thank Jean-Philippe and Kazuhide for laying the extraordinary groundwork of fuel cells and ionic liquids, respectively, for myself and other researchers to further build upon in our laboratory. My good friend, Iolanda, has been an amazing cohort since my permanent transfer into the lab group and her organizational assistance is unforgettable for us establishing the first graduate
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The ever-growing human population of the world is in dire need of renewable energy for the surge of new electrical-powered technologies. The present energy supply is not enough as the human population rapidly rises on each continent of the first and developing worlds (Cohen, 1995) along with old and new electrical devices becoming more mobile every year that continue to permeate the open market. These mobile devices must meet this ever-burgeoning energy demand, which is impracticable with finite fossil fuels as the power source (Simbolotti & Kempener, 2012). The energy consumption of the world has risen exponentially with no signs of decreasing; now at the moment the world has a demand of energy primarily from fossil fuels consisting of oil, coal, gas, and some nuclear sources. Renewable energy sources are becoming more important everyday in our society; especially when old and new imminent countries are in need to secure foreign fossil fuels, such as Brazil, Russia, India, China, and Korea, known internationally as the collective B.R.I.C.K. countries (NREL-U.S. DoE, 2013). The present mature technologies are powered by 91% fossil fuels and only 9% renewable energy in the United States as seen in Figure 1.1 and even at a slightly smaller percentage overall worldwide (U.S. EIA, 2014):
The top greenhouse gas producing countries are of North America, Europe, and Asia that are consuming oil at a soaring rate. They put a strain on the limited fossil fuels and also produce large quantities of carbon dioxide gas that is extremely detrimental to Earth’s atmosphere (de Souza, Padilha, Gonçalves, & Rault-Berthelot, 2006). We are living within an extraordinary era where as a human species we recently entered the Information Age of the 1990’s transgressed into the Great Recession and now the beginning of a Renewable Energy Age. The main argument is the debate over the well-established fossil fuels versus the newly developing renewable energies.

The benefits of energy “going green” are:

• sustainability
• recyclability
• less polluting
• more energy efficient

While the disadvantages of fossil fuel energy sources the finite, less efficient, and heavily polluting when processed for production and consumer usage.

1.2 Fossil Fuels

The *Industrial Revolution* initially commenced in Great Britain back in early 19th century before spreading to the United States. The various uses of crude oil, e.g. gasoline and diesel, were further refined by John Rockefeller under the Standard Oil Company (Ladenburg, 2007). Gasoline is a petroleum-based liquid mixture from crude oil consisting mostly of aliphatic, saturated hydrocarbons at 35 MJ/L and 4–12 carbons per chain. Aromatic hydrocarbons such as benzene and toluene are added to increase the octane rating in internal combustion engines. Diesel is also a petroleum-based liquid mixture from crude oil yet additionally consisting of aromatic, saturated hydrocarbons at 41 MJ/L and 8–25 carbons per chain; this is the heaviest, factional distillate from crude oil (Hansen, Zhang, & Lyne, 2005). A major contributing factor to the resistance of progression by the dominant oil industry is the mature infrastructure remaining stagnant utilizing fossil fuels. The cost per barrel has steadily rising oil per barrel prices since 1995 shown in Figure 1.2; and the $100-200 per liter cost during unforeseen oil spill cleanups such as the recent incident of the BP Corporation in the Gulf of Mexico (Fingas, 2001):
Figure 1.2 Average price per barrel of crude oil in the United States from 1945-2013; price spike around 1980 due to the “oil crisis” (U.S. EIA, 2014).

1.3 Biofuels

Biofuels are a supposedly the next generation of liquid energy from certain renewable sources. This liquid energy is similar to an extent to common fossil fuel derivatives such as gasoline and diesel (Schubert, 2006); the pure biofuel does not contain enough energy per unit volume of a gallon as compared to them. Bioblends are when ethanol and diesel are mixed together to create a percentage blend solution (Ribeiro & Pinto, 2007). A blend of 15% ethanol into diesel will slightly decrease the energy per volume from 41 kWh/gal down to 35 kWh/gal (pure ethanol is 25 kWh/gal). The blend of 15% ethanol into gasoline is known commercially as E85 producing 25% net energy balanced from production while soybean biodiesel
generating 95% more energy (Hill, Nelson, Tilman, Polasky, & Tiffany, 2006). The country of Brazil is a formidable representation of an independent, fuel economy with their domestic ethanol being produced from their abundant, staple crop of sugar cane (Heaton & Voigt, 2004; Marris, 2006). The energy prices to produce these biofuels are not a significant net gain when sold in the market at the pump (Sanderson, 2006). For example, ethanol cost ~$58/barrel to produce from the corn being grown all the way to its final refining processes.

1.4 Hydrogen Gas Economy

Hydrogen gas will be an energy source of the future for fuel cells as it has more than 3x as much energy at an astonishing 1.4 MJ/g as compared to diesel. Yet with the present tanks the storage capacity is about four times less in energy per unit volume of gallon as compared to diesel. With further research developments this will be a competitive fuel, as additionally it has no carbon dioxide emissions but only pure water vapor when utilized by an electrical device. On-site hydrogen gas generation for instant fuel utilization is being further explored by regenerative fuel cell (RFC) systems, also referred to as electrolyzers, where the necessary electricity would have to come from a renewable energy source to be considered a sustainable process (Thomas & Zalbowitz, 1997). This principle concern of how the hydrogen gas is being produced by the present traditional, less efficient method with fossil fuel sources (Zehner, 2012) versus from the greener, cleaner renewable energy sources.
1.5 Solar & Wind Economy

Presently, these solar and wind renewable energy sources require secondary-type batteries for energy storage in on-grid and off-grid solutions. Solar and wind energy have been identified as some of leading focus points of sustainability towards renewable energy sources to date; yet combined just comprising only 17% of the overall renewable energy market as mention above. The United States Department of Energy (U.S. DoE) has allocated significant funding to the government laboratories and the private sectors to research and develop viable products for near future utilization (van Valkenburg & Vaughn, 2005). This revolutionary concept dates back as far as 2,300 years ago when the philosopher Socrates proposed utilizing sunrays to heat water or now denoted as passive solar-thermal heating (Lea, 2010); it was commercialized in the late 19th century in America then became a popular method to heat water at some point in time giving credence to the old adage that history repeats itself.

1.6 The Power Grid of the United States

The U.S. power grid is divided into three main separate sections: East Interconnection – West Interconnection – and the separate Texas Interconnection (Siluk, 2014). The grid power supply must be steadily available for on-demand power surges as needed, e.g. power spikes to businesses and homes throughout the weekdays. In this day of age technology moves at the speed of business and consumes the required energy just as fast hence solar and wind renewable energy sources must be further aided by secondary battery systems to store the excess
produced energy then supply to the power gird as maintaining trend consistency with additional boosts of power for these peak periods to prevent unpredictable power overload on the grid. This is the extremely crucial area of consistency that solar and wind energies have been lacking because although they may be renewable sources,

“If the sun isn’t showing and if the wind isn’t blowing then the economy is slowing.”

Hence brown-outs occurring would be absolutely unacceptable during business hours on a primarily renewable energy supplied grid system; especially for American cities during the emergence from beneath the Great Recession for gaining global economical traction, e.g. Phoenix, AZ (Ross, 2012). Ideally, the batteries would be charged from the excess energy produced during low peak hours normally at nighttime then discharged during peak hours in the day for consistent power grid delivery.

The key issues to circumvent are how to:

- Integrate renewable technologies into the existing power infrastructure
- Further develop these technologies enhancing electrical output efficiencies
- Construct them with cheaper yet durable materials by mass production
- Reliability of these renewable energy sources for everyday, practical usage

These renewable energy sources rely on Mother Nature to keep the wind blowing at maximum flow and the skies completely clear of overcast to maximize sunrays. Expectedly on Earth now this is not possible as the weather changes with
the seasons hence the low power dips or high spikes during fluctuations depicted by the plateau in the plot here:

![Diagram showing power grid fluctuations](image)

Figure 1.3 The proposed renewable source-based power grid utilizing secondary batteries for energy storage then discharged for electricity compensation during peak periods (Gyuk, 2008).

The proposal of convincing the society is stressed here because thus far renewable energy has not been able to demonstrate its consistency and robustness as the present, more mature fossil fuel technologies. These new electrical devices will have to meet the required dimensions for stationary units and also weight specifications for mobile purposes.

1.7 Rechargeable Battery Systems

Rechargeable, industrial-size battery systems are the foremost integral component to coincide with solar/wind systems as to provide power for overcast or
still air durations, respectively, and aid the peak power situations. This time-shift paradigm is where the batteries create their impact by allowing the renewable energy system to be independently decentralized from the main power grids (Gyuk, 2008). The sodium-ion batteries are becoming more viable as the secondary battery systems that will likely alleviate the problem of dependable power storage and steady energy consumption. Sodium-sulfur (NaS) battery systems are already stationed throughout the world as undisruptive power systems operating at high temperatures of 350°C (Sudworth, 1984). For example, the 1.2 MW NaS battery system in Charlestown, WV was the first of its kind installed in the United States in summer of 2006. This system operated during peak load conditions that reduced heat buildup in the transformer and demonstrated no upgrades were required in a 3-year period with the unit saving ~$10k USD per month due to efficiency as instantaneous, readily available power as shown here:

Figure 1.4 Coal-fired power plants and the heat engine, e.g. internal combustion engine requires an ignition/combustion process multiple steps for final energy utilization versus the instantaneous, more efficient conversion from chemical storage to electrical usage of the electrochemical device, e.g. portable battery (Pilwon, 2008).
Another type is sodium nickel-chloride batteries (Li et al., 2012) that can be a competitive system in the energy market when compared to the present, ubiquitous lithium-ion batteries and the formidable lead-acid batteries. Lithium batteries are expensive and lead-acid batteries are cheaper with a relatively short 120 cycles lifespan even with the latest advances (Martha & Hariprakash, 2006). The abundant metals such as the element sodium are mined at lower cost hence less expensive materials for construction. The ability to replace Li$^+$ with Na$^+$ will significantly reduce the production cost due to sodium metal’s preferred accessible global deposits, e.g. sodium chloride is common household table salt. Lithium metal is a somewhat rare alkali-metal, also where the largest reserves are of mining deposits outside the borders of the United States. The battery technology must be modified then optimized for energy storage as these molten salt systems presently must operate well above 300°C to operate efficiently (Dustmann, 2004).

There were 3 principle focal points, which have been under world-wide investigation for proprietary purposes are: 1) Enhancing the sealing properties for separation of the individual internal compartments of the sodium-ion battery, while eliminating the absorption of atmospheric water 2) Substituting nickel chloride in the electrolyte for other favorable materials for improved conductivities 3) Abating the cell temperature of operation of the electrolyte for the sodium-ion batteries.

These sodium-ion types of batteries are all of the alkali-metal category. They have excellent electrochemical stability, incredible charge/discharge rates, and as mentioned prior the high specific energy density. Na-NiCl$_2$ batteries are the most established and researched of the sodium-ion batteries (Ratnakumar, Attia, & Halpert, 1991). Also alkaline-earth metal (Lv et al., 2013) and aqueous-based
batteries are of interest (Wu, Mohamed, & Whitacre, 2013). Nowadays, lithium-ion batteries have been meeting this demand with their high energy to weight density ratio hence light carrying for travel, e.g. smart phones and laptop computers. Also their ability to operate at relatively low temperature of around ambient, which has continually progressed commercially since their release in 1991 by the Sony Corporation (Sony Corp, 2001). Lithium-ion batteries and sodium-ion batteries have better energy efficiency as storage units than fossil fuels, but still presently have high energy density advantage overall as potential energy (Son et al., 2013). Sodium ion batteries have the ability to deliver the same or even greater power over time at a much cheaper price. Na-NiCl2 (ZEBRA) type batteries are known to have overall lesser cost for mobile purposes such as for vehicles in the transportation sector (Gerssen-Gondelach & Faaij, 2012).

1.8 Thesis Statement

The conclusive research of this dissertation focused on sodium-ion based ionic liquids of exceptional conductivity as electrolytes for alkali-metal type battery systems operated at low to moderate temperatures to meet or to supersede energy storage benchmarks when compared to well-known secondary battery systems.
2.1 Introduction to Molten Salts

Molten salts (MSs) have been in existence over 200 years in modern society. Humphry Davy had aided in the discovering of some elements amongst the periodic table through the process of electrolytic separation: by applying a dc (direct current) electrical current to a common salt thus freeing the sodium ions into a heated liquid of sodium chloride creating the first known molten salt (Austen Angell, Ansari, & Zhao, 2011).

Throughout history, electroplating for semi-precious metals has been an energy intensive and expensive process due to the utilization of aluminum alkyls in organic solvents and high temperature molten salts. The metal industry presently utilizes electrowinning and electrorefining techniques based on the independent processes Hall and Héroult in 1886 then further developed by Hoopes of Alcoa (Aluminum Company of America) in the 1930’s to produce high metal purities of aluminum, cooper, zinc, and etc. (Patterson, 1933; Curtain & Naab, 2001).
These industrial systems always operate at high temperatures so as to reach the threshold for maximizing ion mobility by decreasing the viscosity of the electrolyte hence enabling enhanced diffusivity to the electrodes. These types of methods emit harmful carbon monoxide, carbon dioxide, fluorinated compounds, and etc. byproducts into the surrounding environment. Additionally, other complications decrease and even inhibit production when dendrites growing from the cathode connect to the anode and short-circuit the cell (Pradhan & Reddy, 2012).
2.2 The Ideal Molten Salt

By definition, the ideal molten salt has random yet evenly distributed anions and cations approximating a quasi-lattice structure. The thermodynamics of ionic liquids and their mixtures, in particular the entropy of mixing, was first analyzed by Russian scientists (Temkin, 1945). Presently, monovalent ion conducting materials have been mostly utilized for solid electrolytes such as in lithium-ion (Li⁺ ion) rechargeable batteries and solid oxide fuel cells at high temperatures (> 620°C). The scientific community plans to utilize the same monovalent materials for future sodium-ion (Na⁺ ion) battery technologies at low-moderate temperature ranges of 100-180°C.

Favorable qualitative properties are:

- Vapor pressure
- Fluidity
- Conductivity
- Thermal stability
- Glass forming capability

The molten salts utilized in the industrial Hoope process aforementioned are governed by Lewis acidity. To further reiterate electrochemistry, this branch of chemistry is specifically focused on the electronic behavior and electron transfer processes between chemical compounds for a desired electrochemical reaction or to better comprehend the redox properties. An electrophile is an atom or chemical species that has an electroaffinity, i.e. an affinity to receive electrons from some
neighboring chemical species known as nucleophile to create a stronger binding of the ionic interaction as expressed here:

$$X_{\text{base}} + Z_{\text{acid}}Y_{\text{base}} \rightarrow Y_{\text{base}} + Z_{\text{acid}}X_{\text{base}}$$

Equation 2.1

For example, AlCl$_3$ is prime chloride ion acceptor when added to a molten salt containing more basic chlorides like FeCl$_2$ or even SbCl$_3$, and the withdrawal of electron density from the environment of redox species by the AlCl$_3$, increases the redox potentials of any redox couple in the liquid, e.g. Fe(II)/Fe(III) or Sb(III)/Sb(V), in the liquid, in addition to raising the Lewis acidity as demonstrated by Mamantov and co-workers (Chapman, Smith, Sørlie, Petrovic, & Mamantov, 1984). The halide ion stability is in descending order for hard Lewis complexes: F $>>$ Cl $>$ Br $>$ I and the reverse order for soft Lewis complexes (Pearson, 1963).

The ability of AlCl$_3$ to form anionic species by chloride complexing in ionic liquid and molten salt systems is also important to the ionic conductivity. The ionic conductivity is mainly dictated by the reduction in Coulomb energy accompanying the complexing of the mobility of the alkali-metal cation within the system (Ostvold, 1971). A notable concern with AlCl$_3$ is that even though the melting point of the anhydrous material is 192.4°C, it will begin to sublime as the dimer Al$_2$Cl$_6$ at $\sim$180°C, hence altering the stoichiometry of the remaining solution. The compositional balance is vital in determining whether the liquid will be basic, neutral, or acidic in the Lewis sense, because the chloride ion activity changes so rapidly across the stoichiometric composition as reported in Pb$^{2+}$ ions (Bennett & Angell, 1985).

The well-studied acidic melts have major products of AlCl$_4^-$ and Al$_2$Cl$_7^-$ and minor constituents of Al$_3$Cl$_{10}^-$ and Al$_4$Cl$_{13}^-$ (Pradhan & Reddy, 2012). The acidic
melts have deep eutectic temperatures, such strongly Lewis acid melts undergo an exothermic reaction upon mixing with alkali-metal chlorides just above ambient temperature (Lui & Angell, 1996). The dimeric chemical form of AlCl$_3$ is Al$_2$Cl$_6$, which when reacted with a molecule containing a chloride gives rise to the anionic species Al$_2$Cl$_7^-$ (aluminum-chloride bridging) where it further contributes to the ionic conduction of the entire salt as depicted below:

![Figure 2.2](image)

Figure 2.2 Molar fraction of AlCl$_3$ of a chemical species significantly changes the Lewis acidity along with physicochemical and electrochemical properties (Boon, Wilkes, & Lanning, 1991). Permission granted for reprint.

This can be an elusive species as it is formed during melting into the liquid state or not, depending on the excess of aluminum chloride present in the molten salt or ionic liquid. Additionally, the composition can be elusive as it is generally
quantified through plotting phase diagrams and indirect measurements of vapor pressures (Liu & Angell, 1996).

2.3 Chemical Activity Control by Stoichiometry

These molten salts are of great interest due to their highly conductive properties. Unfortunately, at elevated temperatures around 300°C, they are known to exert vapor pressures, due to the AlCl₃ anionic component. Specifically, the popular melt NaAlCl₄ is known to have a vapor phase as reported separately by Dewing, Øye, Viola, and co-workers (Robelin, Chartrand, & Pelton, 2004). The systems with compositions containing more than 50 mol% of aluminum chloride exhibit a sharp decreased activity of chloride ion (pCl) that is a characteristic of any acid-base titration (Tanemoto, 1982); the same would be true of liquids in the NaBr + AlBr₃ systems.

The use of mixed halide systems for lowering the melting point from high temperatures above 300°C is also a part of developing a more cost effective aluminum plating process eliminating the requirement of volatile, organic chemical components as reported by Hussey and co-workers (Wang & Hussey, 2013).
2.4 Introduction to Ionic Liquids

An ionic liquid (IL), as defined by most researchers in this field at the moment, is a liquid composed completely of ions that has a freezing point below 100°C. ILs have been well known for more than a century now, the first deliberately synthesized case being that of ethylammonium nitrate (EAN) by Paul Walden in 1914. The melting point of the water-free EAN is 14°C, and its “simple” ionic character is revealed by its high ionic conductivity (Plechkova & Seddon, 2008). Later, Hurley and Wier discovered ionic liquids based on salts containing a cyclic cation, ethylpyridinium bromide, mixed with excess aluminum chloride as the anion, 1:2 [EtPyr]Br·AlCl₃ (Tₘ = -40°C). This electrolyte was utilized for metal deposition at low temperature of operation, decreased potential expenditure, and stronger metal adherence after the processing (Hurley & Wier, 1951). The research interest, driven by innovative applications, has been rising exponentially since the beginning of the 21st century.

ILs possess many qualitative characteristics:

- Negligible volatility
- Thermal stability
- Low viscosity
- Non-flammability
- High ionic conductivity
- Wide electrochemical windows
The ionicity is an important feature of ionic liquids to be recognized for its impact in the electrochemical properties of battery and fuel cells that continue to be explored. Protic ionic liquids have a variable ionicity, which determines the ability of the IL to conduct ionic current. It is important to have a way of determining the degree of proton transfer that occurs in the formation of an ionic liquid between a given protic acid and the base that accepts the proton. The equilibrium reaction that determines the ionicity can be written:

\[ AH + B \leftrightarrow BH^+A^- \]  

Equation 2.2

Where \( AH \) is the acid, \( B \) is the base, \( A^- \) is the deprotonated acid, and \( BH^+ \) the protonated base.

It can be beneficial to quantitatively determine the elusive rate of the actual mechanism of ionic conductance between the liquid states of the protic ionic liquids (PILs) or aprotic ionic liquids (AILs) as expressed as the equilibrium constant; here the ionization constant below:

\[ K_i = \frac{[BH^+][A^-]}{[AH][B]} \]  

Equation 2.3

Where \( K_i \) must be a large number for the ionicity to be high (Johnson, 2007). The experimental methods of obtaining estimates for the ionicity of ionic liquids using Walden plots and etc. will be discussed in later chapters.

The ionic conductivity is so important in many electrochemical applications of ionic liquids are controlled by both the ionicity and the viscosity of the liquid. The viscosity is determined by all the factors that determine how cohesive the liquid is as the temperature is increased the cohesion decreases; simultaneously the viscosity decreases and the conductivity increases. A beneficial way of seeking the viscosity is
to determine the glass transition temperature, which is a sort of cohesion indicator. This characteristic can be simply measured and its behavior analyzed in terms primarily of the relation between *Coulombic forces* for the charge-charge attractions and the *van der Waals forces*.

2.5 Attractive Forces amongst Molecular Liquids

It is best to comment first on the case of molecular liquids, where van der Waals forces act between molecules to determine the cohesion, viscosity, and glass temperatures; plus there are no charged particles to consider. Inspection of viscosity or glass temperature data for molecular liquids shows immediately that the attraction forces increase as the molecules become larger (view Figure 2.3). This is relatively easy to follow because the larger the molecules are then the larger are the number of electrons in each molecule combining to determine the van der Waals attractions.
Figure 2.3 Dependence of glass temperature on molecular weight (MW): molecules all have comparable density so increasing MW corresponds to increasing molecular volume and respective glass transition (Angell et al., 1980’s). Permission granted for reprint.

Molecular liquids are comprised of covalently bonded molecules loosely held together by weak van der Waals forces. The weak linkage amongst the molecules are the primary cause of the high vapor pressures associated with these liquids referred to as volatile organic compounds (VOCs). Presently, VOCs are the dominating liquid medium for conducting industrial electrochemical reactions for chemical production. These liquids were sought for their conductive properties and inexpensive materials, but their drawbacks such as exerting high vapor pressures, redox properties, and toxicities are unfavorable.
2.6 Dependence of Viscosity on Charge and Ion Size Factors

Turning to the case of ionic liquids, it is seen in Figure 2.4 that the cohesion energy (indicated by glass transition temperature, $T_g$) first decreases with increase in size of the ions (indicated by the molar volume, $V_m$) as the long-range electrostatic attractions between positive and negative ions decreases before it starts to increase. Thus, the cohesion energy goes through a minimum at an intermediate volume where the decreasing Coulomb forces that vary inversely with the charge separation balance of the increasing van der Waals attractions. This volume (~250 ml/mol for liquids) with singly charged cations and anions is where the smallest viscosities at a given temperature will be found as seen below in Figure 2.4:
The “packing” forces in the liquid state usually cause structural perturbations to the molecules hence less symmetrical packing obtained, which can lower the melting point under certain conditions (Ostvold, 1971). Besides the phase state, the volume expansion of a chemical species changes as a function of temperature depending on the rate, where a crystalline phase is heated to the melting point threshold to a phase transition into a liquefied state of a larger volume. The liquid when cooled rapidly (supercooled) will pass the freezing point to the glass transition into varied forms of glassy states of a smaller volume (Ediger, Angell, & Nagel, 1996). Yet if the cooling rate is faster than the normal of the ability of the molecules to pack symmetrically then the liquid phase transitions into an amorphous phase more commonly known as glasses. This rapid rate as described is also known as “quenching” (Zallen, 1983). Large cations and anions are favorable to decrease the cohesion energy hence lowering the viscosity of the system, but the larger ionic radii increase the van der Waals interactions.

Hydrogen bonding (H-bonding) is another type of attractive force. H-bonding has a significant role when concerning ion mobility in cyclic ring containing ILs; just as important for hydrated species (Hodge & Angell, 1978). The ionic bonds between the cations and anions of these species are further supplemented by different types of H-bonding. There are three main types of H-bonding that are dictated by their
relative positions, i.e. in the imidazolium ring structure. The order of interaction strength: ring hydrogens > first alkyl chain hydrogens > second alkyl chain hydrogens. Recently discovered that not only the C-H···Cl- interacts with the halide but, another weaker attraction type occurring strictly between the C···Cl- that exhibits longer interaction distances uniquely described by Skarmoutsos and co-workers (Skarmoutsos, Dellis, Matthews, Welton, & Hunt, 2012).

**The Free Energy.** The highest energy state of the solid when melted has a large lattice energy that when quenched would have not solidified upon rapid cooling, but transition into a glassy state (Angell, 1991). The lowest energy state of the solid has the least amount of lattice energy hence melting first. The amount of Gibbs free energy remains relatively same throughout the solid-to-solid phase transitions, but the solid-to-liquid phase transition decreases trending away from the melting point. This free energy value is also approximately equal to the equation expressed here:

\[ \Delta G = -RT \cdot \ln \Delta pK_a \]

Equation 2.4

When rearranged the free energy value is also approximately equal to the pKₐ value obtained as expressed here:

\[ \Delta pK_a = \exp \left(\frac{-\Delta G}{RT}\right) \]

Equation 2.5

Where \( R \) is the gas constant and \( T \) is the temperature.

In prior research by this laboratory group (Belieres & Angell, 2007) showed that the excess of the combined component boiling points composed of the PIL is
correlated to a quantity that is a proportional value to the free energy of protic transfer between the *Gurney* energy levels on acids and bases as shown below:

### Table: Acid Electrolytes

<table>
<thead>
<tr>
<th>Acid Electrolytes</th>
<th>Occupied</th>
<th>Vacant</th>
<th>$pK_a$</th>
<th>$E$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HSO$_4^-$</td>
<td>SO$_3^-$</td>
<td>-10</td>
<td>0.59</td>
<td></td>
</tr>
<tr>
<td>ClO$_4^-$</td>
<td>ClO$_4^-$</td>
<td>-9</td>
<td>0.53</td>
<td></td>
</tr>
<tr>
<td>I$_2$SO$_4^-$</td>
<td>I$_2$SO$_4^-$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HPO$_4^{2-}$</td>
<td>HPO$_4^{2-}$</td>
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<td>H$_3$PO$_4$</td>
<td>H$_3$PO$_4$</td>
<td>2.12</td>
<td>-0.13</td>
<td></td>
</tr>
<tr>
<td>CH$_3$COONH$_4$</td>
<td>CH$<em>3$COO$</em>-$</td>
<td>3.00</td>
<td>-0.18</td>
<td></td>
</tr>
<tr>
<td>IF$_4^-$</td>
<td>IF$_4^-$</td>
<td>3.75</td>
<td>-0.22</td>
<td></td>
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<tr>
<td>CF$_3$COOH</td>
<td>CF$<em>3$COO$</em>-$</td>
<td>4.75</td>
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### Table: Neutral Electrolytes

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<th>$E$ (eV)</th>
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<tr>
<td>NH$_4^+$</td>
<td>NH$_3$</td>
<td>9.23</td>
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<td>Et$_2$NH$_2^+$</td>
<td>Et$_2$NH$_2$</td>
<td>10.63</td>
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<tr>
<td>Bu$_2$NH$_2^-$</td>
<td>Bu$_2$NH$_2$</td>
<td>11.25</td>
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### Table: Basic Electrolytes

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<th>Basic Electrolytes</th>
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</thead>
<tbody>
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<td>NH$_3$</td>
<td>NH$_2$</td>
<td></td>
</tr>
<tr>
<td>OH$^-$</td>
<td>O$_2^-$</td>
<td>28</td>
</tr>
</tbody>
</table>

Figure 2.5 *Gurney* energy level diagram for protic acid-base couples, where the greater the energy difference between the proton donor (occupied level) and acceptor species (vacant level) the more ionic will be the ionic liquid product (Belieres & Angell, 2007). Permission granted for reprint.
The ΔpKₐ values from this energy level diagram will correlate not only with ionicity but also with boiling points of chosen PILs.

2.7 Types of Ionic Liquids

Presented here are the main types from the expanding field of ionic liquids.

Figure 2.6 Classification of ionic liquids: e.g. 1-butyl-3-methylimidazolium (BMI) dicyanamide (DCA) all organic ionic liquid (Pringle et al., 2002) guanidinium organic cation (Zhao, Ueno, & Angell, 2011) and all inorganic solvate ionic liquid.

2.7.1 Room Temperature Ionic Liquids (RTILs)

The room temperature ionic liquids (RTILs) achieve ambient temperature melting by the cation being composed of large molecules, which inherently lowers
the Coulombic energy force interactions hence lowers melting point of the entire molecule. This destabilization effect reduces the ability of the necessary ion packing of the molecule to crystallize. This can be proven on the typical Arrhenius plot of viscosity over inverse temperature: depicts the compounds with inorganic cations exhibiting lower melting points than when composed with organic cations. Therefore correlating weaker cohesive energy strengths to the inorganic anions.

The cation-anion pair interacts weakly hence having a low symmetry is crucial to the properties of an ionic liquid. The cationic portion: a cyclic ring with resonating pi-bonding charge of the 1-ethyl-3-methylimidazolium (EMI⁺). The anionic portion: tetrahedral structure with an inductive negative charge, evenly distributed throughout the halides of tetrachloroaluminate (AlCl₄⁻) or tetrafluoroborate. The weak bond association and spherical shape of the anion to the planer shape of the cation along with the projecting alkyl groups awkwardly disrupt the crystallization process for packing effectively into a solid therefore remains a liquid at room temperature. The uniform distribution of negative charge around positive centers of the ionic molecule is responsible for the decrease in free energy, this unique feature is called Madelung energy, which is the potential required to overcome the lattice crystal structure (W. Xu et al., 2003).

Typically, aqueous solutions at room temperature are about a half an order up to a full order of magnitude higher conductivity than RTIL, such as LiCl·6H₂O (10⁻⁰.⁷₅ S/cm) over [EtNH₃][NO₃] (10⁻¹.⁷₅ S/cm) at 25°C. Yet RTIL, [NH₄][HF₂] (10⁻⁰.₅ S/cm), is slightly more conductive at 110°C with a negligible vapor pressure when compared to the described aqueous solution just mentioned here.
2.7.2 Aprotic Ionic Liquids (AILs)

By far, the aprotic ionic liquids in particular are the most researched that is exemplified as an exponential surge in the latter years of the past century. The dialkyl imidazolium ring ions of the organic AILs class are amongst the originals discovered of the cyclic rings, which are popular and have remained favored due to the planar cyclic structure of the ring along with the pendulous alkyl groups disrupting the geometric packing-order and the carbon-nitrogen charge delocalization. Overall, decreasing the ion-ion interactions and lowering the melting or eutectic points (Pringle, Howlett, MacFarlane, & Forsyth, 2010). Aprotic ionic liquid formation is expressed here in the equation below:

\[ BX + M \leftrightarrow B^+MX \leftrightarrow B^+ + MX \]  

Equation 2.6

Inorganic, binary ionic liquids containing ammonium cations have been widely known to have low melting points and high ionic conductivities, which are excellent for proton transfer applications. Additionally, the low vapor pressure attributed to the Coulomb ordering provides evenly distributed cohesion energy throughout the quasi-lattice structure of the system. These types of molten salts that have been explored in previous investigations by Belieres and co-workers as ionic liquid electrolytes for fuel cell purposes such as \( \text{NH}_4\text{Tf}\text{NH}_4\text{NO}_3 \) (40-60 mol%), \( \text{NH}_4\text{TFAc}\text{NH}_4\text{SCN} \) (60-40 mol%), and \( \text{NH}_4\text{TFSI}\text{NH}_4\text{HF}_2 \) (40-60 mol%) all with conductivities around \( 10^{-1} \) S/cm above 120°C. One of the lowest liquid forming cation components for inorganic ILs are quaternary ammonium(\text{I}) ions. One of the lowest liquid forming anion components for inorganic ILs are of the imide family, e.g. \text{bis(trifluoromethanesulfonyl)amide(III)} ion.
2.7.3 Protic Ionic Liquids (PILs)

The protic ionic liquids are of immense interest for their design tuning purposes for electrochemical devices, i.e. fuel cells. They differ from aprotic ionic liquids in that the Brønsted acid transfers its proton to the Brønsted base for a weakly associated ionic bond versus the transfer of an alkyl group. PILs have been reported to have more fluidity therefore ionic conductivities are an entire order of magnitude higher than AILs. PILs have been the primary focus as proton-conducting electrolytes for fuel cell systems while AILs for battery systems as well as prospective replacement mediums of volatile organic compounds (VOCs) in industrial synthesis processes. A PIL achieves this increased hydrogen proton transfer preferably by Grotthuss proton-hopping mechanism, which can in brief be described as a proton quickly transferring from one molecule of the electrolyte to another molecule (to be explained in more detail in Chapter 3). Protic ionic liquid formation expressed in this equation:

\[ B + HA \leftrightarrow BH^+A^- \leftrightarrow BH^+ + A^- \]  

Equation 2.7

PILs have a uniform dispersion of the negatively charged anions ionically attracted to the positively charged proton hence lowering the vapor pressure: a descriptive property of all ILs and some MSs. This correlation is the lower glass transition temperature of the PIL usually translates into a lower melting point around ambient temperature, which can be quantified by the pK\(_a\) as reported by Friesen and co-workers (Bautista-Martinez et al., 2009).

The design properties of ionic liquid properties are tunable for desired outcomes depending on the consisting ions (Ueno & Tokuda, 2010). The ion mobility
and ionic conductivity are related by the ability of the ion $i$ to migrate, as represented by the Stokes-Einstein equation:

$$D^i = \frac{u_i k T}{k_B T}$$

Equation 2.8

Where $D^i$ is the diffusion coefficient of an ion, $u_i$ is the ion mobility, $k$ is the Boltzmann’s constant, and $T$ is the absolute temperature.

2.7.4 Inorganic Ionic Liquids (IILs)

The completely inorganic class of ionic liquids is definitely the smallest in size and less explored as compared to the aforementioned classes. Conveniently, IILs can be either aprotic or protic and could be considered more related to molten salts in nature as their cations and anions are completely inorganic. For example, the organic, cyclic cation is substituted for an inorganic, tetrahedral species. This study in particular focused on characterizing the physicochemical properties for their enhanced thermal stability of enduring moderate to high temperatures when coupled with the strong Lewis acidity of aluminum chloride based species. Also their larger electrochemical windows make them favorable for battery applications (Katayama, Konishiike, Miura, & Kishi, 2002).

A brief mention of another relatively new and more compact class are solvate (or chelate) ionic liquids, which are basically solvated ions of molten salts that are typically composed of inorganic components. The solvate molecules abate the temperature of the liquid phase similar to RTILs as an advantage, but the disadvantage is there have been some stability issues, e.g. evaporation of the aqueous solution. Presently, they are being further researched to extent their
overall longevity by Watanabe and co-workers (Ueno, Zhao, Watanabe, & Angell, 2012).

2.7.5 “Ionic Oils” Trihalide Systems

This system would be classified as a completely inorganic ionic liquid (Wang & Hussey, 2013) and the addition of another anionic species to further lower the eutectic temperature inherently increasing the viscosity is ideal of an “ionic oil” at room temperature (Xu & Angell, 1995). The stability of the trihalide is increased when the cation is larger and evenly symmetrical. The inorganic trihalides have been known to be less stable than tetraalkylammonium salts (Wiebenga et al., 1961). The melting point is decreased due to the trihalide anion being less interactive with the cation, which is typically a stronger ionic bond than of most ILs. These trihalides, IBr₂ > Br₃ > ICl₂, reported for their exceptional polarization capability coinciding with their increasing molecular weights. The tribromide (Br₃) of an AIL has the highest conductivity and uniquely, the highest viscosity of the known trihalides as this counter-correlation (Ohno et al., 2011). The tribromide begins to show signs of degradation at 120°C yet only significant mass loss above 500°C (Bagno et al., 2005). For example, sodium tribromide and sodium polysulphide have been utilized as the positive and negative electrodes, respectively, in redox flow batteries (RFB) (to be explained in further detail in Chapter 3). They can reach an open circuit potential of 1.5V with up to 74% efficiency when coupled with peripheral equipment. These chemicals are relatively inexpensive and abundant for preparation and remain active species when diluted in aqueous solutions.
2.8 The Walden Rule

The Walden Rule governs the product of the equivalent conductivity (molar conductivity) and the viscosity of the studied electrolytes in the liquid state is constant:

\[ \Lambda_m^0 \eta = C, \text{constant or expressed as } \log \Lambda_m^0 = \log C + \log \eta^{-1} \]  \hspace{1cm} \text{Equation 2.9}

Where \( \eta \) is the viscosity and the equivalent conductivity is \( \Lambda = \sigma \ast V_m \), where \( \Lambda \) is mole per charge equal to the specific conductivity, \( \sigma \), multiplied by the molar volume, \( V_m \), to the fluidity of the electrolyte.

The rule is solely obeyed by large, weakly coordinating ions in solutions of nonspecific ion-solvent interactions (Schreiner, Zugmann, Hartl, & Gores, 2010). The viscosity is an important factor for determining a suitable ionic liquid with a high conductivity for electrochemical device applications. The fragile category of viscosity is for any glassy or plastic species that typically has a physical property of high density incurring longer periods of relaxation even despite possessing a large heat capacity. Now opposite properties are categorized as strong glassy or plastic species that when presented typically possess log Arrhenius behavior on a plot of log viscosity over the glass transition temperature; commonly known as the Angell Plot (Angell, 1991). A chemical species of interest with a high viscosity can generally be classified as fragile having a low ionic conductivity. On the opposite end a chemical species of high fluidity is strong and will exemplify a high ionic conductivity near idealism of 1M KCl aqueous solutions as depicted below in the figure compared to the regions in the plot for ionic liquids:
Figure 2.7 Walden plot of log equivalent conductivity over fluidity for ionic liquids (Angell, Byrne, & Belieres, 2007). Permission granted for reprint.

Walden examined the surface tensions of molten organic salts in his earlier works of thiocyanates, halides, and alkylammonium nirates. Also his works sought a correlation of the structure to the degree of alkylation. The salts containing alkali ions generally have more than twice the viscosity than those containing halides. The hydrocarbon chains on the cations allow for a decrease in entropy while the anions separate from these chains hence an increase in entropy. The tetraalkylammonium iodides demonstrated these properties when examined by Levkov et al.
The anionic portion is considered an electrophile being the *Lewis-acid* willing to donate its electrons to the cationic portion that is *Lewis-basic*. This ionic bonding along with the molecular size/weight interactions of the species are prime contributing factors to determine the viscosity. The *Hildebrand* solubility parameter \( \delta_H \) is utilized to determine the compatibility of various chemical species creating ionic liquids, which is equal to the square root of the cohesive energy:

\[
\delta_H = \sqrt{\frac{\Delta_{vap}H - RT}{V_m}} \tag{Equation 2.10}
\]

Where this cohesive energy is dictated by the \( \Delta_{vap}H \) where is the enthalpy of vaporization, \( V_m \) is the molar volume, \( T \) is the absolute temperature, and \( R \) is the gas constant.

The higher the cohesive energy then the stronger the *Coulombic* interactions that are essentially governed by the enthalpy of vaporization. The ionic concentration is the more accepted value closely correlated to this solubility parameter and the physicochemical properties: 1) viscosity, 2) surface tension, and 3) enthalpy of vaporization. The molar volume (known density/molecular weight) has been a parameter linked to the ionic concentration (Ueno & Tokuda, 2010). The *Vogel-Fulcher-Tammann (VFT)* equation is used as fitting parameters for the conductivity and viscosity measurements supporting the *Walden* rule (Schreiner et al., 2010).

*Lewis Acidity & Basicity.* This process of electron exchange is measured in strength of the Lewis acidity of the respective electrophile and nucleophile involved within the interaction. Simply stating that hard acids bind strongly to hard bases:
and soft acids bind strongly to soft bases (Pearson, 1963). The Figure 2.8 below depicts the common single-replacement adduct for a base to an acid of strengthening electroaffinity on the Lewis acidity scale below:

![Lewis Acidity Scale](image)

Figure 2.8 Ionicity, Type I: weakly Lewis-acidic cation with a strongly Lewis-basic anion. Type II: weakly Lewis-acidic cation with Lewis-basic anion. Type III: strongly Lewis-acidic cation with a weakly Lewis-basic anion. Type IV: weakly Lewis-acidic cation with a weakly Lewis-basic anion (Ueno & Tokuda, 2010). Permission granted for reprint.

<table>
<thead>
<tr>
<th>Hard Class</th>
<th>Soft Class</th>
</tr>
</thead>
<tbody>
<tr>
<td>H⁺ Li⁺ Na⁺ K⁺ Mg²⁺ Sn²⁺ Al³⁺ Co³⁺ Fe³⁺ Si⁴⁺ Ti⁴⁺ VO₂⁺ SO₃²⁻ Cl⁻ HX (hydrogen bonding molecules)</td>
<td>Cu⁺ Ag⁺ Au⁺ Hg⁺ Cs⁺ Pd²⁺ Cd²⁺ Pt⁺ I⁺ Br⁺ HO⁺ RO⁺ I₂, Br₂, O, Cl, Br, I, M₀ (bulk metal atoms)</td>
</tr>
<tr>
<td>Intermediate Class</td>
<td>Fe²⁺ Co²⁺ Ni²⁺ Cu²⁺ Zn²⁺ Pb²⁺ SO₂, NO⁺</td>
</tr>
</tbody>
</table>

Table 2.1 Lewis Acidity Classifications (Pearson, 1963).
The higher the ionization potential then the lower the opportunity for polarization of the chemical species, therefore defining its hardness and vice versa; where the lower the ionization potential then the higher the polarization opportunity of the chemical species hence defining its softness.

2.9 Industrial Applications

BASF chemical company along with Queen University’s Ionic Liquid Laboratories (QUILL, established by Seddon and co-workers) was one of the first companies to explore a large-scale industrial process for biphasic acid scavenging utilizing ionic liquids in 2003, called the BASIL process. The alkoxyphenylphosphine products generated are crucial precursors for screen-printing type materials. In the past the general reaction generated the products via an in situ method and the byproduct hydrochloric acid as seen here then producing an ionic liquid:

\[ \text{PhP(R)Cl} + \text{R'OH} \rightarrow \text{PhP(R)R'O} + \text{HCl} \]

\[ \text{then to MI}m + \text{HCl} \rightarrow \text{H[MI}m\] \] \hspace{1cm} \text{Equation 2.11}

The BASF research group simply substituted a base that would neutralize hydrochloric acid to precipitate a salt for the heterocyclic compound, 1-methylimidazole (MI)m. The new IL, HMIIm (Tm = 75°C), would form in-situ as when MIIm readily mixed with HCl which then could be separated from product by density hence creating a lower pure product layer and above an upper ionic liquid layer. Later, the freshly protonated H[MIIm], would be recycled therefore this newly refined process was less wasteful as an alternative method. There are similar patented
methods such as the *Dafisol* process of the French Institute of Petroleum, where they utilized the ionic liquid [BMIm][AlEt₂Cl₂] as the solvent and Lewis acid in the presence of nickel(II) metal as the catalyst (Seddon, 2003). Note: BMIm is 1-buyl-3-methylimidazolium.
3. Introduction to Batteries

The market of energy utilization for residential, commercial, and personal devices is constantly evolving with energy storage in battery systems leading the way because the demand for portable power is increasing voraciously everyday for the latest in technological advancements. For each new battery generation the ultimate goal is to assemble smaller in size, lighter in weight, more powerful, and longer-lasting characteristics (Dell, 2000).

Battery chemists have focused on new chemical components to simplify the internal redox processes of system operation and enhance the overall battery performance longevity since the 1800’s ((Science, 1889); Wade, 1902). This section focuses on the thesis for the utilization of ionic liquid electrolytes for specific use in alkali-metal ion battery systems operating at low temperature around 100°C (Angell & Martin, 2010; Xu, Zhang, & Angell, 1996). The overall critical traits that must be enhanced to achieve higher energy densities, specifically for sodium-sulfur and sodium nickel-chloride, rechargeable batteries are by:

- Lower the temperature of operation to around 100°C
- Reduce the corrosive properties of the electrolyte in the catholyte
- Increase tolerance to over charge/discharge and eliminate self-discharge
• Ability to easily manufacture the sodium-ion battery in the discharged state
• Enhance safety parameters when internal components experience issues

3.2 History of Batteries

The history of battery electrochemistry even further predates American and European research projects with the discovery of the “Baghdad Battery” by archaeologist, Wilhelm Konig in 1938. These ancient batteries were dug up in the area of Khujut Rabu nearby Baghdad, Iraq of the Middle East and dated as far back to 200 B.C. (Gevorkian, 2010). The battery itself was five inches tall with an iron rod centered inside with the copper around it. The vase was filled with an acidic liquid possibly vinegar or juice to create the necessary potential difference to provide power.

The term battery originated in North America; given by Benjamin Franklin in 1748 when he discovered that an array of glass plates carried a charge (Krider, 2006). The fundamental principle of electrochemistry had a significant contribution by Dr. Luigi Galvani of the University of Bologna in Italy of the 1790’s in biological comprehension of the electrical signals in muscle contractions of deceased frog legs.

These electrical signals were indeed nerve impulses from the brain that he discovered and created the electrophysiology field (Bresadola, 1998; Piccolino, 1998). Besides biological systems he began to experiment with metallic materials and noticed electrical discharging when two dissimilar metals were in contact with each other.
3.3 Wet Cell Battery

The “wet” cell battery was invented by Alessandro Volta in 1800 at University of Pavia in Italy. The battery consisted of a voltaic pile, which was constructed of alternating discs of zinc and copper with brine soaked cloth sheets between the metal discs. The electric current produced travelled through a metallic arc; as this was the first practical method to produce reliable, steady-state electricity (Smith, 1945). In 1836, John Fredrick Daniell, sought out to continue Volta’s research and make a similar yet more simplified voltaic pile with better performance (Gevorkian, 2010). This breakthrough provided stationary power for individual devices such as telegraph, telephone, and bell-ringing systems prior to the development of the national power grid system, i.e. The Electric Storage Battery Co. (Wohlleben, 2010). Here are the electrochemical reactions of a Daniell Cell displayed below:

![Daniell Cell Diagram](image)

Figure 3.1 Daniell Cell, the spontaneous oxidation of zinc metal electrode to release two electrons to be conducted through the external wire then reduced at the copper metal electrode producing a 1.1V cell potential (Splung Physics, 2014).
An electrochemical cell using zinc and copper metals as the anodatic and
cathodic electrodes, respectively, where these electrodes had a salt bridge separator
(Bard & Faulkner, 2001). The zinc metal has a higher electrical potential than
copper or hydrogen in the electrochemical series therefore zinc will spontaneously
oxidize releasing two electrons that will travel through the current collector to the
copper metal. There they reduce the free cupric ions from aqueous solution at a
lower electrical potential to deposit copper on the electrode. The electrodes form
solid zinc sulfate at the anode terminal as expressed in the equation:

\[ \text{Anode electrode (−): } \text{Zn}_{\text{metal}} \rightarrow \text{Zn}^{2+}_{\text{aq}} + 2e^{-} \text{ at } -0.76V \]  \hspace{1cm} \text{Equation 3.1} \\

\[ \text{Cathode electrode (+): } \text{Cu}^{2+}_{\text{aq}} + 2e^{-} \rightarrow \text{Cu}_{\text{metal}} \text{ at } +0.34V \]  \hspace{1cm} \text{Equation 3.2} \\

\[ \text{Overall reaction: } \text{Zn}_{\text{metal}} + \text{Cu}^{2+}_{\text{aq}} \rightarrow \text{Zn}^{2+}_{\text{aq}} + \text{Cu}_{\text{metal}}, E_0 = 1.1V \]  \hspace{1cm} \text{Equation 3.3} \\

Michael Faraday, the protégé of Humphry Davy, is considered the
grandfather of modern electrochemistry. He established the laws pertaining to the
flow of electrons through the external circuit from the electrode are equivalently
coupled with the flow of ions through the electrolyte (Hunt, 1979; Thomas, 1992).

The most mature technology and still prevalently used battery in automobiles
is the lead-acid battery cell, which was invented by Gaston Plante of France in 1859.
Besides being the precursor to today’s car battery it was also one of the first
rechargeable batteries. In between 1867-77, George Leclanché in France invented
the first “dry” battery cell that was irreversible. This primary battery was further
refined over time to be the most easily known and frequently used battery cell that
people commonly associate battery technology for electronic devices (Fricke, 2007).
It was not until 1898 that the first commercial dry cell battery debuted on the market by Eveready Battery, originally founded as National Carbon Co., that still today manufacturers the Energizer Brand of battery cells (Energizer Corp, 2012).

Thomas Edison led his research team, which included a major contribution of the light bulb filament further development by Lewis Latimer. The team assisted with pioneering commercial usage of the direct current (dc) form of electricity first in the New York metropolitan area for street lighting purposes. Edison and his team also invented an alkaline dry battery cell from a period of 1898-1915 (Carlson, 1988). Here are some notable U.S. patents of Thomas Edison and Nikola Tesla, whom once was a researcher under the Edison team in Menlo Park of New Jersey.

Nikola Tesla, immigrated from Europe for work as a member of the Edison team then later branched off to further develop his alternating current (ac) form of electricity in Colorado Springs, Colorado. His laboratory developed ac electrical transmission (Wysock, Hardesty, Corum, & Corum, 2001) and his research is the predecessor of wireless electrical transmission for the present wireless charging stations. Also present day dc electricity from a battery or stationary source is converted into ac electricity for everyday power for devices such as lamps and televisions. At the time, this relatively new electrochemical phenomenon was now illuminating the streets out in the open for public view from behind the scientific curtain, which burgeoned the electrochemical field of physical chemistry due to the possible applications.

3.4 Electrochemical Devices for Mobile Applications

Electrochemical devices for mobility has always been at the forefront of new technology more so in the late 19th Century and well into the 20th Century than the dominant petroleum-based mobile machines, where present day internal combustion engines for diesel are ~44% efficient (Van Blarigan, 2001). The demise of mobile electric devices dwindled by the 1920’s, because batteries could not provide enough reliable storage energy (Armand & Tarascon, 2008) and coinciding with the oil tycoons encouraging the mass production of the Model T by Henry Ford in 1908 for obviously a gasoline demand still ever-present today (Tidd & Bessant, 2009).

Present day, the intercalation processes for lithium-ion batteries (Whittingham, 1978) utilized to electrically power laptops, smart phones, and etc
were first discovered by Michael Whittingham et al at Exxon Corp in the 1970’s (Whittingham, 2004) then the rechargeable version developed by John Goodenough et al at Oxford University and Bell Labs. The first commercial lithium-ion battery produced by the Sony corporation in 1991 utilized a layered-oxide (Li$_{1-x}$MO$_2$) as the anode with the transition metal typically cobalt, manganese, or nickel and graphite (Li$_x$C$_6$) as the cathode immersed in a LiPF$_6$ EC-DMC electrolyte. These batteries stored 180 Wh/kg and operate at 3.8V (Sony Corp., 1991).

A charged battery cell stores potential energy where upon circuit completion a chemical reaction ensues releasing electrons from the negative anodic chamber to the positive cathodic chamber.

Battery cell is composed of three principle parts:

- Anode, higher electrical energy state
- Separator, ion conductor (electrical insulator)
- Cathode, lower electrical energy state

These electrons are negatively charged particles, which is the makeup of everyday electricity. Electricity can exist as a collection of charged particles of either electrons or protons. The electricity can only travel along a conductor (not an insulator) that can create a magnetic field, which produces an electromotive force and activates redox processes or by simply generating heat in resistive conductors (Williard, He, Hendricks, & Pecht, 2013). The traditional delivery of electricity as the current via a conductor is dynamical (moving) while the accumulation of charge on surfaces then delivered as static (stationary) electricity.
Figure 3.3 Electromagnetic field: the ac electrical current travels through the conducting wire or rod while perpendicularly the voltage produced an electric field along with a rotating magnetic field produced by the current.

Voltage is an electromotive force (emf) or a potential difference capable of doing work expressed as a measure of charge per unit in a galvanic cell (voltaic cell). Volts determine how forceful electrons are sent through a circuit wire. Current is the rate at which electricity moves through a circuit wire capable of doing work as here expressed:

\[ E - Ir = IR, \text{ when rearranged } E = I(r + R) \]  
\[ \text{Equation 3.4} \]

Where \( I = \frac{E}{(r+R)} \), therefore \( EI = I^2r + I^2R \)  
\[ \text{Equation 3.5} \]
3.5 Types of Batteries

There are many different types of batteries with varying chemical components for varying load outputs for electrical devices. The two main types are primary and secondary batteries along with others as shown in the figure below:

![Classification of Batteries](image)

Figure 3.4 Classifications of varying battery types (including a fuel cell) and present commercial applications.

Primary batteries are irreversible, disposable batteries that are assembled in the charged state then upon usage of expending the energy the internal chemical components are transformed then unable to revert back to their original states.

Reversible batteries are typically assembled in the discharged state then an electrical current is applied to raise the energy state uphill thereby transforming the chemical components for storing electrons then upon demand the electrons are discharged as electrical energy. Typically, this process is cycled repeatedly many times until over time the internal chemical components begin to degrade into
permanent, irreversible forms that cannot be reversed anymore. Additionally, energy is wasted as heat into the battery cell surroundings due to the structural vibrations of the permanently transformed molecules unable to chemically react as once prior (Dell, 2000).

Table 3.1 Performance and operating parameters of popular battery systems.

<table>
<thead>
<tr>
<th>Rechargeable Battery type:</th>
<th>Specific energy, Wh/kg</th>
<th>Energy density, Wh/L</th>
<th>Life cycles</th>
<th>Operating temp, °C</th>
<th>Electrolyte type</th>
<th>Losses, % per month</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead·Acid, car battery SLI (starting, lighting, ignition)</td>
<td>35</td>
<td>70</td>
<td>200 – 700</td>
<td>-40 to 55</td>
<td>aqueous</td>
<td>20 – 30</td>
</tr>
<tr>
<td>Lead·Acid, portable battery (e.g. ebike)</td>
<td>30</td>
<td>90</td>
<td>250 – 500</td>
<td>-40 to 60</td>
<td>aqueous</td>
<td>4 – 8</td>
</tr>
<tr>
<td>Nickel·Cadmium</td>
<td>30 – 40</td>
<td>40 – 80</td>
<td>500 – 2,000</td>
<td>-40 to 60</td>
<td>aqueous</td>
<td>10 – 20</td>
</tr>
<tr>
<td>Nickel·Iron</td>
<td>30</td>
<td>55</td>
<td>2,000–4,000</td>
<td>-10 to 45</td>
<td>aqueous</td>
<td>20 – 40</td>
</tr>
<tr>
<td>Nickel·Zinc</td>
<td>50 – 60</td>
<td>80 – 120</td>
<td>500</td>
<td>-10 to 50</td>
<td>aqueous</td>
<td>&lt; 20</td>
</tr>
<tr>
<td>Silver·Zinc</td>
<td>105</td>
<td>180</td>
<td>50 – 100</td>
<td>-20 to 60</td>
<td>aqueous</td>
<td>5</td>
</tr>
<tr>
<td>Silver·Cadmium</td>
<td>70</td>
<td>120</td>
<td>300 – 500</td>
<td>-25 to 70</td>
<td>aqueous</td>
<td>5</td>
</tr>
<tr>
<td>Nickel·Hydrogen</td>
<td>64</td>
<td>105</td>
<td>1,500–6,000</td>
<td>0 to 50</td>
<td>aqueous</td>
<td>&gt; 30</td>
</tr>
<tr>
<td>Nickel·Metal·Hydride</td>
<td>75</td>
<td>240</td>
<td>300 – 600</td>
<td>-20 to 50</td>
<td>aqueous</td>
<td>15 – 25</td>
</tr>
<tr>
<td>Lithium·Ion</td>
<td>150</td>
<td>400</td>
<td>1,000+</td>
<td>-20 to 50</td>
<td>organic</td>
<td>2</td>
</tr>
<tr>
<td>Lithium·Polymer</td>
<td>500</td>
<td>600</td>
<td>2,000+</td>
<td>-20 to 60</td>
<td>organic</td>
<td>&lt; 1</td>
</tr>
</tbody>
</table>

3.5.1 Battery Synopsis

The alkaline battery is utilized most commonly in small portable devices. The electrodes are zinc metal as the anode and manganese oxide as the cathode with an alkaline paste as the electrolyte. The zinc-carbon battery (standard carbon
battery) also known as the dry cell is most commonly utilized in small portable devices (Fricke, 2007). The electrodes are zinc metal as the anode and carbon as the cathode with an acidic paste as the electrolyte.

The nickel-cadmium (NiCad) rated at 1.2V each cell is typically configured as a commercial battery utilized in hybrid vehicles (Wu, Mohamed, & Whitacre, 2013). The electrodes are nickel hydroxide as the cathode and cadmium metal as the anode with potassium hydroxide as the electrolyte.

The lead-acid battery is most commonly utilized in motorized vehicles. Each lead-acid battery produces 2V per cell for a total of 12V per battery. The electrodes are of lead metal as the anode and lead oxide as the cathode with aqueous sulfuric acid as the electrolyte (Martha & Hariprakash, 2006).

The lithium-ion batteries are ubiquitously utilized in majority laptop computers, tablet devices, and smart phones, as they are preferred for their rechargeability. Lithium metal batteries are for disposable purposes after powering electronics such as watches and lighting devices (Doh & Veluchamy, 2010).

The sodium-ion batteries presently operate at high temperatures between 250-350°C are presently utilized commercially as large-scale stationary power devices also being designed for future electric vehicular applications (Kim et al., 2004).

Redox flow batteries have their fuel sources pumped inside instead of being traditionally contained within the battery system encasing. The electrochemical reaction occurs when the chemicals in the liquid phase flow contacting the internal ion-selective membrane for a passive oxidative state change to release the electrons. These redox flow battery systems are under intense research and development for
the commercial interest due to the quick, convenient ability to regenerate the fuel source once depleted (Chakrabarti et al., 2014).

*Portable Batteries.* There are two main types of batteries: 1) the first kind is the primary cell, which is called the disposable battery because after consuming the energy it is discarded and 2) the second kind is the secondary cell or better known as the rechargeable battery because the discharged cell can be charged with an accommodating electrical source of electrons that reverse the electrochemical redox reactions to restore the potential energy inside the cell.

The best-known rechargeable batteries are lithium-ion, lead-acid, nickel metal hydride, and nickel cadmium. These secondary batteries will eventually cease to recharge after many cycles depending on the conditions. The nickel cadmium batteries are a prime example of decreased energy storage capacity and cyclability if the cell is not reconditioned properly such incomplete discharging and overcharging when complete; this irreversibility in performance degradation is called the “memory effect” of the internal chemical structure (Manimekalai, Harikumar, & Raghavan, 2013). This primary zinc-manganese battery was introduced to the consumer market in 1959 to replace zinc-carbon batteries (Energizer Corp, 2012).

### 3.5.2 Dry Cell Battery

The “dry” cell is categorized as a primary battery containing zinc-manganese materials. Technically, not a water-free battery, but utilized a semi-aqueous based paste moist enough (no liquid sloshing around inside) just to allow the flow of
electrons upon discharge virtually within any directional orientation. The metallic zinc serves a dual purpose as the functional anode and the protective exterior container. The electrolyte is a mixture of zinc chloride and an ammonium chloride; a watery paste where it dissociates into aqueous ammonium, protons, and chloride ions. The interior cathode consists of a manganese dioxide and carbon powder mixture where the carbon powder serves as the electrical conductor for the electrons from the oxidization of the zinc metal. The manganese is reduced from a higher oxidation state to a lower state releasing two oxygen ions to conduct through the positive terminal; also consisting of a carbon rod inserted directly into the cathodic chamber within this electrolytic paste. This carbon rod centered in the cell container is usually the best cost effective choice of electrical conductors as to avoid corrosion due to the acidic nature of the electrolyte (Fricke, 2007). There are multiple variations of electrochemical steps for the intermediate/final products in the cathode for electrolyte, ammonium chloride, hence a varying electropotential range in the cathode. Below are the electrochemical reactions upon discharge:

**Anode electrode (−):** \( \text{Zn}_{\text{sol}} \rightarrow \text{Zn}^{+}_{\text{aq}} + 2e^- \) at 0.76V  

**Cathode electrode (+):** \( 2\text{Mn}^{IV}_{\text{sol}} + 2\text{NH}_4^+ \text{Cl}^-_{\text{aq}} + 2\text{H}_2\text{O}_{\text{liq}} + 2e^- \rightarrow 2\text{Mn}^{III}_{\text{sol}}(\text{OH}) + 2\text{NH}_4(\text{OH})^-_{\text{aq}} + 2\text{Cl}^- \) at 0.5V

**Overall reaction:** \( \text{Zn}_{\text{sol}} + 2\text{MnO}_2_{\text{sol}} + 2\text{NH}_4\text{Cl} \rightarrow \)

\[ \text{ZnCl}_2(\text{NH}_3)_2 + \text{Mn}_2\text{O}_3_{\text{sol}} + \text{H}_2\text{O}_{\text{liq}}, E_0 = 1.26\text{V (up to 1.54V)} \]  

*Equation 3.6*  

*Equation 3.7*  

*Equation 3.8*
3.5.3 Lead-Acid Battery

The lead-acid battery is a categorized as a secondary battery and is most commonly known as the “car battery” amongst automobile consumers. The electrodes are composed of metallic lead and lead oxide at the anode and cathode, respectively. The electrolyte is sulfuric acid and dissociates into protons and sulfate ions. They have 78% energy efficiency and an extremely low energy to weight/volume ratios, yet what makes them so attractive is there high instantaneous power delivery for startup surges (Stevens & Corey, 1998). Below are the electrochemical reactions upon discharge:

Anode electrode (-): \( \text{Pb} + \text{SO}_4^{2-} \rightarrow \)

\[
Pb^{II}SO_4 + 2e^{-} \text{ at } 0.356V \tag*{Equation 3.9}
\]

Cathode electrode (+): \( \text{Pb}^{IV}O_2 + \text{SO}_4^{2-} + 4H^+ + 2e^{-} \rightarrow \)

\[
Pb^{II}SO_4 + H_2O \text{ at } 1.685V \tag*{Equation 3.10}
\]

Overall reaction: \( \text{Pb} + \text{Pb}^{IV}O_2 + 2H_2SO_4 \rightarrow \)

\[
2Pb^{II}SO_4 + 2H_2O, E_0 = 2.041V \tag*{Equation 3.11}
\]

3.5.4 Lithium-Ion Battery

They are a type of rechargeable battery that after oxidation the ionized molecule being lithium migrates through the electrolyte to the cathode while the electrons flow externally to power the electrical device in the discharge (insertion) process. The charging (extraction) process is the reverse action pathway where the lithium ion migrates from the cathode back to the anode to be reduced with an electron from a power source (Fricke, 2007). Li-ion batteries should not be mistaken
for lithium batteries as their primary anode material is entirely lithium metal. Another differentiating factor are the materials as the anode and the cathode are graphite and lithium metal oxide, respectively, cathodes consist of cobalt oxide (CoO\textsubscript{2}), manganese oxide (MnO\textsubscript{2}), or iron phosphate (FePO\textsubscript{4}). The layered metal oxide of the lithium molecule is what is actually oxidized and reduced during discharge and charge, respectively. The material of the electrolyte is an ether solvent with a lithium salt of either lithium hexafluorophosphate (LiPF\textsubscript{6}), lithium tetrafluoroborate (LiBF\textsubscript{4}), or lithium perchlorate (LiClO\textsubscript{4}). Below are the battery chemical reactions upon discharge:

Anode electrode (-): Li\textsubscript{x}C \rightarrow C + xLi\textsuperscript{+} + xe\textsuperscript{-} \quad \textit{Equation 3.12}

Cathode electrode (+): Li\textsubscript{1-x}CoO\textsubscript{2} + xe\textsuperscript{-} \rightarrow Li\textsubscript{1-x}CoO\textsubscript{2} \quad \textit{Equation 3.13}

Overall reaction: Li\textsubscript{1-x}CoO\textsubscript{2} + Li\textsubscript{x}C \rightarrow C + Li\textsubscript{1-x}CoO\textsubscript{2} at \( E_0 = 3.6 \text{V} \) \quad \textit{Equation 3.14}

Excessive discharging supersaturates the cell with lithium oxide salt:

\begin{align*}
\textit{Cathode electrode: Li}^+ + 1e^- + LiCo\textsuperscript{II}O_2 & \rightarrow Li_2O + Co\textsuperscript{II}O, \text{irreversible} \quad \textit{Equation 3.15}
\end{align*}

Excessive charging supersaturates the cell with cobalt oxide salt:

\begin{align*}
\textit{Cathode electrode: LiCo}^{III}O_2 & \rightarrow Li^+ + 1e^- + Co^{IV}O_2, \text{irreversible} \quad \textit{Equation 3.16}
\end{align*}

3.5.5 Sodium-Sulfur (NaS) Battery

Present day, the sodium-sulfur (NaS) batteries are utilized in the industrialized commercial sector as secondary energy storage for continual operation. They have been viewed as the future supplementary units that will provide the necessary power stabilization of the fluxing output from the renewable energy
sources of solar and wind. The main points of these batteries are to provide instant, undisrupted power delivery to the device in operation. This reliable backup power is additionally desirable to the ever-growing, ever-evolving sector of information technology as it is a premium market for personal computers and commercial servers. Industrial sized NaS batteries have one of the highest energy densities available of up to 760 Wh/kg. They must operate between 290–360°C thus enabling optimal performance and design lifetime (Weber & Kummer, 2010). They generally have exemplary current efficiency above 86% and 96% within either 2hr or 8hr charge/discharge duration, respectively. The catholyte, sodium polysulfide, upon discharging enters the liquid state around 275°C. These units have been prone to limited longevity due to growth of sodium dendritic formations (Sudworth, 1984). The Na₂S₂ and Na₂S₃ (Park, Ahn, Ryu, Kim, & Ahn, 2006) are typical products while Na₂S₄ is an intermediate cathodic product still soluble within the sulfur electrolyte but the most favored product is the Na₂S₅ as the saturated version that exhibits the highest voltage of >2.0V upon discharge. The Na₂S₃ version is expressed here and below are the electrochemical reactions upon discharge:

Anode electrode (-): \(2\text{Na}_\text{metal} \rightarrow 2\text{Na}^+ + 2e^-\)  \(\text{Equation 3.17}\)

Cathode electrode (+): \(2\text{Na}^+ + 3S + 2e^- \rightarrow \text{Na}_2\text{S}_3\)  \(\text{Equation 3.18}\)

Overall reaction: \(2\text{Na}_\text{metal} + 3S \rightarrow \text{Na}_2\text{S}_5, E_o = 2.09V \text{ (up to 2.28V)}\)  \(\text{Equation 3.19}\)

The NaS stationary battery units require thermal management of internal heaters and fresh air circulators to properly maintain the specified high temperature. This peripheral equipment requires minimal maintenance and routine inspections of the air flow system. This renewable secondary power source would be ideal for
residential use for storing wind and/or solar energy when produced thus enabling on-demand electricity. Even possible as primary sodium batteries for smaller, portable electronics (Will & Mitoff, 1975), which are in the not so far future.

3.5.6 ZEBRA (Sodium Nickel-Chloride) Battery

ZEBRA (ZEolite Battery Research Africa) or also known as (Zero Emissions Batteries Research Activity) were originally developed in South Africa back in the 1970’s and the technology was further refined in Germany in the 1980’s then finally the patents were bought by MES-DEA in 1999 (Coetzer, 1986). These are batteries consisting of two electrodes, a liquid sodium anode and a liquid sodium-nickel chloride cathode, partitioned by a thin solid electrolyte being β” alumina ceramic for sodium ion conduction. The sodium-nickel chloride batteries were originally and most extensively researched amongst the versions of the ZEBRA-type battery cells. They offer qualities of decreased temperature of operation, increased cell potential, overcharging tolerance, less complicated assembly in the discharged state, and minimized safety issues (Trickett, 1998).
Figure 3.5  Durathon sodium nickel-chloride battery for mobile energy storage from Transportation Division of General Electric (GE) consisting of individual cells packed into a single high performance, application specific module (150-200 Wh/L, >2.5k cycles based on 80% efficiency, 99% recyclable non-toxic materials) (GE Energy Storage, 2010).

There has been extensive research concerning the utilization of various transition metal-chlorides of NiCl$_2$, FeCl$_2$, CuCl$_2$, MoCl$_2$, and CoCl$_2$ were under similar conditions in the past (Ratnakumar et al., 1991). Nickel as NiCl$_2$ has reigned as the primary choice due to overall favorable electro-kinetic characteristics, such as NiCl$_2$ does experience a passivation layer upon charging which limits the kinetic capabilities. The ZEBRA batteries are high-energy battery systems that operate at 270-350°C for stationary and mobile electrical applications. These battery cells contain molten salt electrodes composed of sodium nickel chloride with the maximum ability of providing 2.58V of power at 500Ah and a cycle life greater than 1000x for the larger capacity systems. The electrodes require a preheat conditioning which may take up to 24-hrs for the initialization of the system to the get the
operating temperature of the battery cells up to 350°C (Galloway & Dustmann, 2003). Afterwards the thermal manager would also need to utilize 14% of self-produced power to regulate the operating temperature on a daily basis if under continual 24-hour usage. Below are the electrochemical reactions upon discharge:

**Anode electrode (−):** \[2 \text{Na}_\text{metal} \rightarrow 2 \text{Na}^+ + 2e^- \]  
**Equation 3.20**

**Cathode electrode (+):** \[\text{NiCl}_2 + 2 \text{Na}^+ + 2e^- \rightarrow \text{Ni}_\text{metal} + 2 \text{NaCl} \]  
**Equation 3.21**

**Overall reaction:** \[2 \text{Na}_\text{metal} + \text{NiCl}_2 \rightarrow 2 \text{NaCl} + \text{Ni}_\text{metal}, \ E_0 = 2.58V \]  
**Equation 3.22**

Many alkali-metal chlorides have been chemical contributors due to their higher ionic conductivities and lower melting points such as NaBr, LiBr, and LiCl that have been studied. The larger ionic radius of bromide reduces the melting point to 747°C of NaBr as compared to 801°C of NaCl. These combinations all contained excess alkali metal-chloride to prevent the Lewis acidity of the aluminum chloride from degrading the battery system. The conductivity increase could be attributed to additional alkali-metal into the secondary electrolyte hence an irregular structural formation. These deformities within the modified structure create ion channels for increased ion conduction pathways.

Most investigations at lower temperatures of operation focused primarily on overcoming the ohmic resistances of the tubular or β" alumina solid electrolyte (BASE) generally 2mm or less in thickness and lesser attention is given to the secondary electrolyte of NaAlCl₄ (Legers, 2005). Researchers at Pacific Northwest National Laboratory (PNNL) had been able create a micron thin BASE with the aid
of Eagle Pitcher and added chemical additives to the well-studied secondary electrolyte for improving ionic conductivity (Li et al., 2012).

3.5.7 Redox Flow Battery

Redox flow batteries are electrochemical devices that produce electricity from the chemical reactions of the dissolved electroactive ions within the respective electrolytes. The liquid electrolytes continually flow via pumps through the cell to the ion-selective membrane where being directly converted into chemical energy in the cell chamber while the electrical current captured at the solid electrode to provide power to the external load. The flow batteries are considered rechargeable as the depleted electrolyte can be replenished for fresh electrolyte stored in nearby tanks. The larger volumes of electrolyte stored hence more current density and the better the electrolytic conversion cell the more power density:

Figure 3.6 Simplified schematic of the large-scale redox flow battery cell with adjoining fuel tanks (Chen et al., 2014).
The vanadium redox flow battery was discovered in 1978 at Bell Laboratories in Murray Hill, New Jersey (Johnstone, 2008). The charge/discharge of the system is based off of the oxidation-reduction cycling of elemental vanadium at various oxidation states as the liquid electrodes normally around room temperature. The all vanadium with sulfuric acid version is expressed here and below are the battery chemical reactions upon discharge:

\[
\begin{align*}
\text{Anode electrode (−): } & V^{2+} \rightarrow V^{3+} + e^- \quad \text{Equation 3.23} \\
\text{Cathode electrode (+): } & VO_2^+ + e^- \rightarrow VO^{2+} \quad \text{Equation 3.24} \\
\text{Overall reaction: } & V^{2+} + VO_2^+ \rightarrow V^{3+} + VO^{2+}, \ E_0 = 1.4V \quad \text{Equation 3.25}
\end{align*}
\]

VRB Power systems is a Canadian company that designs and constructs these vanadium redox flow batteries and has demonstrated a performance of 75-85% efficiency and 13k regenerative cycles when coupled with power conversion system. The cell stack operates at 40°C and has the ability to charge/discharge simultaneously. Additional advantages are avoidance of toxic heavy metals and the indefinite life of the electrolytes thus no waste generation (VRB Power Systems Inc., 2011). There are many other types of flow batteries such as the zinc-bromine flow battery system (Nguyen & Savinell, 2010) utilizing zinc bromide as the electrolyte. Below are the battery chemical reactions upon discharge:

\[
\begin{align*}
\text{Anode electrode (−): } & Zn \rightarrow Zn^{2+} + 2e^- \quad \text{Equation 3.26} \\
\text{Cathode electrode (+): } & Br_2 + 2e^- \rightarrow 2Br^- \quad \text{Equation 3.27} \\
\text{Overall reaction: } & Zn + Br_2 \rightarrow Zn^{2+} + 2Br^- , \ E_0 = 1.8V \quad \text{Equation 3.28}
\end{align*}
\]
Premium Power launched their version called the TransFlow 2000 system capable of 2.8 MW-hr with a 500kW rating of portable power for industrial load demands. This company has also set goals of introducing the HomeFlow as a residential system for solar energy storage capable of 30kW-hr with a 10kW rating. Their plan is make the unit affordable on the market price (Kanellos, 2010).

3.5.8 Metal-Air Battery

Other emerging battery technologies are the metal-air batteries, which are of immense interest for transportation applications. Zinc-air batteries to be refined to achieve an ideal energy density of 1,084 Wh/kg, but practical energy density of 350 Wh/kg. The cells have electrodes composed of a zinc anode, a porous carbonaceous air cathode, and usually an aqueous-based potassium hydroxide electrolyte (Caramia & Bozzi, 2014). Here are the irreversible (non-rechargeable) battery cell electrochemical reactions upon discharge:

Overall reaction: $\text{Zn}_{\text{metal}} + \frac{1}{2} \text{O}_2 \rightarrow 2 \text{ZnO}$ \hspace{1cm} \textit{Equation 3.29}

The actual potential is limited to around 1.23V as to prevent the decomposition of the water molecules of the aqueous solution in the electrolyte. Most researched zinc-air batteries are not rechargeable at the present moment due to the consumption of zinc metal to form the final product the zinc paste, yet an Arizona based company: Fluidic Energy led by Cody Friesen has laid proprietary claim to the only commercial rechargeable zinc-air batteries for remote, undisrupted power generation suppliers (Zyga, 2009).
Lithium-air batteries presently at ~83% efficiency would help mitigate the present over voltage for oxygen reduction reaction by control of the SEI (solid electrolytic interphase) and ceasing the consumption of pure oxygen gas versus actual atmospheric air along with its contaminants, CO\textsubscript{x} and NO\textsubscript{x} reactants, for realistic conditions (Christensen et al., 2012). Below are the battery cell electrochemical reactions upon discharge:

\[
2 \text{Li}^+ + \frac{1}{2} \text{O}_2 \rightarrow \text{Li}_2\text{O}_2 \quad \text{nonaqueous-based electrolytic system}
\]

\[
2 \text{Li}^+ + \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} \rightarrow 2 \text{LiOH} \quad \text{aqueous-based electrolytic system}
\]

The Li-air cell energy yield is appreciably greater since the oxygen bond does not need to be oxidized by a platinum catalyst as required in hydrogen/oxygen fuel cells where ideally 1000 Wh/kg could be attainable as compared to 400Wh/kg for Li-ion cells. Researchers are focusing on reversible lithium-air battery systems by increasing specific energy and energy density as a battery pack system for automotive purposes.

3.6 β” Alumina Solid Electrolyte

This is an integral battery component called the separator known as β” Alumina Solid Electrolyte (BASE) within the internal system of the Na\textsuperscript{+} battery. The ceramic electrolyte should be as thin as possible without lacking in durability to provide higher power density overtime at ambient temperature, where the typical chemical composition is Na\textsubscript{2}O•11Al\textsubscript{2}O\textsubscript{3} (Farrington, 1982). The BASE separates the heated liquid electrodes within the encapsulation of the battery system. The
material has an exceptional high ionic conductivity of >100 mScm⁻¹ at an operating temperature between 300-400°C as described in the table here.

Table 3.2 Specific conductivity of β” Alumina as a function of temperature. Battery separator ionic conductivities courtesy of Ionotec, Ltd in the United Kingdom.

<table>
<thead>
<tr>
<th>Ionic conductivity (function of temperature)</th>
<th>Na⁺ β” Alumina (Scm⁻¹)</th>
<th>K⁺ β” Alumina (Scm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25°C</td>
<td>0.002</td>
<td>0.0005</td>
</tr>
<tr>
<td>200°C</td>
<td>0.092</td>
<td>0.021</td>
</tr>
<tr>
<td>300°C</td>
<td>0.24</td>
<td>0.053</td>
</tr>
<tr>
<td>400°C</td>
<td>0.38</td>
<td>0.10</td>
</tr>
</tbody>
</table>

β”-alumina is comprised mainly of aluminum oxide (Al₂O₃) with sodium ions (Na⁺) narrowly oriented within the planes of the crystal lattice. The aluminum oxides are called conduction slabs when layered with the sodium ions between creating the conduction planes (Lu, Lemmon, Sprenkle, & Yang, 2010). Specifically, the Na⁺ ion species are high mobility through the loosing packing of the mirror plane within the crystalline structure composed of the many mid-oxygen sites between the open Beevers-Ross sites and anti Beevers-Ross sites (Kim et al., 1979).

The sodium ions availability is primarily within the BR open sites then the rest lie in the mid-oxygen open sites when conducting. The Nernst-Einstein equation can be utilized to determine the diffusion coefficient $D_σ$ or the relation rearranged to determine the ionic conductivity $σ$ as expressed below:

$$D_σ = \frac{αkT}{Nq^2}$$

Equation 3.32

Where $σ$ is the ionic conductivity, $k$ is the rate constant, $T$ is temperature, $N$ is the mobile species concentration, and $q$ is the charge.
This chemical compound conducts these present ions and the influx of fresh sodium ions upon charge and/or discharge for battery applications. There are anisotropic conductivity properties when hot pressed where there has been reported a slightly higher resistivity ratio along the parallel plane versus the perpendicular plane and even added resistivity with incremental decrease in grain size from 100 mm down to 2 mm when measured at 300°C (Youngblood, 1978).

\( \beta'' \) Alumina Application. The layers have to be calcined properly and many other recipe tweaks assist in the elimination of mixed \( \beta' \) and \( \beta'' \) phases, which have lower conductivities. There are even a \( \beta''' \) and \( \beta'''' \) solid electrolytes (Matsui, 1981) to diminish separator degradation for NaS battery applications. \( \beta'' \) alumina is a prime candidate for the electrolyte as it is a Na\(^+\) conductor and prevents the reduction of Al\(^{3+}\) into aluminum metal. The NaSICON (Sodium Super Ionic Conductor) battery technology is currently being refined by Ceramatec, founded 1976 in Salt Lake City and now a part of the CoorsTek, owned by Coors Brewing Company. The sintered ceramic electrolyte of NaSICON selectively conducts only sodium ions via particle grain boundaries in solid state as reported (Hasler, 2009). The \( \beta'' \)-alumina can be attacked by the Li\(^+\) ions of the cathodic composition compromising its seal then short-circuiting. It conducts only sodium ions; hence a buildup of lithium ions in the conduction planes creating cracks on the surface occurs when charging is initiated (Petrovic & Mamantov, 1983).

Another alternative is diverting from the specific capacity of the performance but the design overview. There have been recent efforts by researchers at Pacific Northwest National Laboratory (PNNL) to utilize a Na\cdotZnCl\(_2\) catholyte as a less
expensive material and lower operation temperature to 280°C for comparable performance. This system suffers from multiple redox steps with an intermediate species of Na₂ZnCl₄ for a complicate charge/discharge cycle that ultimately consumes the sodium ions into a salt that permanently precipitates out of the liquid state in the cathodic chamber (Lu et al., 2013).

3.7 System Efficiency

The efficiency of a battery system is important for performance and longevity. The Coulombic efficiency (CE) determines the charge/discharge cycling ability of the system as seen here:

\[
CE = \frac{Q_c}{Q_d}
\]

Equation 3.33

Where \( Q_c \) is the charge input and \( Q_d \) is the charge output.

The \( CE \) can decrease for a number of reasons such as internal resistances from irreversible byproducts and slowing of electrochemical kinetics (A. J. Smith, Burns, Trussler, & Dahn, 2010). A principle dispute is the high temperature of operation and continual thermal maintenance. After the initial heating no additional energy is required for the thermal management as the battery cells generate enough heat energy to overcome internal resistances. A battery system with exceptional efficiency would be by utilizing all the generated heat without internal energy losses.
**Alkali-Metal Interfacial “Wetting.”** The interface of the liquefied electrodes to the solid electrolyte known as wetting is a vital aspect for the transfer of ions between the metals regardless of their respective ionic conductivities. The sodium and lithium metals play the roles as anodic materials for batteries, which require optimal wettability to limit the anode effect of polarizing, excess heat buildup, and corrosion during operation (Morel, 1970). For example, pure sodium metal melts at 98°C but still poor interfacial contact with the separator. Typically, enhancing wettability is achieved by increasing the temperature of operation for a conditioning duration until desired stabilization. The contact angle needs to decrease as much as possible (Zisman, 1964) indicating increased spreading of the sodium metal for optimal surface area contact to the solid separator of an alkali-metal anode as expressed here:

\[
\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta 
\]

Equation 3.34

Where \(\gamma_{SV}\) is the interface solid to vapor phases, \(\gamma_{SL}\) is the interface solid to liquid phases, \(\gamma_{LV}\) is the interface liquid to vapor phases.

This equation is the mechanical equilibrium of the three surface tension types of a liquid droplet on a solid plane under normal atmospheric conditions at room temperature. The temperature is the ideal method to increase the sodium interfacial wetting along with pressure within a battery system. The sodium metal interface increases when current pass through it as well (Wang, 2010).
3.8 Electrolytic Additives

Hydrochloric acid, HCl (Smith, Dworkin, Zingg, & Pagni, 1989) and thionyl chloride, SOCl₂ (Kim, Lang, & Kohl, 2005) and are well-studied additives to the NaAlCl₄ molten salt of the catholyte in the sodium-ion battery for enhanced kinetics of Na⁺ mobility at low temperatures.

![Diagram](image)

Figure 3.7 The chloride bond interaction of the additives A: thionyl chloride and B: hydrochloric acid weakening the Lewis acidity of the tetrachloroaluminate to free the sodium ion at low temperatures (Kim et al., 2005).

3.9 Battery Materials

The raw materials of the ZEBRA battery system are reasonable priced yet the market value of this unit for a practical offset of the cost is suitable for units only greater than 20kWh. Also enhance the reliability of the power grid and allow new innovations access to participate in the electrical market. It is crucial new services are provided to regulate power systems and technological advances in storage charge and discharge for instantaneous response times during unpredictable situations. The Ceramatec division of Coors Tek has developed a battery system
with backup power storage for a maximum of 20 kW in 4 hours (5 kW/h), which is enough to supply a medium sized house. The first generation unit would cost around $2k USD with a 10 year lifespan or 3.65k cycles therefore around 2.5c/kWh: a stark contrast to 8c/kWh when purchased from the conventional power grid (Green et al., 2013). The principle challenges are lowering the cost of production for homeowners while within the size constraints of a typical refrigerator and a manageable operating temperature at 45°C (or 113°F).

<table>
<thead>
<tr>
<th>Cost per ZEBRA (Na/NiCl₂) Battery percentage</th>
<th>Cost per kWh percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell materials 39%</td>
<td>Nickel materials 63%</td>
</tr>
<tr>
<td>Manufacturing 32%</td>
<td>Iron materials 17%</td>
</tr>
<tr>
<td>Controller system 16%</td>
<td>β” alumina 12%</td>
</tr>
<tr>
<td>Battery casing 13%</td>
<td>Electrolyte 6%</td>
</tr>
<tr>
<td></td>
<td>Copper wiring 2%</td>
</tr>
</tbody>
</table>

*Nanomaterials.* These nano-sized structures are being developed to increase the surface area for enhanced SEI (solid electrolytic interface) conduction plus the nano-infused electrodes can be coated to avoid unwanted redox processes and prevent decomposition or damaging stresses (Xue, Xia, Tucker, Fu, S. Zhang, Li, Zhang, 2013). These nano-electrodes have the capability of achieving higher capacity due to reduced interfacial resistances (Tokuda, Tabata, Susan, Hayamizu, & Watanabe, 2004). There are now aqueous-based electrode portions that significantly increase the ionic conductivity within electrolytic polymers by improving the interfacial grain-boundary areas and less sensitivity to atmospheric water (Lu, Goodenough, & Kim, 2011). Additionally, the use of hydrophobic ionic
liquids would eliminate the water issues, but for feasible utilization ionic liquids must be able to exhibit high conductivity at low temperatures and have a low-cost of production (Appetecchi, Scaccia, Tizzani, Alessandrini, & Passerini, 2006).

3.10 Alternative Electrodes & Electrolytes

Magnesium and aluminum metals as the mobile species utilized in sulfur/oxygen and graphite fluoride scaffolds, respectively, could be alternative high capacity battery systems (Armand & Tarascon, 2008). There are two principle methods for ion exchange: molten salt bath or the salt vapor phase atmosphere (Satter et al., 1986). This could avoid the requirement of anhydrous battery systems, hence less stringent constraints on the sealants for protection against moisture. NaTi$_2$(PO$_4$)$_3$ with water molecules is an aqueous electrolyte in the cathodic compartment interfaced with new novel BASE (b” alumina solid electrolytes) separators that can be gently moistened while conducting sodium-ions (Wu, Mohamed, & Whitacre, 2013).

3.11 Safety Concerns

Of course, the battery longevity factor requires enhanced conductive of the chemical components and thinner (less resistive) separators. Unfortunately, the narrower separator heightens the risk of cell compromise then the inevitable short-circuiting of the battery and the possible safety concern of igniting a chemical fire. This system has been identified to be more tolerant to short circuiting malfunctions as the individual cells can be replaced when deemed necessary within the cell stack;
hence less susceptible to cell failures inducing chemical fires as in the general case of sodium sulfur battery systems. Occasionally upon accident, laptop Li-ion batteries that pressurized within their encasing catch fire.

The most recent troublesome cases of consumer safety were the Li-ion batteries aboard the new Boeing 787 Dreamliner airplanes of overheating to where premature landings were needed. The primary concern is to dissipate the heat generated limited to only that dysfunctional cell undergoing cell failure in a battery system. If not controlled the adjacent cells in the housing will absorb the detrimental heat causing overheating then eventually cell failure of a once fully functional cell then spreading the heat to the next adjacent cell then so on. This cascading effect is known as “thermal runaway” in the battery industry and has the hazard of the materials melting and possibly igniting into flames (Williard et al., 2013).

This battery technology is in its infancy stages and unexpected events do occur. On September 2011 in Ibaraki, Japan the NGK battery system installed at Mitsubishi Materials Corp.’s Tsukuba plant caught fire for an 8 hour burning duration until declared extinguished by local authorities (Irfan, 2011). Hence, when the energy is crammed into an unfavorable area when naturally wanting to be an area of a lower energy state. Therefore when this energy is stored over time there looms a possibility of an energy escape by means of a slow leak or suddenly as an explosion relatively proportionate to the stored energy volume (Wesoff, 2011).

Yes, renewable energy can have its problems and these types of battery failure occurrences as aforementioned will grow ever so gradually in parallel as this sector increases worldwide. Yet the safety issues and bodily risks are just as equal
or more dangerous for fossil fuels. These risks are much more common and widely acceptable as mature technologies of these traits have the so-called grandfathered-in-clauses amongst the market of producers and consumers.
3.12 Introduction to Fuel Cells

The alkaline fuel cell (AFC) was first utilized in the aerospace sector by NASA, where this technology provided electricity and water in a spacecraft of the Project Gemini and Apollo missions to the moon. Later in the 1970’s, the phosphoric acid fuel cell (PAFC) further developed by the United Technologies Corporation (UTC) was the first commercialized fuel cell unit to provide large-scale stationary power. Towards end of the 20\textsuperscript{th} century the latest developments of proton exchange membrane fuel cell (PEMFC) in the automotive industry were by Daimler Chrysler-Mercedes (Dicks & Larminie, 2003). Most recently in the early 21\textsuperscript{st} century the Phantom Works, a subdivision of Boeing, focused on the latest PEM fuel cell innovations to integrate with current aircraft technology (Coppinger, 2007).

![Fuel cell-powered light aircraft](image)

Figure 3.8 Light aircraft powered by a proton exchange membrane fuel cell (PEMFC) by Phantom Works of the Boeing Corp. (Sawhney, 2012).
New fuel cell technology such as the solid oxide has the ability to use significantly less fuel at 60% up to 85% efficiency as compared to a standard gas turbine engine of an aircraft, where this technology could be used to power the 500kW energy demand required for flight (Santin, Traverso, Magistri, & Massardo, 2010). Present day there is a resurgence of the solid oxide fuel cell (SOFC) utilizing thinner membranes for the planar-type system with the reversible benefit of become an electrolyzer as well have been developed by the General Electric Corporation (Nyugen, 2011).

3.13 Fundamental Operation of a Fuel Cell

The fundamental principles of the fuel cell was discovered by German scientist, Christian Schönbein, in 1838 from there the basic technology was further developed by British scientist and judge, Sir William Grove, in 1839 (Grove, 1839). A fuel cell is an electrochemical device known as a Galvanic cell that converts the molecules of an inlet fuel source, e.g. hydrogen gas, into their stoichiometric quantities of electrons and ions as illustrated below:
Initially, the electrons are spontaneously liberated by oxidation on the catalytic surface called HOR (hydrogen oxidation reaction) of the negatively charged anode at the triple point of contact site, which is where the fuel-catalyst-electrolyte convene for the electrochemical reaction. The electrolyte partitioning the chambers is electrically insulated thus the electrons are forced to migrate from the anodic chamber by the conductive wire collector to provide power to the external device as the electrical current flows through it to complete the circuit back into the internal cathodic chamber of the fuel cell. Simultaneously, as the electrons are powering the device by the liberated ions (hydrogen protons) of the triple point redox reaction are
conducting from the anodic chamber through the electrolytic membrane (solid or liquid) into the cathodic chamber, which is the inlet of the oxidant source (e.g. oxygen gas). Finally, the ions and electrons converge at the triple points on the catalytic surface ORR (oxygen reduction reaction) of the positively charged cathode for a reduction reaction as expressed here:

\[
\text{Anode (-): } \quad 2H_2 \rightarrow 4H^+ + 4e^- \quad \text{(oxidation)} \quad \text{Equation 3.35}
\]

\[
\text{Cathode (+): } \quad O_2 + 4e^- + 4H^- \rightarrow 2H_2O \quad \text{(reduction)} \quad \text{Equation 3.36}
\]

Hence, the electrochemical reaction produces the stoichiometric quantities of pure water vapor that flows through the outlet exhaust port. The hydrogen gas is the limiting reagent where \(\sim 80\%\) undergoes HOR (Kolb, 2008). Therefore, the typical gas flow (\(\eta\)) of the oxidant oxygen is an excess of \(\lambda\) is \(>1\) as depicted here:

\[
\lambda = \frac{\eta_{O_2}}{2\eta_{H_2}} \quad \text{Equation 3.37}
\]

A fuel cell with power supplied to it will operate reversibly hence producing hydrogen and oxygen gases when immersed in water; the process is called electrolyzation.

3.13.1 Protonic Migration & Conductance

Thus far, Nafion is the benchmark standard of the electrolytes of PEM fuel cell testing. The versions of 115 and 117 serve their primary function as a proton exchanger that must be readily hydrated to maintain optimal efficiency when operating around room temperature (Mota et al., 2006; Adanur et al., 2006). The Nafion material is a sulphonated acid polymer electrolyte that transports the
hydrogen proton by a water molecule creating a positively charged hydronium ion by a process called Vehicular mechanism. The hydronium migrates via the sulphonated groups that are negatively charged for repulsion as seen here:

Figure 3.10 Typical polymeric chemical structure (perfluorosulphonic acid) of Nafion by DuPont for Vehicular mechanism to migrate protons via water molecules (Slade, Campbell, Ralph, & Walsh, 2002).

Specifically, the NRE-212 by Dupont is composed 20% Pt/C and 30% polytetrafluoroethylene (PTFE) commonly known as Teflon (Chen et al., 2008). If the membrane commences to dehydrate it causes greater proton resistance hence less power and if the membrane beings to flood then less electrochemical reactions due to less site activity of the triple-points hence again less power. Water management for Nafion (Slade et al., 2002) is extremely important to provide consistent hydration, which could be balanced by electroosmotic pumps to control the water flow therefore further complex the fuel cell system and increasing the cost.

Overall, the present technology increases complexity of the design, unit dimensions, and maintenance costs of the general fuel cell. Consequently, the proton exchange membrane (PEM) must be further modified to endure dehydrating stresses during its operation as required for the Vehicular mechanism that
transports the protons by water molecules. This can be achieved through an anhydrous electrolyte in a PEM fuel cell. This superior conducting material embedded in a polymer transports the hydrogen protons via Grotthuss mechanism, which differs by the protons rapidly hopping then transferring the adjacent proton to the next molecule to span through the entire electrolyte (Agmon, 1995) as seen here in the figure below:

![Figure 3.11 Ideal conception of the Grotthuss mechanism where the entering proton demonstrating the protonic displacement then anion rotation per molecule for protonic conduction through the electrolyte of a phosphoric acid fuel cell (PAFC).](image)

3.13.2 Protonated Electrolytes

Currently, protic ionic liquids (PILs) are being tested as the electrolytes. These novel electrolytes for fuel cells are being developed to optimize the proton transfer, cell lifetime, safety, and environmental friendliness such as non-toxicity. PILs are liquids that consist entirely of ions that melt below 100°C and often equal or lower than room temperature. Watanabe and co-workers first demonstrated the utilization of PILs as electrolytes for fuel cell purposes then refined the practicality under non-humidified conditions (Lee, Ogawa, & Kanno, 2010). These PILs specifically all have a proton transfer between an organic cation (Brønsted acid) and normally an inorganic anion (Brønsted base). Protic ionic salts and molten salts
exhibit similar properties as a PIL, but melts above 100°C up to between 400-800°C, respectively. They all have unique properties of interests such as increased proton transfer, low volatility, fluidity, and charge neutrality thus making them attractive for electrolytes in fuel cell operations (Belieres et al., 2006).

3.13.3 Polymer Membrane Electrolyte

The compound can also be suspended within a polymer matrix to create a thin, flexible membrane, e.g. polyvinyl pyridinium phosphate (PVPP). A polymer with hydrophobic properties would provide more mechanical stability then future performance than enhances the thermal and electrochemical stabilities without degrading the ionic conductivity of the composite electrolyte during fuel cell operation. Typically, this polymer membrane state increases durability but slightly decreases the ionic conductivity. There has been continuous research approaches for alternative polymers can maintain or even enhance the ionic conductivity under anhydrous conditions at elevated temperatures above 100°C for higher overall efficiency (Lee & Yasuda, 2010). Furthermore, the thinner the membrane the lesser resistance due to the shorten proton conduction path distance hence more opportunity for energy density.

3.13.4 Fuel Cell Stack & Peripheral Equipment

A fuel cell stack is the combination of the individual fuel cells interfaced with each other by the conductive graphite bipolar plates. The plates can also be mass-produced from a plastic, acrylonitrile-butadiene-styrene, and copper ribs for
conductive interconnects (Chen et al., 2008). The stack is connected together to deliver a higher voltage potential as a series circuit or to deliver a stronger current as a parallel circuit. As of now the materials are the competitive standards but could be changed to be lighter, more durable, smaller thermal coefficients, and more conductive for less resistance in the fuel cell stack. An example would be copper current collector connections instead of graphite bipolar plates. The increase of the active surface areas to provide more energy yet countered by more resistances from the fuel cell stack. The net power output would decrease as more power would be needed to supply the peripheral equipment such as electro-osmotic pumps to maintain the proper hydration of Nafion membrane as typically used as seen here in this diagram below:

Figure 3.12 Flow diagram of a generalized fuel cell stack along with the required peripheral equipment emphasizing the water balance control of the system (Yilanci, Ozturk, Atalay, & Dincer, 2007).
For example, this peripheral equipment also includes the hindrances of added dimensions and excess weight for transportation purposes, which are very crucial for cargo storage and travel fuel economy. Also pressurized system inherently requires stronger sealants of the fuel cell system hence the integration of the pumps would complex the fuel cell thus increasing engineering design cost.

3.14 Types of Fuel Cells

There are many different types of fuel cells with varying chemical components for varying load outputs to provide direct electrical conversion for electronic devices. The two main types are low and high temperature fuel cells corresponding to a liquid or solid electrolyte.

<table>
<thead>
<tr>
<th>Fuel Cell Type, (FC = fuel cell):</th>
<th>Electrolyte Type:</th>
<th>Cell Temp:</th>
<th>Fuel</th>
<th>Mobile species</th>
<th>Oxidant</th>
<th>Electrical efficiency:</th>
<th>Energy output:</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFC, alkaline</td>
<td>Potassium hydroxide</td>
<td>25 – 90°C</td>
<td>H₂</td>
<td>← OH⁻</td>
<td>O₂</td>
<td>60 - 70%</td>
<td>300W – 5kW</td>
</tr>
<tr>
<td>PEMFC, proton exchange membrane</td>
<td>Hydrated membrane, e.g. Nafion</td>
<td>25 – 80°C</td>
<td>H₂</td>
<td>H₃O⁺ →</td>
<td>O₂ (H⁺ via Vehicular mechanism)</td>
<td>40 – 70%</td>
<td>1kW</td>
</tr>
<tr>
<td>DMFC, direct methanol</td>
<td>Hydrated membrane</td>
<td>25 – 90°C</td>
<td>CH₃OH</td>
<td>H⁺ →</td>
<td>O₂ ethanol, gasoline</td>
<td>20 – 30%</td>
<td>1kW</td>
</tr>
<tr>
<td>PAFC, phosphoric acid</td>
<td>Phosphoric acid: or in PBI matrix</td>
<td>180 – 220°C</td>
<td>CO₂, H₂</td>
<td>H⁺ →</td>
<td>O₂ Reformed: methane gas</td>
<td>55%</td>
<td>200kW</td>
</tr>
</tbody>
</table>

(Table 3.4 cont. next page, 79)
<table>
<thead>
<tr>
<th>Fuel Cell Type</th>
<th>Electrolyte Material</th>
<th>Operating Temperature</th>
<th>Fuel Reformed:</th>
<th>Power Efficiency</th>
<th>Power Output</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCFC, molten carbonate</td>
<td>Molten mix, alkali-metal carbonates</td>
<td>620 – 660°C</td>
<td>CO, H₂</td>
<td>65%</td>
<td>2MW – 100 MW</td>
</tr>
<tr>
<td>SOFC, solid oxide</td>
<td>YTZ, yttria stabilized zirconia</td>
<td>800 – 999°C</td>
<td>CO, H₂</td>
<td>60 – 65%</td>
<td>100 MW</td>
</tr>
<tr>
<td>SAFC, solid acid</td>
<td>e.g. Cesium hydrogen phosphate</td>
<td>120 – 280°C</td>
<td>H₂</td>
<td>42%</td>
<td>-----</td>
</tr>
<tr>
<td>RFC, regenerative</td>
<td>e.g. Sodium (tri)bromide + polysulfide</td>
<td>25°C</td>
<td>Na₂S₂</td>
<td>60 – 93%</td>
<td>-----</td>
</tr>
<tr>
<td>BFC, biological</td>
<td>e.g. Sodium sulfate, urea and dextrose</td>
<td>25°C, inside body</td>
<td>NADH</td>
<td>30 – 50%</td>
<td>-----</td>
</tr>
</tbody>
</table>

3.14.1 Alkaline Fuel Cell (AFC)

The alkaline fuel cell (AFC) was discovered by Sir Francis Bacon in the early 1960’s. These archaic fuel cells utilized potassium hydroxide as the liquid electrolyte for better solubility than sodium hydroxide and cheaper cost purposes. There were limited demonstrations of the viability but in the end as the user the deciding factors were the retail price, power reliability, durability, and safety along with the high temperature of 260°C or lower down to 70°C of operation for the fuel cell system (Dicks & Larminie, 2003). NASA was the prime example of usage for the alkaline fuel cell, then later they were replaced for another low temperature functioning at 80-90°C PEM fuel cells in the upcoming Orbiter spacecraft. Below are the fuel cell electrochemical reactions upon fuel consumption for power generation:

Anode (-): \[ 2H_2 + 4OH^- \rightarrow 2H_2O + 4e^- \]  \hspace{1cm} \text{Equation 3.38}

Cathode (+): \[ O_2 + 4e^- + 2H_2O \rightarrow 4OH^- \]  \hspace{1cm} \text{Equation 3.39}
3.14.2 Phosphoric Acid Fuel Cell (PAFC)

The phosphoric acid fuel cell (PAFC) operates around a medium temperature of around 190-220°C and uses a phosphoric acid solution as the electrolyte for hydrogen proton conductor. The PAFCs were the first commercialized fuel cells and assisted setting the electrical power standards for these stationary electrochemical power source devices (Dicks & Larminie, 2003). Below are the PEMFC and PAFC electrochemical reactions upon fuel consumption for power generation:

*Anode (−):* \[ 2H_2 \rightarrow 4H^+ + 4e^- \]  
Equation 3.40

*Cathode (+):* \[ O_2 + 4e^- + 4H^+ \rightarrow 2H_2O \]  
Equation 3.41

3.14.3 Direct Methanol Fuel Cell (DMFC)

The direct methanol fuel cell is another alternative choice. The main difference is the fuel source as it is methanol liquid instead of hydrogen gas yet the oxidant remains to be oxygen gas. The electrolytic component consists of an ionomer (polymer membrane). This fuel cell operates at a low temperature range 60-100°C and additionally has a byproduct of carbon dioxide gas within the water vapor (Srinivasan, 2006). It is capable of generating power output up to 1MW with only 20% system efficiency. Integrating peripheral equipment such as a reformer to process the fuel initially into hydrogen gas and carbon monoxide. The system would have a significant increase in efficiency of 40% if it was required to operate between 250-300°C at significantly less power output and supplemental dimensions for the peripheral equipment. It is a prime candidate for portable power applications in
electronics and transportation. Below are the fuel cell electrochemical reactions upon fuel consumption for power generation:

\[ \text{Anode} (-): \quad CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \quad \text{Equation 3.42} \]

\[ \text{Cathode} (+): \quad \frac{3}{2}O_2 + 6H^+ + 6e^- \rightarrow 3H_2O \quad \text{Equation 3.43} \]

3.14.4 Proton Exchange Membrane Fuel Cell (PEMFC)

The proton exchange membrane fuel cell (PEMFC) or at times polymer electrolyte fuel cell (PEFC) is current the primary choice as a potential power source for larger scale applications such as an aircraft. The miniature scaled PEM fuel cell would be an excellent power source for micro-aerial vehicles. It consumes hydrogen gas as the fuel and oxygen gas as the oxidant. The electrolytic component consists of a PEM (proton exchange membrane), which is typically Nafion, a polymer product of DuPont chemical company. The fuel cell stack would have a power output of up 500kW and 50% system efficiency (EG&G, 2004). Below are the fuel cell electrochemical reactions upon fuel consumption for power generation:

\[ \text{Anode} (-): \quad 2H_2 \rightarrow 4H^+ + 4e^- \quad \text{Equation 3.44} \]

\[ \text{Cathode} (+): \quad O_2 + 4e^- + 4H^+ \rightarrow 2H_2O \quad \text{Equation 3.45} \]

3.14.5 Molten Carbonate Fuel Cell (MCFC)

This fuel cell operates between 600-700°C utilizing alkali carbonates in the liquid state as the electrolyte. The catalysts within the anode and cathode chambers
are composed of nickel metal rather than platinum metal due to reduced energy required for oxidation and reduction at that high of temperature. The fuel cell system require more initial time to properly heat hence not a quick startup, which is why these types of fuel cell are used for stationary power sources. The fuel source undergoes steps prior to entering the anode chamber as the methane gas is reformed into hydrogen gas or just carbon monoxide gas could be substituted. The carbonate ion migrates across the electrolyte to the anode from the cathode then reacts with hydrogen gas to create water vapor, carbon dioxide, and the released electrons needed to deliver power to that device. The newly formed carbon dioxide is recycled directly back to the cathodic chamber as oxygen and carbon dioxide gases react together to form the carbonate ions. The molten carbonate electrolyte is extremely corrosive and causes rapid degradation of the stack materials (EG&G, 2004). Below are the fuel cell electrochemical reactions upon fuel consumption for power generation:

\[
\text{Anode (−): } \ 2H_2 + 2CO_3^{2−} \rightarrow 2H_2O^+ + 2CO_2 + 4e^- \quad \text{Equation 3.46}
\]

\[
\text{Cathode (+): } \ O_2 + 2CO_2 + 4e^- \rightarrow 2CO_3^{2−} \quad \text{Equation 3.47}
\]

Or when the fuel source of hydrogen gas is substituted for carbon monoxide gas chemical reactions:

\[
\text{Anode (−): } \ 2CO + 2CO_3^{2−} \rightarrow 4CO_2 + 4e^- \quad \text{Equation 3.48}
\]

\[
\text{Cathode (+): } \ O_2 + 2CO_2 + 4e^- \rightarrow 2CO_3^{2−} \quad \text{Equation 3.49}
\]
3.14.6 Solid Oxide Fuel Cell (SOFC)

The solid oxide fuel cell is also a leading choice as a potential power source that would also consume hydrogen gas as the fuel and oxygen gas as the oxidant. The electrolytic component usually consists of ceramic material of either zirconium dioxide or lanthanum nickel oxide. The electrolytic functionality contrasts by an oxide ion conducting reversibly across the membrane as compared to hydrogen proton conduction of the typical fuel cell systems. Ideally, the newer planar electrode-electrolyte designs of SOFC system separates itself from the older tubular designs that operate at intense temperature range of 650-1000°C. The system could generate power output of up to 100MW and 60% system efficiency (Dicks & Larminie, 2003). Below are the fuel cell electrochemical reactions upon fuel consumption for power generation:

Anode (-): \[ 2H_2 \rightarrow 4H^+ + 4e^- + 2H_2O \] \hspace{1cm} \text{Equation 3.50}

Cathode (+): \[ O_2 \rightarrow + 2O^- + 4e^- \] \hspace{1cm} \text{Equation 3.51}

3.14.7 Regenerative Fuel Cell (RFC)

The regenerative fuel cell (RFC) systems, also referred to as an electrolyzer, which is simply a fuel cell operated in reverse requiring electricity unlike the spontaneous (energy-free) redox process of \( \text{H}_2 \) into \( 2\text{H}^+ \) at platinum metal of the anodic electrode. That process requires 1.23V minimum of energy on platinum electrode, which is the optimal metal for lowest electropotential to oxidize a liquid water molecules splitting it into separate hydrogen and oxygen gases.

Anode (-): \[ 2\text{H}_2\text{O}_{\text{liq}} \rightarrow O_{2g} + 4\text{H}^+_{\text{aq}} + 4e^- \] \hspace{1cm} \text{Equation 3.52}
The growing class of regenerative fuel cell is also known as the redox flow battery (RFB) where this electrochemical device has its liquid fuel source pumped into it to provide large-scale compensation power during peak hours of a facility on the electrical grid. The chemical reactants are of different oxidation states in water separated in external tanks; allowing the systems to be easily scalable for power-demand purposes. In the past there have been various chemical solutions primarily vanadium-based, some iron/chromium, and now polysulfide/bromine solutions. These charged aqueous solutions are flowed into the fuel cell by thorough stoichiometric mixing, where the anodic reactants seek the lower electrochemical potential hence releasing electrons then the ion passing through the membrane to form a more stable species in the progress as formulated here (Dicks & Larminie, 2003). Below are the fuel cell electrochemical reactions upon fuel consumption for power generation:

\[
\text{Cathode (+)}: \quad 4\text{H}_2\text{O}_{\text{liq}} + 4e^- \rightarrow 2\text{H}_2 + 4\text{OH}_{\text{aq}} \quad \text{Equation 3.53}
\]

\[
\text{Anode (-)}: \quad 2\text{Na}_2\text{S}_2 + \text{Na}_2\text{S}_4 \rightarrow 2\text{Na}_2\text{S}_4 + 2\text{Na}^+ + 2e^- \quad \text{Equation 3.54}
\]

\[
\text{Cathode (+)}: \quad \text{NaBr}_3 + 2\text{Na}^+ + 2e^- \rightarrow 3\text{NaBr} \quad \text{Equation 3.55}
\]

3.14.8 Biological Fuel Cell (BFC)

This fuel cell technology is the latest product within the progression of the miniaturization and portability of electrical devices (Logan et al., 2006). They have the desirable qualities of operating at room temperature and achieving high-energy
conversion efficiency as when compared to modern implants. Additionally, these biological fuel cells (BFC) also known as enzymatic fuel cells (EFC) are designed specifically to function within living tissues such as the human body from organic renewable fuel sources within the human body. The enzymatic-based catalysts of the electrodes in the anode oxide naturally occurring sugars and alcohols then reduce the ions into liquid water and hydrogen peroxide. BFCs and EFCs have emerged as evolving energy technologies as having the ability to further scale down in size due to the elimination of chemical reactant storage of implantable batteries as well longevity hence less invasive surgical maintenance requirements (Luckarift et al., 2014). Below are the fuel cell electrochemical reactions upon fuel consumption for power generation:

Anode (-): \[ 2\text{NADH} \rightarrow 2\text{NAD}^+ + 2\text{H}^+ + 2e^- \]  

Equation 3.56

Cathode (+): \[ \text{O}_2 + 4e^- + 4\text{H}^+ \rightarrow 2\text{H}_2\text{O} \]  

Equation 3.57

Figure 3.13 BFC (biological fuel cell) redox reaction of NADH (Nicotinamide adenine dinucleotide) by the oxidase enzyme to release the electrons to power the small electrical device, i.e. pacemaker, and the protons conduction through membrane to be reduced into a water molecule.
3.14.9 Solid Acid Fuel Cell (SAFC)

In particular, the solid acid fuel cell utilizes a proton conductive electrolyte in the solid-state unlike the liquid-state electrolytes. The fuel source is hydrogen gas into the anodic chamber as oxygen gas into the cathodic chamber as the PEMFC and PAFC, where the same redox reactions occur to produce an electrical potential and water vapor. These new types of fuel cells are attractive due to the solid electrolyte for durability, the ability to utilize dry gas feeds, and enhanced conductivity of super protonic conduction states reported by Haile and co-workers (Uda & Haile, 2005). For example, cesium hydrogen sulfate (CsHSO₄) is an acidic salt compound that can be utilized for protonic conductivity. It has been proven to have a super conductive phase transition at approximately 145°C (10⁻² S/cm), which decreases resistivity and enhances proton conductivity as a solid electrolyte due to structural phase transformation from monoclinic to tetragonal crystallinity (Haile & Chisholm, 2007).

The solid state has the advantages of being less permeable to hydrogen gas fuel crossover, catalyst carbon monoxide or sulfur fouling acquiescent to less platinum metal for HOR and ORR electroactivities with conductive values between 45-150 mS/cm at 100-200°C for 5% Al-doped SnP₂O₇ under anhydrous conditions as reported by Hibino and co-workers (Tomita, Kajiyama, Kamiya, Nagao, & Hibino, 2007). No humidification is required hence less dependency for a gas diffusion layer and less peripheral equipment. Also, it is more robust for mobility and a moderate temperature of operation therefore less expensive materials required. This compound has been categorized as a mixed ionic and electronic conductor (MIEC) at
times depending the stoichiometric composition (Hirabayashi et al., 2004). These systems are competitive with phosphoric acid fuel cell (PAFC) with similar function.

*Heat Engine Efficiency.* These varying types of fuel cells are in direct competition with the heat engine, which is a mature technology developed during the industrial revolution. The efficiency parameters of Gibbs free energy are valid even though efficiency is not constrained by enthalpy of formation as in typical thermal cycles of internal combustion engines. The efficiency of the fuel cell will never obtain 100% as it abides by the Second Law of Thermodynamics (Paula & Atkins, 2006).

Electrochemical devices provide instantaneous energy from conversion of chemical substances directly into energy versus the lagging, multiple steps of the heat engines of transforming the chemical substances into combusted products then into thermal energy for mechanical force to move a turbine or piston. The thermal energy is converted into mechanical energy with an upper temperature from the system releasing exhaust heat (along with water vapor and carbon dioxide gas) into a lower temperature of surrounding, which is usually ambient temperature, 25°C or 298K. This process is known as the Carnot cycle as expressed here:

\[
\eta = \frac{W_E}{Q_R} = \frac{(T_2 - T_1)}{T_2}
\]

Equation 3.58

Where \( \eta \) is the theoretical efficiency, \( W_E \) is the mechanical energy (work), \( Q_R \) is the thermal energy (reaction enthalpy), \( T_2 \) is the upper temperature, and \( T_1 \) is the lower temperature.
The Carnot cycle limits the maximum efficiency for a heat engine to 50% and is actually much lower due to other energy losses such as friction of the moving components of the heat engine. The exhaust heat is irretrievable as expressed here:

\[ Q_C = \frac{T_1}{T_2} \cdot Q_R \]  

Equation 3.59

Where \( Q_C \) is the irretrievable Carnot heat.

3.15 Fuel Cell Efficiency

The system efficiency of a fuel cell in general is at 45% (without CHP = coupled heat production), which is greater than the mature technology of an internal combustion engine fueled by gasoline or diesel with net efficiencies < 40% (Barclay, 2006). The efficiency is overall the *Gibbs* free energy is determined by the released electrons as electricity to power the electrical device minus the required activation energy. The overall redox equation is \( 2H_2 + O_2 \rightarrow 2H_2O \) with the reaction enthalpy of \(-285.8 \) kJ/mol. However, the *Gibbs* free energy has a maximum electrical energy of \(-237.1 \) kJ/mol thus the maximum efficiency is 83% for an individual fuel cell (Bagotsky, 2009). The *Nernst* equation gives the reversible open circuit voltage of the \( H_2/O_2 \) fuel cell as expressed here:

\[ E = \frac{-\Delta G_f}{2F} \]  

Equation 3.60

Where \( E \) is electromotive force (emf), \( -\Delta G_f \) is the Gibbs free energy of formation, and \( F \) is Faraday’s constant (96,485 coulombs).

The theoretical max is 1.23eV at 25°C with the actual max open circuit voltage (OCV) are 1.18eV for a PEMFC at 80°C; and 1.14eV for a PAFC at 200°C.
After the initial spontaneous oxidation (no activation energy required) of the hydrogen gas these cell efficiencies have to include the final step of having to overcome the required activation energy barrier of the oxygen reduction overpotential to complete electrochemical reaction to create water vapor. The general schematic of the occurrence as displayed below here:

![Schematic diagram of electrochemical reaction](image)

Figure 3.14 After the initial spontaneous (energy free) oxidation of the hydrogen gas for ionic conducting protons across the membrane then the required activation energy, $E_a$, from the electrons reduces the protons with oxygen gas to produce water vapor molecules.

The efficiencies increase to 60% when the heat is coupled for utilization in the unit. They have the highest operational efficiencies at low power densities when supplying pure reactants of hydrogen and oxygen gases, in which the current efficiency (Bard & Faulkner, 2001) can be calculated to determine the optimal gas flow of hydrogen gas usage, $X$ (mL/min) derived from the Ideal Gas law, $PV = nRT$, as displayed below here:

$$X = \frac{n k R T}{P}$$  \hspace{1cm} \text{Equation 3.61}
Where \( n \) is moles (mol/sec), \( k \) is flow rate conversion (sec/min), \( R \) is the gas constant of 82.057 (mL·atm)/(K·mol), \( T \) is the temperature (K), and \( P \) is the pressure (atm).

The fuel cell efficiency is indirectly proportional to the voltage output. The more power demand then the increase in current density that is directly proportional to the decrease in cell voltage inducing lower efficiency. This is expressed in the equation of Ohm’s law:

\[
V = IR
\]  

Equation 3.62

Where \( V \) is voltage, \( I \) is current, \( R \) is resistance.

This equation is important to determine the voltage loss during operation from the resistance of the fuel cell materials. This voltage loss is added to the voltage potential in the process called \textit{IR correction} (Page, Anbuky, Krumdieck, & Brouwer, 2007). The IR corrective compensation solely analyzes the electrochemical aspects of the electrolyte and interface at the electrodes, which are the focus of this project excluding the resistances of the cell and lead wires. For example, 85% ortho-phosphoric acid is the research benchmark of performance hence the control sample for H\(_2\)/O\(_2\) fuel cells.

The actual open voltage potential of the PEM fuel cell is ~0.9V depending on fuel quality, gas flow, temperature, and pressure yet the theoretical voltage potential is 1.23V. The difference in fuel cell potential losses is explained by three principal factors: 1) Activation loss, 2) Ohmic loss, and 3) Mass transport loss (Ramani, 2006). A basic phosphoric acid fuel cell for this laboratory control utilizes 85% ortho-phosphoric acid as a liquid electrolyte at 140°C under H\(_2\) and O\(_2\) gases flowing at 18 and 24 mL/min, respectively, as depicted here:
Figure 3.15  Fuel cell polarization curve at OCV (open circuit potential) where upon testing the initial activation losses, followed by the ohmic losses, then finally mass transport losses to zero potential or polarity reversal.

1) The open circuit voltage induces a sharp activation loss that is overpotential from the electrons statically charging to overcome the electrical double layer then cross at the interface of the triple point site. 2) The gradual ohmic loss is resistance from the electrons migrating through the conductive materials at varying distances thus impeding their velocity rates. 3) The sharp mass transport loss is basically under potential from the electrons unable to compensate needed current for the increased voltage potential demand by the electrical device due to depletion of fuel reacting at the triple point site (Kolb, 2008). Besides, the catalytic efficiency the hydrogen gas production for fuel cell usage as well as the hydrogen gas store are prime factors for the overall efficiency of this new emerging infrastructure.
3.16 Overpotential Issue

Thus far the noble metal, platinum, has been tested and proven to be the most catalytically active material for spontaneous hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR) (Nørskov et al., 2004). The theoretical cell potential of 1.23V at room temperature would be more attainable if it weren’t for the “overpotential” in energy required for the ORR with hydrogen ions and electrons to form water. The oxygen reduction has an enormous overpotential of ~0.3V compared to hydrogen oxidation of around 0.1V (Barclay, 2006). This overpotential has been identified with the platinum electrodes in fuel cells, where the dire improvement of the material is the catalytic activity at the cathode. The oxygen reduction process accounts for the most significant loss of energy efficiency in a fuel cell system (Liang, 2005).

3.17 Electrocatalytic Activity of Platinum Nanoparticles

Electroactivity of the catalysts is much more efficient of platinum (Pt) per unit mass by increased utilization of its surface area such as nanoparticle dispersion throughout the carbon nanotube supports (Kang 2011; Shi, Jiang, & Pan, 2011). Platinum particles between 2-3 nm diameters are the optimal candidate for both hydrogen and oxygen gases. The adsorption processes are dependent on the influential structure of the platinum, which differs in the dominant crystal planes and average Pt-Pt intercrystalline distances (Torre, Aricò, Alderucci, Antonucci, & Giordano, 1994).
**Nanocarbon Support for Catalysts.** Novel materials of carbon support for precious, noble metals provide new opportunities in fuel cell technology such as nanofibers, nanohorns, nanocoils, and the highly publicized nanotubes (Maiyalagan et al., 2005). Carbon nanotubes (CNTs) consist of carbon atoms bonded to form graphene sheets that are rolled into cylindrical structures of various diameters, lengths, and wrapping vectors as depicted below:

Figure 3.16 E-Tek carbon cloth supporting platinum particles as catalysts for present H₂/O₂ fuel cell research. TEM image courtesy of Denish Medpelli.
Figure 3.17 Multi-walled carbon nanotube (MWCNT) supporting platinum nanoparticles, where darker spots are denser regions of the observable fine dispersion. TEM image courtesy of John Gustafson.

These are being thoroughly investigated for applications into energy conversion devices such as hydrogen storage, electrochemical capacitors, photovoltaic cells, thermoionic emitters, thermoelectric power generators, polymer membranes, and fuel cell electrodes (Narayananamoorthy et al., 2007). Experiments with CNTs in DMFCs have been cited in numerous publications (Srinivasan, 2006).
Overall, the cell voltage potential should increase 30% coinciding with a 20°C increase in temperature. The cathodic reduction activity suffers extreme overpotential but the Pt/CNTs have been able to decrease it slightly compared to the optimum E-Tek Pt/C electrodes (Shaijumon, 2006). The electrode performance is to be examined for effects of electrode fouling by carbon monoxide at 50 ppm that is expected to improve due to significant improvement electrocatalytic activity. The carbon material itself exhibits good covalent bond stability, electronic conductivity, and corrosion resistance, which no other material may compare equally. The electronic properties are controlled by this folding of the graphene sheet. The conductivity is determined by the intersecting of the valance and conduction bands at the apex of each carbon atom (Lindsay, 2010).

3.18 Fuel Crossover

Fuel (gas) crossover occurs in the fuel cell system when the hydrogen and oxygen gases fed into anodic and cathodic chambers, respectively, do not undergo catalysis at the surface of the electrode-electrolytic interface thus the diatomic molecules penetrate the electrolyte (Ramani, 2006). The gases freely flowing through the structure of the electrolyte generate frictional heat that is released into the immediate area. Observably, the entire fuel cell block temperature rises slightly depending on the amount of fuel crossover. Inherently, the OCV lowers along with a drop in cell efficiency upon load testing.
**Fuel Cell Conditioning.** The preliminary fuel cell testing was conducted using small-scale conditioning similar as large-scale systems. This will give valuable hands-on insight about their complete operations and how to maximize overall efficiencies and cell longevity. The protocol of fuel cell conditioning (break-in routine) are also used for battery systems by research and development teams to optimize efficiency and load sequencing will be specific to governmental and industrial standards. For example, an experimental protocol for fuel cell conditioning is listed below:

Table 3.5 Fuel cell conditioning and testing protocol:

<table>
<thead>
<tr>
<th>Break-in routine</th>
<th>System Pressure:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Setup Setup</td>
<td>Teflon Fuel Cell: Inlet Gases:</td>
</tr>
<tr>
<td><strong>Cell Info</strong></td>
<td>Fuel: 99% H₂, dry</td>
</tr>
<tr>
<td>Active area: 0.5 cm²</td>
<td>Thickness: 0.3 cm Oxidant: 99% O₂, dry 40 psi, tank regulator</td>
</tr>
<tr>
<td>Electrodes: ETEK O₂ 2-3x more in gas flow</td>
<td>cell block inside under 1 atm</td>
</tr>
<tr>
<td>Pt load: 0.5mg/cm²</td>
<td>Non-Humidified Gas</td>
</tr>
<tr>
<td>#</td>
<td>Temp Operation: Fuel Cell Potential: Time (hours):</td>
</tr>
<tr>
<td>1</td>
<td>Heat @ 140°C inside of oven 0.0V, no H₂/O₂ gas flow RUN EIS TEST 8hrs minimum, wire leads w/ gas connections completed</td>
</tr>
<tr>
<td>2</td>
<td>Cool @ 120°C ~0.9V, OCV gas opened 2hrs later</td>
</tr>
<tr>
<td>3</td>
<td>Heat @ 120°C RUN LOAD TEST OF PSTAT PROGRAM time elapsed (in minutes), required recovery period</td>
</tr>
<tr>
<td>Break-in verification</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Heat @ 120°C REPEAT SAME TEST 1hr later, time elapsed (min), required recovery period</td>
</tr>
<tr>
<td>Polarization Curves</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Heat @ 120°C RUN LOAD TEST 3x within 1hr then 1hr ramp</td>
</tr>
<tr>
<td>6</td>
<td>Heat @ 140°C RUN LOAD TEST 3x within 1hr then 1hr ramp</td>
</tr>
<tr>
<td>7</td>
<td>Heat @ 160°C RUN LOAD TEST 3x within 1hr then 1hr ramp</td>
</tr>
<tr>
<td>No.</td>
<td>Action</td>
</tr>
<tr>
<td>-----</td>
<td>-------------------------</td>
</tr>
<tr>
<td>8</td>
<td>Heat @ 180°C</td>
</tr>
<tr>
<td>9</td>
<td>Heat @ 200°C and above, 250°C max</td>
</tr>
<tr>
<td></td>
<td>Polarization Curves</td>
</tr>
<tr>
<td>10</td>
<td>Cool @ 180°C</td>
</tr>
<tr>
<td>11</td>
<td>Cool @ 160°C</td>
</tr>
<tr>
<td>12</td>
<td>Cool @ 140°C</td>
</tr>
<tr>
<td>13</td>
<td>Cool @ 140°C</td>
</tr>
<tr>
<td></td>
<td>Cell Reconditioning</td>
</tr>
<tr>
<td>14</td>
<td>Cool @ rm temp, shut down oven</td>
</tr>
</tbody>
</table>

3.19 Potentiometric Scanning

Potentiometry or simply known as constant current is a type of testing that is crucial for determining the stability of the choice electrolyte and the longevity of the performance of the desired fuel cell system. The fuel cell was heated to the optimal temperature then operated as normally with dry H₂/O₂ gas feed then inlet flow adjusted for the maximum OCV value (Wahdame et al., 2007). The constant current of choice is 50mA/cm², which is around the necessary power of 30W for either 2 fluorescent light bulbs or one small portable stereo. These tests performed in this lab ran for 24-hour durations at moderate temperature ranges without any gas humidification nor cell block pressurization (Tang, Wan, Pan, & Jiang, 2007). Industrial research of mid to large-scale fuel cell systems average between 5-20k hours of constant current testing under strained conditions, which are primarily for commercial vehicular purposes (Jiang et al., 2001).
3.20 Fuel Cell Applications

Fuel cells in general have a variety of power applications for large-scale stationary and small-scale mobile purposes. Initially, the AFC and PAFC had the government and private industrial commercial sectors utilization, respectively, but now the PEMFC and SOFC are of primary focus for the private sectors. Lightweight, low-powered (10W-3kW systems) PEMFCs would be suitable for cordless household appliances, outdoor tools, auxiliary generators, and etc. The mid-range fuel cells would be utilized for conceptual vehicles and residential units operating from 8-10kW for 3,000 to 6,000 sq ft homes (Curtin, 2010). The principal advantage of PEMFCs are their higher power density outputs versus energy storage batteries and the internal combustion engines. The principle disadvantages are utilizing platinum electrodes and hydrogen gas to achieve this advantage due to cost along with the demanding volume of dangerously flammable gas storage aspects (Büchi et al., 2003).

3.21 Fuel Cell Materials

The pricing for overall PEMFC systems has dropped from $20k/kW 14 years ago down between $3.5-4k/kW presently for commercial applications, which are only plausible through government subsidies and private sector funding. The PEMFC was mandated to attain an operating potential of 650mV and a power density of 600mW/cm² for mass production of minimum of 500,000 units (Carlson et al., 2005). Nafion is a much more expensive choice at $622/m² but operates at a lower temperature range of 50-120°C.
Table 3.6 Typical cost for a 80k H₂/O₂ PEM fuel cell system (Carlson et al., 2005).

<table>
<thead>
<tr>
<th>#</th>
<th>80kW H₂/O₂ PEM fuel cell component, total cost of $5,640:</th>
<th>Price percentage:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fuel cell stack</td>
<td>56% total, breakdown of the fuel cell stack listed below:</td>
</tr>
<tr>
<td>1</td>
<td>Electrodes</td>
<td>69%</td>
</tr>
<tr>
<td>2</td>
<td>Membrane</td>
<td>9%</td>
</tr>
<tr>
<td>3</td>
<td>Bipolar plates</td>
<td>7%</td>
</tr>
<tr>
<td>4</td>
<td>Gas diffusion layer</td>
<td>7%</td>
</tr>
<tr>
<td>5</td>
<td>Sealing of system</td>
<td>2%</td>
</tr>
<tr>
<td>6</td>
<td>BOS (balancing of system state)</td>
<td>2%</td>
</tr>
<tr>
<td>7</td>
<td>Fuel cell stack assembly</td>
<td>6%</td>
</tr>
<tr>
<td></td>
<td>(Table 3.6 cont. next page, 97)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>BOP (body of plant)</td>
<td>44% total, breakdown of the body of plant listed below:</td>
</tr>
<tr>
<td>1</td>
<td>Air compression/filtration</td>
<td>15%</td>
</tr>
<tr>
<td>2</td>
<td>Sensors, valves, pipework</td>
<td>8%</td>
</tr>
<tr>
<td>3</td>
<td>H₂ gas blower/ejector</td>
<td>5%</td>
</tr>
<tr>
<td>4</td>
<td>Membrane humidifier</td>
<td>5%</td>
</tr>
<tr>
<td>5</td>
<td>Enthalpy wheel humidifier</td>
<td>4%</td>
</tr>
<tr>
<td>6</td>
<td>Coolant Pumps and Fans</td>
<td>5%</td>
</tr>
<tr>
<td>7</td>
<td>BOP assembly</td>
<td>2%</td>
</tr>
</tbody>
</table>

The system costs would need to further decline to $400-750/kW to be market viable, e.g. residential fuel cell units (Curtin, 2010). The private transportation sector desired to utilize PEMFCs for vehicles under the U.S. DOE allotted target of $125/kW for 2005. These costs are crucial for a quality fuel cell system manufactured abundantly at a market price to be competitive to fossil fuels.
Laboratory Materials. The materials and equipment utilized in this investigation were either ordered or readily available in the lab. After receiving the ordered chemicals they were stored under a nitrogen atmosphere in a VAC glove box before opening. The glassware was rinsed placed in a base bath (3M NaOH aqueous solution) for extended periods then washed with deionized water then lightly with acetone (Truman, 2009). These cleansed weigh bottles and glass rods for mixing, avoiding metal spatulas, were only used during the preparation to avoid contamination of the electrolyte from any impurities as much as possible. Also a minimal coating of vacuum grease was used at the ground glass joints on the lids before capping the weigh bottles for storage within a rubber-sealed desiccator containing CaSO$_4$ or MgClO$_4$ powders.

4.1 Synthesis of Molten Salts

The creation of the molten salt commenced as a simple method of first placing the vacuum-dried NaX (X = halide) powder into the glass weigh bottle under an inert Ar$_g$ atmosphere then adding the stoichiometric amount of the anhydrous AlX$_3$ powder. The powders in the bottle were sealed with a ground-glass joint lid then heated to 250°C overnight or until reacted to completion for a homogenous molten
solution. Finally, the molten salt, NaAlX$_4$ and the ionic liquid, [EMI]AlX$_4$ (EMI$^+ = 1$-ethyl-3-methylimidazolium) with for the desired molar ratios. This pouring order was vital as to avoid sublimation of vaporous AlCl$_3$ leaving the bottle during the exothermic reaction, inadvertently changing the stoichiometry of the desired molar ratio. The slightest change in the stoichiometry then the melting point of, i.e. NaAlCl$_4$, changes dramatically as evident on the steep temperature of fusion depicted in the binary phase diagram hence changing the eutectic temperature of the overall desired electrolyte, [EMI]AlX$_4$:NaAlX$_4$ 1:1 (Wilkes, 1994). Note: 1-Ethyl-3-methylimidazolium chloride has been recognized to have a plethora of abbreviations such as EMICl, EMImCl, ImCl, MEIC, and EMIMCl.

Figure 4.1 Sodium chloride, $T_m = 801^\circ C +$ aluminum chloride, $T_m = 192^\circ C \rightarrow$ sodium tetrachloroaluminate, $T_m = 151^\circ C$ (Levin et al., 1969).

Figure 4.2 1 mole of sodium chloride, $T_m = 801^\circ C +$ 2 moles of aluminum chloride, $T_m = 192^\circ C \rightarrow$ sodium heptachlorodialuminate.
Figure 4.3 Sodium bromide, $T_m = 1377^\circ C + \text{aluminum bromide, } T_m = 255^\circ C \rightarrow \text{sodium tetrabromoaluminate, } T_m = 192^\circ C$ (Kendall, Crittenden, & Miller, 1923).

Figure 4.4 1 mole of sodium bromide, $T_m = 1377^\circ C + 2$ moles of aluminum bromide, $T_m = 255^\circ C \rightarrow \text{sodium heptabromoaluminate, } T_m = 94^\circ C$.

4.2 Synthesis of Ionic Liquids

1-Ethyl-3-methylimidazolium halides, [EMI]X, (X = halide) mixed equimolar with aluminum chloride producing 1-ethyl-3-methylimidazolium metal halides [EMI]MX$_4$ or [EMI] M$_2$X$_7$ (M = metal) thus reduced hygroscopic affinity. The mixed powders were heated at or greater than 120$^\circ$C until melted then stirred into a homogenous transparent solution afterwards further heated to react to completion about 3 days in a ground glass sealed vial under an inert atmosphere.

This specific ionic liquid was produced similar to the founding method of The Frank J. Seiler Research Laboratory of the Air Force Academy in Colorado Springs
since the early 1980’s (Fannin et al., 1984). The electrolyte was synthesized from stock 1-ethyl-3-methylimidazolium halide ([EMI]X) white powder and, common sodium salt (vacuum-dried NaX), and anhydrous aluminum trihalide (AlX₃) white powder. The samples had a relatively simple preparation of uniformly mixing the powders under dry conditions; however described here was the order of mixing. Initially, the [EMI]X powder was placed into a glass weigh bottle under an inert Ar (or N₂) atmosphere of a VAC glove box. Next, the desired stoichiometric amount of AlCl₃ powder was added to reduce vaporous AlX₃ (cautious of sublimation) forming above the surface upon contact with the other powder. The reaction of the solid chemicals was spontaneous and an exothermic melting into a warm transparent liquid then the bottle was sealed with ground-glass joint lid.

The prepared ionic liquid thermal stability, e.g. The [EMI]AlCl₄:NaAlCl₄ (<50 mol% NaAlCl₄) was only able to endure a conductivity measurement by the transient heating ramp (1K/min) as function of temperature to ~150°C without decomposing the organic cationic portion, 1-ethyl-3-methylimidazolium. Interestingly, the pure [EMI]AlCl₄ solution decomposes at 270°C as reported by Stuff (Stuff, 1989) also an affiliate of the U.S. Air Force Academy, yet apparently the temperature of decomposition is significantly abated when the organic cation mixed with the inorganic anion portion of > 50 mol% of AlCl₄⁻ creating Al₂Cl₇⁻ therefore increasing the Lewis acidity (Mamantov & Petrovic, 1992). This is a principle disadvantage of organic cations in these ionic liquids in general. The advantage of the organic cation is the cyclic-planar structure disrupting the more thermodynamically favorable crystalline structuring to the AlCl₃ tetrahedral structure.
Figure 4.5 1-ethyl-3-methylimidazolium chloride, $T_m = 78^\circ C$, mixed equimolar with aluminum chloride, $T_m = 192^\circ C$ producing 1-ethyl-3-methylimidazolium tetrachloroaluminate, $T_m = 8^\circ C$ (Wilkes, 1994).

Figure 4.6 1-ethyl-3-methylimidazolium bromide, $T_m = 74^\circ C$ mixed equimolar with aluminum bromide, $T_m = 255^\circ C$ producing 1-ethyl-3-methylimidazolium tetrabromoaluminate for possible ability as a low-temperature electrolyte for industrial metal deposition (Boon et al., 1991).

Figure 4.7 1-ethyl-3-methylimidazolium chloride, $T_m = 78^\circ C$ mixed equimolar with iron chloride, $T_m = 306^\circ C$ producing 1-ethyl-3-methylimidazolium tetrachloroferrate, $T_m = 16^\circ C$ (Lipsztajn & Osteryoung, 1985).
Figure 4.8 1-ethyl-3-methylimidazolium chloride, T_m = 78°C mixed equimolar with cupric chloride, T_m = 496°C producing 1-ethyl-3-methylimidazolium trichlorocuperate, T_m = 48°C (Chen & Sun, 1999; Leong, Sun, Deng, Wu, & Chen, 2008).

Figure 4.9 Phosphorus pentabromide, T_b = 106°C mixed equimolar with aluminum bromide, T_m = 255°C producing phosphorus tetrabromide tetrabromoaluminate, T_m = 98°C (Coleman, Nieuwenhuyzen, Rutt, & Seddon, 1995).

Figure 4.10 1 mole of phosphorus pentabromide, T_b = 106°C mixed 2 moles of aluminum bromide, T_m = 255°C producing phosphorus tetrabromide heptabromodialuminate, T_m = -73°C.
Figure 4.11  Phosphorus pentachloride, $T = 167^\circ C$ mixed equimolar with aluminum bromide, $T_m = 255^\circ C$ producing phosphorus tetrabromide tetrachloroaluminate.

Figure 4.12  1 mole of phosphorus pentachloride, $T_m = 167^\circ C$ mixed 2 moles of aluminum bromide, $T_m = 255^\circ C$ producing phosphorus tetrabromide hexabromodialuminate chloride.

Figure 4.13  1 mole of sulfur dichloride, $T_m = -80^\circ C$ mixed 2 moles of aluminum bromide, $T_m = 255^\circ C$ producing sulfur monochloride hexabromodialuminate chloride, where the oxidation states of sulfur(II) are more stable and reversible at higher temperatures above 160$^\circ C$ (Marassi, 1976).
Physicochemical Characterization:

4.3 Differential Thermal Analysis (DTA)

This physical characterization was crucial for determining the temperature of the liquid phases of the synthesized chemical species as aforementioned. Differential Thermal Analysis (DTA) is a well-established physical chemical technique utilized to determine a physical state and phase transitions of the sample being studied. The increase of temperature can produce kinetic energy to increase the interparticle space of a solid transitioning above its heat of fusion (melting point) into a liquid (Hatakeyama & Quinn, 1999).

4.3.1 Equipment Setup & Data Interpretation

This DTA testing apparatus is a replica of a new portable model of inexpensive equipment (Martínez, Videa, & Mesquita, 2013) to be described later in this section. This portable model has the ability to test 3 samples and 1 standard control sample simultaneously with the proper software manipulations; but for our purposes only a 1 sample and 1 standard control sample setup was utilized. The designers are previous researchers of this lab group whom contributed prior work (Videa & Angell, 1999) of molten salts for battery applications therefore very versed for seeking the physical properties of these chemical compounds with sensitivities to moisture.
Both the sample and control were packed under an inert gas the tubes sealed with Teflon tape to prevent water absorption as many of these samples are water-sensitive. The heating cartridge connected to the transformer provides the heat transfer to the metal block to perform the experiments as a function of temperature. The aluminum block was submerged in a dry ice acetone bath for sample measurements below zero down to -70°C then the temperature was ramped up to around 20 K/min. The control is typically dried aluminum oxide (Al₂O₃) packed in the exact same manner into a separate glass capillary tube with a sheathed K-type thermocouple as shown below here:
Figure 4.15  DTA capillary glass tube with sample, enlarged is the glass sheathed K-type thermocouple resting in the sample then placed in the aluminum block for testing (Martínez et al., 2013). Permission granted for reprint.

The heat capacity of aluminum oxide is a standard choice as a control due to a higher melting point as fitting reference such as similar sample heat capacities are required for optimal results (Hodge & Angell, 1978). The noise during scanning will be abated when utilizing chemical powders with similar heat capacities (Angell & Sare, 1970). The measurements are primarily linear with the exception of slight background noise from low voltage fluxes over a period of time.
Figure 4.16 DTA (differential thermal analysis) scan interpretation of a sample: The slight slope with larger insert view is heat capacity of the below glass transition temperature, $T_g$. The exothermic peak is crystallization temperature, $T_c$. The endothermic peak is the fusion (melting point) temperature, $T_m$. The endothermic spike is due to evaporation (boiling point), $T_b$ or temperature of decomposition, $T_d$ (Martínez et al., 2013). Permission granted for reprint.

*Phase Boundaries.* Binary phase diagrams are the simplest graphical representation of two individual components in their purest forms mixing with each other at varying chemical compositions to where phase changes will occur. Ternary phase diagrams are the graphical plot representation of three components enduring the various phases typically as a function of molar composition at standard atmospheric pressure.
The three chemical components are typically more favorable for molten salts as to further lower the eutectic (or liquidus) temperatures similar to ionic liquids (Ohira & Inagaki, 1992). The graphical representation is an equilateral triangle with the three separate chemical components at each vertex. The ternary diagram has a center where all the components converge at a single point as a liquid or vapor of the system, which are known as the melting point (temperature of fusion) and boiling points (temperature of evaporation), respectively (Robelin et al., 2004). The Inverse Lever rule uses equilateral tie lines divided by the equilateral sidelines of the triangle to get the phase percentages (Campbell, 2012). This research investigation purposely avoided the crystalline state of these materials for battery purposes, yet the solid state is only practical in a durable, flexible polymer (Lascaud, Perrier, Vallée, Besner, & Prud’homme, 1994) if deemed for fuel cell applications.
This is known as congruent melting due to the enthalpy of mixing being lowered for a mixed alkali-metal effect (Rasmussen, Hamma, Eriksen, & Hatem, 2004). A peritectic can be more observable in ternary systems than a eutectic point or at times similar features (Kubota, Nohira, Goto, & Hagiwara, 2008). This heating ramp will provide enough energy for the system to phase transition into the gaseous state or decompose as generally expressed here as a non-ideal gas:

\[ P = \frac{nRT}{(V-nb)} - \frac{n^2a}{V^2} \]  \hspace{1cm} \text{Equation 4.1}

Where \( V \) is the volume, \( n \) is gas moles, \( b \) is gas molecules, \( R \) is the gas constant, \( T \) is the temperature, and \( \frac{n^2a}{V^2} \) is related to the van der Waals intermolecular forces of attraction.

The vapor pressure is the gaseous layer above the system of either a solid or liquid for AlCl₃ (Viola, Seegmiller, Fannin, & King, 1977) of these molten salts and ionic liquids as expressed here:
\[ \log p = \left( \frac{A}{T} \right) + B \]  

Equation 4.2

Where \( A \) is 5900.71 and 1956.06 for solid to vapor and liquid to vapor, respectively. \( B \) is 15.88462 and 7.43530 for solid to vapor and liquid to vapor, respectively.

The vapor pressure is greater for the liquid than a solid as an increasing function of temperature.

4.3.2 More Physicochemical Characterization Techniques

Another similar technique is Thermogravimetric Analysis (TGA), which determines any weight changes of the material being studied. The phase changes from either a solid or liquid into a gas phase leave the open sample tray changing the measured weight as a function of temperature over a specified time period. This can either mean just a gaseous phase change or chemical decomposition (Hatakeyama & Quinn, 1999). The Differential Scanning Calorimetry (DSC) technique provides more thermo-physical data such as heat capacity shown here:

\[ C_p = \frac{\Delta H}{T} \]  

Equation 4.3

Where \( \Delta H \) is the change in enthalpy and \( T \) is the temperature.

4.4 Viscosity Measurements

The viscosity measurements were performed on a Brookfield LV-1 specific for its range of operation governed by Newton’s Viscosity law (Wilke, Kryk, Hartmann, & Wagner, 2000):
\[ \nu = \frac{D}{\tau} \]  

Equation 4.4

Where \( \nu \) is the kinematic viscosity (dynamic viscosity, \( \eta \), over the fluidic density of the material), \( \tau \) is shear strain, and \( D \) is the shear rate.

After setup of the equipment the unit was initially calibrated with a Cannon standard solution (Angell, Ngai, & McKenna, 2000) at room temperature from there the specific spindle was attached then descended into the aluminum metal container. The electrolytic samples were preheated by a Staco transformer with a sleeved slot for the provided cylindrical container. The calibration measurements were made up to 100°C as a function of temperature utilizing a Barnett temperature controller to heat the container holder during testing as depicted below:

Figure 4.19 Arrhenius plot of viscosity measurements as a function of temperature of the Cannon standard solution for the Brookfield viscometer unit calibration.
For testing the air-sensitive samples to prevent unwanted contamination a special glass dome was constructed with a N\textsubscript{2g} inlet and gas outlet that also served at the spindle entrance.

4.5 X-Ray Diffraction (XRD)

A Siemens D5000 XRD (Powder X-Ray Diffraction) technique would characterize the solid acidic powders. The unit used a CuK\textalpha\textsubscript{1} radiation beam and graphite monochromatic operation at 45kV, 40mA then scanned at 1.2 K/min with a scan step of 0.02 K from range 2-90° (Shaijumon, 2006; Wang, 2006). The diffraction pattern consists of three crucial criteria to procure the chemical species individual powder x-ray identification 1) number of observed peaks, 2) peak positions, 3) peak intensities.

The 20 angles are where the intensity of the peaks are at their maximum of constructive interference in the diffraction pattern governed by Bragg’s law as the diffraction of the x-ray beams from the parallel planes of the chemical structure where a pattern is described from the constructive interference:

\[ n\lambda = 2d\sin\theta \]  

Equation 4.5

These alkali-metal chloride samples express intense, thinly sharp peaks indicating crystallinity as where less intense, broader peaks are of amorphous materials. The observed peak correlate to the symmetry of the unit cell and their respective intensities are the amount of atoms repeating in the planes (Geselbracht, 2008). The patterns are interpreted by their lattice parameters to denote the designated crystalline symmetry of the system:
• Cubic
• Tetragonal
• Orthorhombic
• Monoclinic
• Triclinic
• Hexagonal
• Triagonal

4.6 Nuclear Magnetic Resonance (NMR)

Nuclear Magnetic Resonance was simultaneously developed at Stanford and Harvard universities in the mid-1940’s. The technique measures the chemical shifts of isotopic element within the chemical structure of the sample. The sample in the sealed capillary tube was where a magnetic field is applied stimulating the nuclei of the sample. The energy absorbed is limited to the eigenvalues raising the nuclei to excited eigen states to be detected. The energy is detected as a resonance where the high frequency transmitter simulated and amplified as a spectral line better known as the resonance peak signal (Günther, 1998).

Each signal is different and what uniquely identifies every element separately. NMR is governed by quantum mechanics. The magnetogyric ratio, \( \gamma \), is the ability of the proton in the nuclei possessing angular momentum, \( P \), limited by the its magnetic moment, \( \mu \), as expressed here as a “quantized” value:

\[
\gamma = \frac{\mu}{P} \quad \text{Equation 4.6}
\]
The eigen functions are related to the wave functions of the Schrödinger equation, which explain the quantum mechanics involved for an atomic system. The \( \alpha \) and \( \beta \) have the same energy corresponding to the nuclei half spins, \( \frac{1}{2} \) and \( -\frac{1}{2} \), respectively. The change of energy, \( \Delta E \), is quantified by the degeneracy of the nuclei half spins being destroyed by the static magnetic field, \( B_0 \), interacting with the magnetic moment simultaneously along the z axis plane shown here (Günther, 1998):

\[
\Delta E = 2\mu_x B_0 = \gamma h B_0
\]

Equation 4.7

Where \( h \) is \( h/2\pi \) and \( h \) is Plank’s constant, \( 6.6261 \times 10^{-34} \) J-s.

Figure 4.20  RF (radio frequency) pulse used to resonate the chemical species translated into magnetic moment and angular momentum along the magnetic field from the NMR (Kühl, 2014).
The experimental protocol began with the calibration adjustment, e.g. range from 100kHz to 50kHz for \(^1\)H proton measurement to the 400MHz Bruker NMR. Typically, the instrument is calibrated with a control of TMS (tetramethylsilane) depending on the sample of interest.

Electrochemical Characterization:

4.7 Electrochemical Impedance Spectroscopy (EIS)

This physical characterization was crucial for determining the temperature of the liquid and few solid phases of the synthesized chemical species as aforementioned.

4.7.1 History of Impedance Spectroscopy

The early vector diagrams and complex quantities of electrical resistance were graphed by Kennelly and Steinmetz, which further refined the newly founded electrochemical technique of impedance spectroscopy by Oliver Heaviside in 1872. It was Nernst that utilized the electrical bridge by Wheatstone with dielectric methods for measurements to establish the electrochemical impedance spectroscopy (EIS) field in 1894 (Orazem & Tribollet, 2008). In the beginning impedance was a great technique to record the capacitance double layer buildup. Later on more techniques were encouraged to measure the electrode processes and electrode-electrolyte interfacial complexes. The mere term of “impedance” was cited ~1.5k times in articles from the establishment to 1993 (Lasia, Bockris, & White, 1999) then 12
years later exploded exponentially to ~1.5k alone by 2005 and more contributions have risen exponentially ever since.

4.7.2 Fundamentals of Impedance Spectroscopy

The guiding principle of electrochemical impedance spectroscopy (EIS) is the ability to send electrical current through a material of interest either being solid or liquid then measure the modulus impedance $Z$ response, more commonly known as the ohmic resistance $R$. This measurement is amidst the current at a specified dc (direct current) potential $U$ while scanned at varying timed frequencies $\omega t$ with an overlapping fixed ac (alternating current) signal $I$ of low amplitude that subsequently provides the phase shift $\varphi$ (Orazem & Tribollet, 2008) as depicted:

![Diagram](image)

Figure 4.21 The sinusoidal DC potential ($U$) input followed by the ac current ($I$) response indicating the phase angle at a timed frequency $\omega t$ (Lasia et al., 1999).
In ionic conductivity the current is measured by the ions migration from the bulk solution, which is the electrolytic medium, to the charged electrodes. Ions in solution deemed as strong electrolytes dissociate completely into cations and their respective anions hence allowing all the ions to migrate. Therefore, the faster the ions migrate to the electrodes the less the impedance or smaller resistance. The lower the resistance thus the higher the conductance as expressed here in this equation to obtain an arbitrary signal:

\[
E(t) = i(t)R + \frac{q(t)}{C} = i(t)R + \frac{1}{C} \int_0^t i(t)dt
\]

Equation 4.8

Where the voltage potential as a function of time \( E(t) \) can be sought when equaled to the current \( i(t) \) times resistance \( R \) plus the stored charge as a function of time \( Q(t) \) over the capacitance \( C \).

EIS delivers a sinusoidal signal to the material of interest to receive an electrical response as expressed below:

\[
E = E_0 \sin(\omega t)
\]

Equation 4.9

Where \( E \) is the desired potential equal to the signal amplitude \( E_0 \) multiplied by the \( \sin(\omega t) \), in which \( \omega \) is the angular frequency and \( t \) is time.

An undesirable effect can occur when the ac amplitude is increased for stronger sample perturbation then the delivered potential is larger, which then will polarize the testing electrodes. This phenomenon is known as the Wien effect to where a longer waiting period is required for the electrodes to trickle discharge to rid of the induced polarization (Kaiser, 2013).
4.7.3 Ionic Conductivity

EIS is a complimentary technique that should be used in tandem with other methods to measure sample interfacial processes as it will not provide all the resolutions concerning sample characterization (Lasia et al., 1999). The electrodes pass an alternating current from one electrode to the other through the electrolyte. The measurement of the impedance, or ohmic resistance, is proportional to the conductance of the material being studied. The input from the potentiostat is the potential and the output response from the electrolyte in the conductivity cell is the current; when these values are known the resistance can be found as expressed here in Ohm’s law:

\[ V = IR \text{ or rearranged to equal } R = \frac{V}{I} \]

Equation 4.10

Where \( V \) is the provided potential, \( I \) is the response current, and \( R \) is the overall resistance of the entire system.

The ionic conductivity of the electrolyte is further sought by calculating the dimensions of the active area \( A \) of a single electrode along with the cell electrolytic path length \( l \) directly between the pair where the measurement would take place shown below:

\[ \sigma = \frac{l}{RA} \]

Equation 4.11

Where \( \sigma \) is the conductivity, \( l \) is the cell electrolytic path length, \( R \) is the ohmic resistance of the electrolyte sample, and \( A \) is the active surface area of the electrode.
Conductivity Parameters. The non-specific conductivity technique can be dependent by multiple variables of the conditions in place as indicated by influential factors above. Some prominent factors contributing factors to the conductivity of the electrolytic sample are:

- ion size mobility (valence of ions)
- solution concentration (homogeneity)
- cell contamination
- thermal stability

Other additional contributing factors of the system besides the electrolytic sample include (Gomadam & Weidner, 2005):

- interfacial polarization
- electrode geometry
- cable lead length
- frequency range
- ac amplitude

Nyquist Plot. A Cole-Cole plot or seldom called a complex plane plot, but normally referred to as a Nyquist Plot. This plot depicts the imaginary part \( Z'' = -1/wC \) of the y-axis over the real part \( Z' = R \) of the x-axis plot displaying the general Debye complex-plane responses as where the capacitance effects are usually more pronounced than the induction effects. It was Krumer-Kronig that introduced the time constant concept to the Debye response, the semicircle graphical representation (Agarwal et al., 1992). The Debye semicircle response recorded
represents the high frequency intercept initial point then the full capacitance at the apex and finally the low frequency intercept point from the relaxation time of the charge dissipation (Macdonald, 1992). The high frequency of 100kHz characterizes the surfaces of the electrode-electrolyte interface but any frequency higher can induce admittance in the potentiostat leads (Gamry Instruments, 2008).

Figure 4.22  Debye response: initial sample resistance $R_s$ of the double layer crosses at 10Ω on the real x-axis then again at 110Ω of the sample resistance plus the charge transfer resistance $R_{ct}$ creating the semicircle with the apex as the electrolytic capacitance.
4.7.4 Randles Equivalent Circuit

The *Simplified Randles* circuit is a plain and recognizable interpretation of impedance data as the electrical equivalent (K. R. Cooper & Smith, 2006). The capacitive resistance, $C_{dl}$, builds up at the electrode-electrolyte interface forming a double-layer charge along with the reaction resistance, $R_s$, that is inversely proportional to the reaction constant. Other resistances such as the charge transfer, $R_{ct}$, are associated with the mobile ion diffusion rate and the adsorption at the electrode. The potentiostat unit requires external calibration to ensure accurate and precise measurements.

![Image of the Simplified Randles circuit]

Figure 4.23 The *Simplified Randles* circuit is the purely electrical representation of the electrolytic bulk solution resistance then the double layer capacitance and charge transfer resistance of the electrode.

4.7.5 Capacitance Double Layer

The surface electrochemistry is extremely important to include and compensate loss voltage from the double capacitance layer $C_{dl}$ at the interface of the
electrode-electrolyte in the active area as expressed as the *Helmholtz* model (Wang, 2000):

\[
C_{dl} = \frac{\varepsilon_0 \varepsilon_r A}{a_0}
\]

Equation 4.12

Where \( \varepsilon_0 \) is the dielectric constant, \( \varepsilon_r \) is the dielectric constant of the electrolyte, \( A \) is the electrode active area, and \( a_0 \) is the radius of the mobile ion.

Therefore, the double capacitance layer is a potential difference spurred by an adherence of electrons from the bulk electrolyte onto the surface of the metallic electrodes that separates them from the ions in the electrolyte and creates a capacitance effect. This parallel plate capacitance is expressed as:

\[
C = \frac{\varepsilon A}{d}
\]

Equation 4.13

Where \( C \) is the capacitance, \( \varepsilon \) is the dielectric constant \((8.84 \times 10^{12} \text{ F/m})\), \( A \) is the active surface area of the electrode, and \( d \) is the distance between the parallel electrodes (Orazem & Tribollet, 2008).

4.7.6 Warburg Linear Diffusion

The *Warburg* impedance reaches a minimum of \( E_{1/2} \) with an intercept at \( R \) along the phase angle equal to \( -45^\circ \) as well as being governed by *Fick’s* law of diffusion towards semi-infinite linearization. The Warburg diffusion ventures straight up within an ideal blocking electrode occurring at a \( 0^\circ \) from the resistance \( R \) intercept. The ideal plot representation of absolute impedance \( |Z| \) at a perfect \( 45^\circ \) phase angle of the imaginary part \( (Z”) \) over the real part \( (Z) \) on a Nyquist Plot.
The total faradaic impedance $\tilde{Z}_f$ is comprised of the sum of the charge transfer $R_{ct}$ plus the Warburg impedance $\tilde{Z}_W$, which is semi-infinite linear ideally at a slope of unity. The representative semicircle completion terminating nearby the low frequency regime depends on the mass transfer limits of the electroactive species during the measurement of the electrolyte as expressed below:

$$\tilde{Z}_f = R_{ct} + \tilde{Z}_W = R_{ct} + \tilde{Z}_{W,O} + \tilde{Z}_{W,R}$$  \hspace{1cm} \text{Equation 4.14}$$

Where $\tilde{Z}_f$ is the faradaic impedance, $R_{ct}$ is the resistance of the charge transfer, $\tilde{Z}_W$ is Warburg impedance or the redox processes are the summation of the oxidative $\tilde{Z}_{W,O}$ and the reductive $\tilde{Z}_{W,R}$ impedances.

Figure 4.24  Warburg diffusion impedance enters the mass transfer control region after the charge transfer resistance $R_{ct}$ from the capacitance buildup at the electrode-electrolyte interface of the solution $R_s$ of the kinetic control region. The intersection at the real axis ($Z'$) intercept is the overall resistance of the system.
**Bode Plot.** The Bode Plot represents the log phase angle (log $Z$/deg) and/or absolute resistance (log $|Z|$) vs. log frequency (log $f$/Hz), which is desired for a complete circuit analysis as they share all the signal parameters on the plot. The log $|Z|$ of the plot typically depicts dual bends indicating the cell plus electrolyte and solely electrolyte resistances as a function of frequency $f$ (Jiang et al., 1997).

**Two-Electrode Conductivity Cells**

An ac signal is applied to the electrodes then the potential (voltage) is measured across the electrolyte. The effective area of the electrodes must be completely immersed in the electrolyte and centered in the cell to avoid field line effects for an accurate measurement. Cell constants determined in this lab for low conducting electrolytes have smaller cell constants under 5/cm and over 20/cm for highly conductive electrolytes as there is a longer electrolytic path length required.

4.7.7 **Dip Test Cell**

The EIS measurements were performed in these specific conductivity cells designed at this lab and fabricated on campus. The twin electrodes are typically symmetrical where the planar sides are aligned in parallel next to each other thus ensuring an optimal response of the electrode kinetics. Two electrode cells performing conductivity tests are typically encouraged for electrolytes of low viscosity and low conductivity around 1.0 S/cm or lower.
4.7.8 Capillary Test Cell

This new capillary (cap) conductivity cell was designed in our lab and fabricated on the campus; itself is comprised of three main parts: 1) the analytical chamber, 2) the bottom electrode, and 3) the top electrode. The chamber houses the electrolyte and is in direct contact with aluminum block. The electrodes are stacked together then placed inside the chamber for an air tight, ground glass fit further sealed with vacuum grease and iron-weld paste for an entirely closed system. The chamber houses the electrolyte of about 2.5 ml in volume and the electrolytic pathway between the electrodes is 2.2 cm (22 mm). The cell is Pyrex glass and the active areas of the electrodes are platinum arc-welded to chromel or copper wire.
leads. The most inner cavity of the cell houses the k-type thermocouple separated from the top portion of the electrolyte by a shielding glass tube.

![Diagram of capillary cell components](image)

**Figure 4.26** Left, a) glass tube sample holder b) K-type thermocouple in glass sheath c) platinum electrodes d) leads for potentionstat with plastic insulation e) ground-glass joints f) electrolyte sample. Right) Ionic conductivity testing in capillary cell where seg.3 fits inside seg.2 then both inside seg.1 for a ground glass seal; segment 1) glass tube containing the electrolyte; segment 2) capillary testing pathway length above bottom platinum electrode; segment 3) glass sheathed K-type thermocouple just above exposed top platinum electrode.

The capillary cell is positioned inside an aluminum block heated by cartridges. The entire cell within the Al block is placed inside a tin can then further insulated with fiber glass wool. A tin lid covers the top with a small entry hole for the potentiostat leads, thermocouples, and heating cartridges.

**Platinized Electrodes.** Platinized electrodes are encouraged for more precise data points recorded. These types of platinized (ptz) electrodes increase the surface area therefore more specific active area for the electrolytic interface within the conductivity cell (Feltham & Spiro, 2013). A conductivity cell with platinized
electrodes will exhibit much better behaved (stabilized) measurements of resistances at lower frequencies recorded on Nyquist plots per desired temperature even upon heat ramp or cool down.

4.7.9 Cell Constant Measurements

Another route to calculate the ionic conductivity is utilizing the cell constant is a value that is to calculate the specific conductivity of the electrolyte within measurement. This value is found by filling measuring the resistance of a known, standard solution such as 0.01M KCl aqueous solution. The specific conductivity of the aqueous solution at the specific temperature can be found in literature as the conductance $G$ in the CRC (Chemical Rubber Co.) Handbook.

Conductivity is $\sigma = G \cdot k$ \text{ Equation 4.15}

Where $G$ is the Conductance and $k$ is the cell constant of the testing system.

Cell Constant is $k = \frac{a}{d}$ \text{ Equation 4.16}

Where $a$ is the effective area of the electrodes and $d$ is the distance between the electrodes.

Conductance is $G = \frac{1}{R}$ \text{ Equation 4.17}

Where $R$ is the ohmic resistance and $1/R = S$, where $S$ is Siemens unit designation.

The new capillary cell had a cell constant determined to be 25.85/cm. The capillary cell was calibrated with known conductivities of LiCl aqueous solutions previously prepared and measured by Bressel and Xu, previous members of this laboratory (Angell, 2002; Xu & Angell, 2003; Moynihan et al., 1971) in Figure 4.27.
Figure 4.27 The ionic conductivity measurements of both investigators, Bressel and Xu, when compared had a ~1% deviation difference of the same 7.718M LiCl solution utilizing the new in-house fabricated capillary cell.

Table 4.1 The air-tight, new capillary cell had a ~1% difference overall average that deviated from the previous studied 7.7M LiCl aqueous solution of Bressel at el.

<table>
<thead>
<tr>
<th>Capillary Cell Accuracy Testing</th>
<th>LiCl Aqueous Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Tucker’s Data</strong></td>
<td><strong>Bressel’s Data</strong></td>
</tr>
<tr>
<td>7.7M, LiCl aq soln</td>
<td>14.286 mol%</td>
</tr>
<tr>
<td>1000/T (K⁻¹) LOG conduct. (Scm⁻¹)</td>
<td>1000/T (K⁻¹) LOG conduct. (Scm⁻¹)</td>
</tr>
<tr>
<td>3.659</td>
<td>-1.039*</td>
</tr>
<tr>
<td>3.609</td>
<td>-0.995*</td>
</tr>
<tr>
<td>3.538</td>
<td>-0.934*</td>
</tr>
<tr>
<td>3.487</td>
<td>-0.891*</td>
</tr>
</tbody>
</table>
In the past, Xu of the Angell group used a dip cell that had a short path length measurement and Bressel had a more favored capillary cell, which had a path length longer by a factor of 10x enabling more precise impedance measurements for highly conductive electrolytes of over 100 mS/cm (Bressel & Angell, 1972).

### 4.7.10 Solid-State Impedance Spectroscopy

EIS experimental measuring became of interest for ionic conduction in solid oxide electrolytes in fuel cells by Bauerle began in the late 1960’s (Jiang et al., 1997) including electrolytes as, fused salts, glasses, polymers, and asymmetrically ionic-bonded single crystal solids with interstitial vacancies. The amorphous glass and polymers materials are dominated by dipolar rotational characteristics of electronic conduction. Additionally, instances of simultaneous ionic and electronic conduction have been recognized in complicated systems (Gomadam & Weidner, 2005). The electrochemical characterization are applicable for electrolytic systems of fuel cells, metal plating, metal corrosion, rechargeable batteries (Wang et al., 2012) and even biomedical applications such as protein identification. Also solar panels and semiconductors for the electronic dominant materials.

<table>
<thead>
<tr>
<th>Value 1</th>
<th>Value 2</th>
<th>Value 3</th>
<th>Value 4</th>
<th>Value 5</th>
<th>Value 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.416</td>
<td>-0.833*</td>
<td>3.416</td>
<td>-0.818</td>
<td>3.416</td>
<td>0.0%</td>
</tr>
<tr>
<td>3.365</td>
<td>-0.793*</td>
<td>3.365</td>
<td>-0.781</td>
<td>3.365</td>
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<td>3.376</td>
<td>-0.800</td>
<td>3.299</td>
<td>-0.727*</td>
<td>3.338</td>
<td>2.28%</td>
</tr>
<tr>
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<td>-0.496</td>
<td>2.914</td>
<td>-0.468*</td>
<td>2.928</td>
<td>0.92%</td>
</tr>
<tr>
<td>2.669</td>
<td>-0.343</td>
<td>2.680</td>
<td>-0.342*</td>
<td>2.675</td>
<td>0.41%</td>
</tr>
</tbody>
</table>

*Extrapolated values from polynomial trendline of the Nyquist Plot in Fig. 4.27

132
Solid Electrode-Electrolyte Interface. Solid electrodes are known as polarizable electrodes as well due to the fact a double-layer capacitance charges builds up on the surface prior to charge transfer thus deviating from ideal conductivity behavior. This capacitance is not dispersed as effectively hence an increased resistance. This is a prominent factor contributed by the surface irregularities or better known as roughness of the electrode (Hirschorn et al., 2010).

The double-layer capacitance can be expressed as the constant phase element (CPE) of the modulus impedance:

\[ Z_{\text{CPE}} = \frac{1}{T(j\omega)^q} \]

Equation 4.18

Where \( T \) is the temperature, \( j \) is the current density, \( \omega \) is the angular frequency, \( \varphi \) is the phase shift.

Figure 4.28  a) solid sample holder b) Teflon cell c) platinum strip electrodes for potentiostat leads d) Viton gasket dual rubber seals e) k-type thermocouple slot f) \( \text{H}_2/\text{N}_2 \) gas slit inlets for attachment to steel harness with mild spring compression.
The through-plane measurements for these studied materials normally have the lesser resistance depending on membrane thickness and anisotropic effects therefore higher conductivity (Soboleva et al., 2008).

4.8 Fundamentals of Cyclic Voltammetry (CV)

Cyclic voltammetry (CV) is an electroanalytical technique utilized to determine the change of current, mA or µA, from the redox processes catalyzed by a desired electrode when sweeping a controlled potential, V (Wang, 2000). A cyclic voltammogram is obtained by the working electrode applying a linear potential (a voltage that will increase or decrease over time) measured by the reference electrode. CV testing of the analyte either oxidizes or reduces it to detect the current (Pine Instrument Co., 2000). The ionic liquids, molten salts, and liquid acids, were prepared then tested under inert, dry conditions in the absence of a supporting electrolyte, e.g. H₂SO₄. Below is an example of the in-house fabricated CV cell with the Teflon lining, which can be improved to having a Viton gasket seal (not shown here) and can withstand higher temperatures without melting the metal lid:
Figure 4.29  CV cell open, Left A) electrolytic sample B) aluminum metal lid with Teflon seal lining C) cell container D) platinum working electrode E) platinum counter electrode F) platinum reference electrode. Right) CV cell closed for testing the electrolyte.

The CV experimental parameters for these aforementioned electrolytes performed optimal at a scan rate of 5-10mV/s with continuous, multi-cycling under normal pressure (Maiyalagan et al., 2005). The electrolytes were purged with either argon or nitrogen gases for 20 minutes prior to testing. The prepared analyte were initially tested at room temperature then pre-heated, raised uniformly up to 120°C to mimic a fuel cell or battery of moderate operation temperature between 120-180°C. The electrochemical stability as a function of temperature is a vital characteristic to determine viable voltage range operation and prevent chemical structural degradation. The alkali-metal chloroaluminate molten salts typically endure electrochemical windows between 4-5V (Xu & Angell, 1995).
Transmission Electron Microscopy (TEM) was performed on a JEOL ARM200F with a Schottky field emission source accelerated at 120kV of operation at room temperature and standard atmospheric pressure. This electron mapping technique provided a visual of the Platinum (Pt) nanoparticle disbursement throughout the carbon paper of the E-Tek electrodes compared to the Pt nanoparticles on the multi-walled carbon nanotubes (MWCNTs) supports (Ismagilov, et al., 2007; Shi et al., 2011). Small samples were loaded onto a copper grid platform immersed in ethanol at 25°C. The electron beam transmitted its electrons through the thinly sliced sample then detected spatially by the charged-coupled device (CCD) camera. The images provided visual information to qualitatively determine the Pt deposition by nanoparticle mean sizes and dispersions on their respective carbon supports.

Furthermore, scanning electron microscopy (SEM) performed on a FEI XL30 with a field emission acceleration operated at 30kV (beam current 21 pA, probe diameter 0.4 nm) was utilized to provide images of the solid acidic electrolytes at room temperature and standard atmospheric pressure. A view of the rough surfaces assisted in the direction to enhance electrode-electrolyte interfaces use in a H₂/O₂ PEM fuel cell, e.g. methanol droplet additions, and understanding pore size for gas flow channels within the chemical structure. A small quantity of sample was sputtered with a thin layer of gold then loaded into the chamber under vacuum for scanning. The images were detected from secondary electrons emitted from the sample surface due to raster-mapping pattern by the electron beam of the unit. Also,
in-situ electron dispersive spectroscopy (EDS or referred to as EDX) can quantify the atoms present in the scanned areas of the sample to specific the chemical makeup.

4.10 Fuel Cell Setup & Protocols

The initial fuel cell testing was performed with Keithley source meters giving simulated load conditions by a current interrupt protocol and a custom LabView program; later utilizing the PAR VMP2 (Biologic EC-Lab software) and PAR 2273 (AMETEK Powersuite software) potentiostats for data measurements as I/V polarization curves for analysis (Russell, 2003). The chronopotentiometric technique on the PAR 2273 was utilized for constant current testing at 50mA to maximum allowable over 24-hour periods to determine electrolytic stability and longevity at moderate temperatures.

Figure 4.30 The liquid electrolyte H₂/O₂ fuel cell version exploded view and the direction of assembly from the Teflon gas inlet/outlet terminal into the liquid reservoir of the Teflon block.
Figure 4.31 Left) Liquid electrolyte H₂/O₂ fuel cell version under mild spring compression ready for testing as a function of temperature inside the oven. Right) The solid gel electrolyte H₂/O₂ fuel cell version ready under mild spring compression ready for testing as a function of temperature inside the oven.

Figure 4.32 Left) Schematic of the solid gel membrane electrolyte H₂/O₂ fuel cell version exploded view. Right) Transparent view of Teflon block insert for a liquid electrolyte testing depicted with overflow reservoirs (Yeager et al., 1992). Permission granted for reprint.

The experimental controls were commercial electrodes with 0.5mg/cm² Pt/C on Toray paper from E-TEK of DeNova materials under BASF. These electrodes mean particle size as Pt catalyst was 2.6nm but micropores nearly 1.0nm width and
with less accessibility for triple-phase interface (gas/electrode/electrolyte). The control electrolyte was 85% ortho-phosphoric acid as a primarily used within a basic PAFC system for research purposes only. The current collectors were dual platinum mesh (Aesar, 52 mesh woven from 0.1mm wire, 99.9%). The Viton gaskets (1-3mm thick, carbon filled PVDF (ployvinylidene fluoride) Eagle Elastomer, Westlake, OH – USA) ensured for closed system as cell sealing for the gel membrane structural integrity during testing then further wrapped with Teflon tape.

Figure 4.33 Fuel cell load testing of a solid pellet as a neat electrolyte, platinum layer coating, mixed with a polymer PVPP (polyvinyl pyridinium phosphate), and compared to the standard electrolyte phosphoric acid.

The protic ionic liquids (PILs) were pipetted into the fuel cell as the experimental electrolyte. The fuel cell (path length 0.3 cm, surface area 0.5 cm²) is constructed completely of Teflon with Viton gaskets for sealing purposes and platinum mesh as current collectors. A steel harness supports the unit and allowed
the piping in of hydrogen and oxygen gases to flow through the inlet/outlet ports without humidification to the anode nor the cathode chambers. The fuel cell testing was be operated inside a Vulcan oven at a low to medium temperature ranges of 80-260°C at ambient atmospheric pressure of 1 atm and dry gases from tanks (40 psi) with gas flow monitoring via Aalborg digital meters.

The solid gels were sandwiched between either E-Tek Pt/C electrodes (0.5mg/cm²) to form the MEA (membrane electrode assembly). Platinum mesh current collectors are placed behind the electrodes and Viton rubber gaskets behind the current collectors then Teflon gas terminals behind the rubber gaskets. Finally, the entire fuel cell is wrapped in Teflon tape to avoid gas leaks. The Teflon fuel cell is placed into the spring loaded steel with the H₂/O₂ gas inlets and outlets connected to plastic tubes. The copper leads are freshly sanded to avoid cell potential disruption from redox processes of impurities adhered to them. The fuel cell is heated to 175°C for 12 hours then cooled as for pretreatment. This heat pretreatment enhances the electrode-electrolyte interface for optimal catalysis during testing. Afterwards the gases are opened and the temp is equilibrated for an hour between each temperature ramping of each test. Cell potential recovery periods are required for maximizing cell performance and efficiency. The protic ionic liquid (PIL) solutions must be incorporated into solidified polymers to be considered for proton exchange membranes when employed within the fuel cell system.
4.11 Battery Capacitance Measurements

The battery capacitance measurements were performed on a Land cell cycler with Lanhe software. The battery cell was an in-house original design. The metal and Teflon materials for the cell were fabricated on the campus at the machine shop. The solid separators, β” alumina and NaSICON, were acquired from Ionotec UK, Ltd. and Ceramatec Corp., respectively, to test the electrolytes. The Viton gaskets for cell sealing were acquired from Thermodyn, Corp. The cell was setup to electrochemically function similar to the ZEBRA battery of slight physical modifications such as sealing and materials. The electrolyte was chemically modified plus additives. The materials were assembled to create a complete battery cell for testing depicted below here:

![Image of battery cell and schematic](image)

Figure 4.34  Left) 3rd generation sodium-ion, nickel-chloride (ZEBRA-type) with β” alumina separator battery cell  Right) schematic depicting the interior cell components of the sodium-ion battery system (Leigang et al., 2014). Permission granted for reprint.

The battery cell was of a 3rd generation design where the anodic and cathodic half cells were constructed of copper and aluminum metal blocks, respectively, and the Teflon screws inserts partitioned the halves from electrical connection. The
fresh electrolyte, e.g. [EMI]FeCl$_4$NaAlCl$_4$, with the cathode, NiCl$_2$ powder, plus the necessary additives into the cathodic chamber and the molten sodium metal along with copper wool for electrical conductivity in the anodic chamber. The solid $\beta''$ alumina solid separator (BASE) was inserted between the respective chambers then sealed with Viton gaskets to prevent atmospheric water being introduced and vapor pressure gas release from the system. The metal springs in each chamber assisted that optimization at the interfaces. The cell was initially heated in a Vulcan furnace at high temperature of 250°C to further optimize “wetting” at the electrolytic interface to the solid separator as in tandem the sodium metal, $T_m = 98^\circ$C, to the solid separator. The cell temperature was held at high temperature then allowed to cool to the operation temperature range between 120°C up to 180°C. The cell cycler leads were connected to the battery then began the charging process as the cell was assembled in the discharged state. The battery capacitance testing began at the state of charge (SOC) at the desired low or moderate temperature of operation. The initial cycle was at a low rate of C/20 to the end of discharge (EOD) for conditioning purposes. Typically, the discharge would be to 40% depth and charging to 90% full for industrial research purposes as required. Afterwards normal test cycles of charge/discharge were at C2 rates for around 10 cycles. Afterwards the cell was allowed to naturally cool for disassembly then internal inspection.
5.1 Introduction

There are many reasons for seeking liquid electrolytes that are free of molecular solvents for electrochemical applications. A leading one is the great reduction in fire hazard that such electrolytes usually offer. Another is the possibility of ionic conductivities competitive with those of the best salt-in-molecular solvent electrolytes. Wilkes and coworkers (Fannin et al., 1984; Wilkes et al., 1982) had long ago in 1984 shown that ionic liquids based on the ethylmethylimidazolium (EMI⁺) cation, with tetrachloroaluminate anions, had conductivities as high as 22 mS/cm at 25°C and 81 mS/cm at 100°C. These were a few percentages higher than the values reported some years earlier (Angell et al., 1976) for the α-picolinium tetrachloroaluminates (61 mS/cm at 100°C) and had the advantage of remaining liquid to ambient temperatures. Both exceeded the conductivities of the "standard" lithium cell electrolyte, LiPF₆ in the mixed cyclic-acyclic carbonate molecular solvents (12 mS/cm at 25°C in EC:DMC, 1:1) (Tarascon, 1994).

Somewhat smaller values (9.1 mS/cm) can now be obtained with air and water-stable ethylmethylimidazolium bis-triflamide [EMI⁺][N(SO₂CF₃)₂] (or EMINTf₂) according to Pan and co-workers, (Pan et al., 2011) who confirm the
earlier values by other researchers (Tokuda et al., 2006; Widegren et al., 2005). Slightly higher values (11 mS/cm) have recently been reported for [EMI\(^+\)][BF\(_4\)](TFA)\(_2\)\(^-\) by Gores and coworkers in a wide-ranging and precise study of fluoroborate-based anion systems (Schreiner et al., 2010).

Kim and co-workers (Kim et al., 2011) have since found that solutions of LiNTf\(_2\) in EMINTf\(_2\) may have conductivities only slightly smaller than those of the EMINTf\(_2\) demonstrating that the pessimism concerning ion trapping of lithium in mixtures of lithium salts with ionic liquids expressed by Cooper and one of us, on the basis of early in 1982, LiX-ILX (X = anion) solution studies (Cooper & Angell, 1983), may have been premature. Evidently, the low basicity (related to polarizability) of the bis-triflamide can overcome much of the lithium ion trapping effect observed in the presence of polarizable anions, that Cooper had sought to overcome using tetrafluoroborate anions. Unfortunately the Li\(^+\) ion remains the least mobile species in these mixtures (Nakagawa et al., 2004; Ye et al., 2007).

Nevertheless, in view of the low basicity of the AlCl\(_4\) anion, there seemed to be some prospect that these melts might provide a means of lowering the operating temperature, without too much sacrifice of conductivity, of cells of the ZEBRA (Na/NiCl\(_2\)) and sodium/sulfur types to the melting point of sodium or even to ambient temperature (Gray et al., 1996) if mixed alkali-metal (Na-K) anodes could be utilized.

Contrary to this aspiration, however, was an observation reported by Wilkes in a 1994 internal (Frank J. Seiler Laboratory) report. There is a rapid decrease in conductivity when NaAlCl\(_4\) is added to [EMI][AlCl\(_4\)] that Wilkes noted,
"Surprisingly, as more sodium ion replaces the large imidazolium ion cation, the conductivity goes down."

see their Figure 5.5 (Wilkes, 1994). The observation was interpreted in terms of the crystal structure of a 1:1 double salt forming in the binary system ($T_m = \sim 35^\circ C$), which revealed enclosure of the sodium ion within a network of tetrahedral anions that 6-coordinated the Na$^+$ cations. This scenario would be consistent with the alkali cation trapping interpretation suggested earlier by Cooper et al.

Unfortunately, no conductivity isotherms were presented and the work was not published in the open literature. Similar observations were later made by the Kohl laboratory (Kim et al., 2005), for the lower-conducting quaternary ammonium tetrachloroaluminate ionic liquid (three alkyls and one benzyl), who made important electrochemical observations (see later) but, again, a complete study to identify the location and depth of the conductivity minimum, was not executed.

With an interest in learning more about this unfortunate behavior, this laboratory decided to repeat the study with the aim of obtaining more detail on the trapping phenomenon and hopefully identifying some means of obviating it. Some encouragement to this end has been provided by the moderate success as reported (Ui et al., 2005) in developing LiAlCl$_4$:EMI[AlCl$_4$] electrolytes for "direct electrolyte" lithium battery technology.

It should be mentioned here that the electrochemical window offered by these electrolytes is highly dependent on the actual electrolyte composition, specifically the Cl/AlCl$_3$ ratio. The acid-base reaction that forms the AlCl$_4^-$ anion from the basic chloride of the EMICl and the Lewis acid AlCl$_3$ is accompanied by a large free energy change. The free energy change accompanying this process was first evaluated for
the alkali halide + AlCl$_3$ cases by laboratories of Mamantov, Bjerrum, and
Osteryoung (Torsi et al., 1972: Breckle et al., 1979: Boxall et al., 1973) using
thermodynamic studies of pCl$^-$, and then supported by observations of the change in
optical basicity (Duffy & Ingram, 1971: Duffy & Ingram, 1976: Pitula & Mudring)
based originally on the $^3$P$_1$ $\leftrightarrow$ $^3$S$_0$ UV spectral shift on crossing the AlCl$_4^-$
stoichiometry of indicator ions doped into the melt. The shift in UV absorption peak
wavelength for probe ions, Pb$^{2+}$ ions, observed by a prior group of this lab (Bennett &
Angell, 1985) when the AlCl$_4^-$ stoichiometry is crossed in the KCl-AlCl$_3$ system, is
extremely abrupt, and amounts to 40.1 nm. This translates to an electronic energy
change $\Delta n$ (= $hc/\Delta l$) of 0.562 eV, which reflects very closely the thermodynamic
change 2.303 RT/F ($\Delta pCl^-$) = 0.57 eV (see also Figure 5.1 of Bennett et al.) for the
direct potentiometric titration in the NaCl-AlCl$_3$ system. The much larger changes
that occur when the EMI$^+$ cation replaces the alkali cation can be appreciated by
comparing titration curve with that from Hussey and co-workers (Hussey et al.,
1986) for the EMICl + AlCl$_3$ case, where the voltage step at AlCl$_4^-$ stoichiometry rises
to more than a full volt.

The widest electrochemical window in these systems is obtained when the
pCl$^-$ is located at the neutral point of the titration, where the pCl$^-$ is changing most
rapidly, which is the exact AlCl$_4^-$ stoichiometry so some means of buffering the
solution at this pCl$^-$ is desirable. Where such means have been studied by different
authors (Koronaios & Osteryoung, 1999: King et al., 1996: Bjerrum, 1971: Smith &
Bjerrum, 1967). The use of insoluble solid CaCl$_2$ and MgCl$_2$ described by Koronaios
and Osteryoung, is a leading example. The control mechanism depends on the fact
that excess Cl$^-$ activity is pre-empted by formation of the soluble MgCl$_{2-}$ anion.
CaCl$_2$ will buffer at a slightly more basic chloride ion activity. Excess, solid alkali-chloride has long been known to buffer near the basic limit for inorganic buffers.

Our first objective in the present study is to quantify the phenomenon of alkali-metal mobility depression, and the obvious first choice of the system is one of the organic cation-based ionic liquids, e.g. EMICl-AlCl$_3$. However to set the problem in perspective, it is desirable to consider the alternative possibilities. An alternative strategy employed for obtaining ambient temperature ionic liquids for electrolytic applications has involved the use of inorganic moieties. Inorganic salts with low melting points, such as hydrazinium nitrate (T$_m$ = 80ºC), have been known for a long time (Sutter et al., 1971). However they are not suitable for alkali battery purposes because of the labile protons typical of proton transfer salts. On the other hand, salts formed by halide transfer, rather than proton transfer, do not have this limitation.

Thus, highly conducting electrolytes have been prepared by using strong Lewis acids, e.g. AlCl$_3$ and BCl$_3$, to extract halide ions from molecular species and thereby to create alternative tetrachloroaluminate liquids (Olah, 1979; Xu et al., 1996). These can be as conductive as the corresponding salts of tetra-alkylammonium cations. An example of this type of solvent-free ionic liquid is [CH$_3$N=PCl$_2$]$^+$[AlCl$_4$] included in Figure 5.1(a) as system II. Its ambient temperature conductivity is 1 mScm$^{-1}$, which can be compared with those of the ambient temperature [NR$_4$]$^+$ based ionic liquids methoxyethylidimethyl ammonium tetrachloroferrate, tetrafluoroborate, and NTf$_2$, all of which are 2-3 mScm$^{-1}$ (Cooper & Angell, 1983; Xu et al., 2003). For further comparison, the best of the alkylpyrroldinidium NTf$_2$ ionic liquid family (MacFarlane et al., 1999), considered
promising for alkali-metal battery applications, has an ambient temperature conductivity of 2x10^{-3} Scm^{-1}. The second most conductive of the five cases in Figure 5.1(a) is the tetrachloroaluminate formed from the fully inorganic moiety Cl₃P=NPOCl₂, which is system IV: it has a 25°C conductivity of ~0.8 mScm^{-1}.

Figure 5.1 (a) Arrhenius plots of chloride transfer quasi-ionic liquids using AlCl₃ and BCl₃ Lewis acids. The most conductive (II) contains the cation CH₃N=PCl₂⁺. Samples (III) and (IV) are all-inorganic. (b) Conductivity isotherms in the binary system [M][AlCl₄] + LiAlCl₄ where M is trichlorophosphazosulfonyl chloride, Cl₃PNSO₂Cl (sample III in Figure 5.1a). The LiAlCl₄ datum at 100°C was obtained by extrapolation of higher temperature data. Sample identities, I: [CH₃SO₂⁺][AlCl₄⁻], II: [CH₃N=PCl₂⁺][AlCl₄⁻], III: [Cl₃P=NSO₂⁺][AlCl₄⁻], IV: [Cl₃P=NPOCl₂⁺][AlCl₄⁻], V: [CH₃CH₂N=PCl₂⁺][BCl₄⁻].

One observes the possibility in Figure 5.1(a) of systematically increasing the conductivity from the 1 mScm⁻¹ of the all-inorganic case IV, by addition of LiAlCl₄ as seen above in Figure 5.1(b). If the LiAlCl₄-LiAlI₄ eutectic temperature, Tₑ= 60°C (Angell et al., 2011) were used as source of Li⁺ cations, the entire composition range would satisfy the ionic liquid criterion. These binary inorganic solutions also appear to have very wide electrochemical windows, and reductive stabilities sufficient to
permit reversible deposition and stripping of lithium (Xu et al., 1996) hence presumably also of sodium.

Despite these favorable properties, the materials of Figure 5.1 are only referred to as "quasi-ionic" liquids (Xu et al., 1996), since reporting of low viscosities suggest that their ionicities might not be ideal. Ionicity refers to the extent to which ions are free from association with species of the opposite charge. It is currently much discussed in the ionic liquids field (Miran et al., 2012; MacFarlane et al., 2009; Yoshizawa et al., 2003), using such measures as (i) conformity to the classical Walden rule (Xu et al., 2003) assessed using a Walden plot (Yoshizawa et al., 2003) or (ii) accord with the Nernst-Einstein equation (Miran et al., 2012), see discussion section. Thus it was deemed preferable for the purposes of the present project to start our study with the organic cation salts since their liquid states are known to be of high ionicity. Furthermore, while they are water and air-sensitive, they are not disadvantaged by toxicity issues.

5.2 Experimental Section:

Materials. Commercial grade NaAlCl4 and 99.5% NaCl were both purchased from Sigma-Aldrich. Anhydrous AlCl3 (99.9%) in sealed ampoules was obtained from Alfa Aesar. 1-ethyl-3-methyl imidazolium chloride (EMICl) was purchased from Arcos Organics. All materials except the NaCl were stored in a drybox, and only opened at the time of use.
5.2.1 Preparation of Chloroaluminates

The commercially obtained NaAlCl₄, when fused, yielded a liquid that was not colorless nor fully transparent so was judged unsuitable for our purposes. By contrast the melt obtained by carefully premixing, and then fusing, pure NaCl and anhydrous AlCl₃ (ampoules, see Materials) in a glovebox, which was of pleasing quality and was used for our further studies.

To obtain the corresponding ionic liquid for conductivity determinations, and for use in preparation of the binary chloroaluminate solutions of this study, the commercial EMICl powder was weighed out in stoichiometric proportions, in a glovebox, and added to a pre-weighed amount of the anhydrous AlCl₃ in a weighing bottle, which was immediately capped. The components simultaneously reacted and fused to yield a clear ambient temperature liquid. Once in the form of [EMI][AlCl₄], the AlCl₃ activity is greatly reduced and the need for great caution concerning exposure to atmospheric moisture is less urgent.

For binary tetrachloroaluminate solution preparations it was possible to add the preformed NaAlCl₄ described above to weighed quantities of the liquid EMIAICl₄. However, it was mostly found more convenient to follow a procedure in which the EMICl and excess AlCl₃ were first mixed, fusing spontaneously, and the stoichiometric mass of NaCl then added, using gentle warming as needed, to achieve the desired tetrachloroaluminate composition.
5.2.2 Conductivity Measurements

(i) Demountable capillary cell. Because of the high conductivities expected from previous measurements (Fannin et al., 1984; Angell et al., 1976) the simple twin electrode dip-type cells that have been used in much of our recent work (Xu et al., 2003; Lee et al., 2012) were deemed inadequate for the accuracy we sought; and a three part capillary cell suitable for use with highly water sensitive electrolytes, was designed. The cell consists of an upper electrode with isolated thermocouple well that mates through a ground glass sleeve with a capillary conducting path component, as illustrated in Figure 5.2(a) and (b). The cell constant, determined completely by the choice of capillary length and bore, was chosen to be near 30 cm⁻¹. These, together, then sleeve into an outer compartment that contains the lower electrode. The sample is added, and the cell assembled, inside the drybox. Once assembled, all further actions can be safely taken outside the drybox. To ensure that the liquid sample rises smoothly through the capillary to immerse the upper electrode, this segment contains a small hole, situated well above the upper electrode, which allows pressure to equalize as the sample rises up the capillary. The assembled cell fits snugly down into a removable cylindrical block which itself inserts into a temperature-controlled, cartridge-heated, aluminum block as seen in Figure 5.2 sitting in a glass wool-insulated container, the upper volume of which is then filled with glass wool to ensure a uniform temperature over the whole cell. The temperature was controlled to ± 0.1°C by a Barnant Co. Model 68900-11 temperature controller, which permitted also the use of a continuous heating ramp.
(ii) Frequency independent conductivity determinations. The measurements of the conductivity as a function of frequency, over the range 0.001-100 kHz, were usually performed in a continuous heating mode at a ramp rate of 1K/min. Data were acquired using a PAR VMP2 potentiostat (Princeton Applied Research) with a frequency range of 0.01 Hz to 1 MHz of which was used only the lowest four orders. After the heating run was complete, further measurements were made during cooling to confirm that the heating rate was slow enough for the data to be collected under effective isothermal conditions (see Results section).

The dc conductivity was determined by the standard complex impedance method. Because of the high conductivity of our samples, most of the impedance measurements were made at frequencies below those at the $Z''$ (imaginary $y$-axis) minimum of the Nyquist plot ($Z''$ vs. $Z'$), meaning that conductivity values would
depend on an extrapolation to $Z'' = 0$. Concern with measurement precision required to be concerned about the details the Nyquist plot in the vicinity of the minimum, because, in the absence of a perfect conductivity vs. frequency plateau, the dc conductivity value must be assessed using a small extrapolation to the zero of $Z''$.

Figure 5.3 shows a set of low temperature data for which the data extend into the domain of the complex impedance arc that is intrinsic to the conductivity relaxation. The complete form of this intrinsic conductivity arc (Kim et al., 2006) is shown as a dashed curve in Figure 5.3. It would seem that the dc conductivity is easily and unambiguously defined from such a plot, however this is where problems can arise. The insert to Figure 5.3 shows a blow-up of the data in the highlighted zone of the main figure. It shows that close to the minimum there is a change of slope, which in some cases can be much more significant than in the case shown. The blow-up shows that data in this "low slope" zone should be omitted from the extrapolation if a precise meeting with the extrapolation of the intrinsic conductivity arc, is to be obtained on the $Z'' = 0$ axis (red and blue dashed lines in Figure 5.3). Otherwise uncertainties in excess of 1% in the conductivity measurement may be incurred. In the case shown, the two extrapolations agree within 0.5%.
5.3 Results

In Figure 5.4 are shown Arrhenius plots of several compositions in the binary system from the present measurements. Comparison is made with the data of Fannin and co-workers (Fannin et al., 1984) for the pure [EMI][AlCl$_4$], and the agreement is seen to be satisfactory in view of the sensitivity of conductivity to the precise composition in the vicinity of AlCl$_4$ stoichiometry, and the fact that neither preparation was buffered at the midpoint pCl$^-$. While there have been a number of electrochemical studies of this particular system concerned with electrodeposition,
not much attention has been given to the conductivity itself since the aforementioned detailed studies.

The highest conductivity in the system is clearly that of the alkali chloroaluminate itself, though the temperature range is limited. The data in Figure 5.4 for NaAlCl₄ extend to well below the thermodynamic melting point, thanks to supercooling. In the case of LiAlCl₄, mixtures with LiAlI₄ can be supercooled to the glassy state with glass temperature of -55°C (Angell et al., 2011). The depression of both end member conductivities by addition of the other seen in Figure 5.1 is quantified by the isotherms shown in Figure 5.5.

Figure 5.4 Arrhenius plots of the data from the present measurements. Comparison is made with the conductivity of an earlier study of the pure [EMI][AlCl₄] (Fannin et al., 1984) and with the conductivities of two Na-ion conducting polycrystalline solids used for separators in sodium battery technology (β/β''-alumina and NaSICON).
Solid symbols are for data taken during slow heating and open symbols for data taken during slow cooling in the same run. Data for cooling run in the case of NaAlCl₄ (and including some supercooled liquid data) were obtained with a small sample dip cell and may not be as precise as the more limited T range heating data.

Although thought to be stable to higher temperatures, [EMI][AlCl₄] in our work proved to be sensitive to temperatures above 140°C, indicated by some discoloration. For this reason seen here below in Figure 5.5, which shows conductivity in relation to mole fraction of NaAlCl₄ at selected temperatures, some compositions near the pure EMIAICl₄ extreme use short extrapolations of lower temperature data for their higher temperature values.

![Figure 5.5 Conductivity isotherms for the present binary system. Lower temperature points for the pure NaAlCl₄ and higher temperature points near pure [EMI][AlCl₄] were obtained by extrapolations of the Figure 5.4 plots (shown as open symbols in each case) where these points typically have larger uncertainties.](image-url)
5.4 Discussion

It is seen in Figure 5.4 that in contrast to the inorganic IL case seen in Figure 5.1(b), there is indeed a serious decrease in the conductivity of the binary solutions as NaAlCl$_4$ is added to the [EMI][AlCl$_4$] IL. The depression maximizes on the NaAlCl$_4$ rich-side of the equimolar composition. It is important for understanding of this behavior that we recall the opposite behavior of the binary solutions EMICl + AlCl$_3$ and the earlier studied solutions of $\alpha$-picolinium chloride + AlCl$_3$ (Angell et al., 1976). In these cases the liquid conductivity goes through a sharp maximum at the 50 mol% composition (Fannin et al., 1984). This is true also in the case of alkali-metal halide system KCl + AlCl$_3$ melts studied at higher temperatures (Boston et al., 1970). In each of these cases, the next nearest neighbor cation to the univalent Na$^+$ is the trivalent Al$^{3+}$ species and the second nearest neighbor cation is another sodium ion. The high charge density of Al$^{3+}$ polarizes the chloride ion electron density towards it, decreasing the coulombic energy of the system making it less viscous and leaving the univalent cation free to move. In the case of the lithium cation the Li$^+$ may even be superionic, see the Walden plot of (Xu et al., 2003) that is reproduced with additional data below. In fact, the simulations of Salanne and co-workers (Salanne et al., 2012) suggest that all the alkali metals in their tetrachloroaluminate melts are weakly superionic with respect to the anion mobility though Li$^+$ is less free than the Na$^+$.

In the mixtures of EMI$^+$ and Na$^+$ tetrachloroaluminates, the same considerations, but this time involving competition between the second nearest neighbor cations lead to the opposite result - a strong decrease in conductivity in the
mixtures. At 50 mol% NaAlCl₄, the decrease in conductivity from its additive value amounts to a factor of 2 at 185°C and increases to more than an order of magnitude at ambient temperature using extrapolated values for the pure NaAlCl₄ conductivity from Figure 5.4. The maximum depression is found on the NaAlCl₄ rich-side of the 1:1 stoichiometry. Although the next nearest neighbor cation is still an Al³⁺, each alkali cation is now competing with a very weak-field second nearest neighbor for the AlCl₄⁻ complex anion taken as a whole. The alkali cation wins, and so creates a self-trap. Indeed, the partial phase diagram (Wilkes, 1994) shows the presence of a mixed crystal with congruent melting point at the 50 mol% NaAlCl₄ composition, the crystal structure of which they determined. It showed the Na⁺ ion enclosed in a cage of AlCl₄⁻ anions.

This is generally in line with expectations from the simple cation competition ion-trapping, scenario advanced long ago for the corresponding phenomenon in mixed iodide ionic liquids (Cooper & Angell, 1983). The line of thought actually has its roots in the early days of inorganic molten salt mixtures, when researchers elsewhere (Kleppa & Hersh, 1961) used the electrostatic argument to interpret enthalpy of mixing data in alkali-metal nitrate binary solutions later refined by a conformal solution theory argument (Reiss, 1962) for the same mixed alkali nitrates. An alternative anion polarization argument (Lumsden, 1961) led to the same expectations. Since the arguments are quite general they should apply to all mixed monovalent cation systems, but be more severe for those systems with highly polarizable anions, thus more serious for alkali iodide + IL cation iodide systems than for the mixtures containing the less polarizable tetrafluoroborates. This was the reasoning that led to the discovery in 1982 of the first water-soluble, air-stable,
ambient temperature ionic liquid, methoxyethylethylidimethylammonium tetrafluoroborate of ionic conductivity 1.7x10^{-3} Scm^{-1} (Cooper & Angell, 1983), which unfortunately was not promoted by its inventors at the time.

There are some problems with this model, however. The competitive electrostatics argument would lead to the expectation that Li^+, with its highest charge/radius ratio, would be the most strongly trapped among the alkali metals while Cs^+, with a much weaker field, would be the least affected. But this is not what is found in the laboratory. The limited data in the report by Wilkes shows that the decrease in conductivity on addition of MAICl₄ to [EMI][AlCl₄] is most rapid where M is the largest alkali cation.

The explanation may lie in the kinetic factor associated with cation size. We know from previous studies of viscosity and conductivity in the case of LiAlCl₄, that the Li^+ motion is not strongly coupled to the motion of the anion except at high temperatures. This can be ascertained from a Walden plot containing data for LiAlCl₄ (Xu et al., 2003) reproduced below in Figure 5.6. The data for LiAlCl₄, taken from a prior investigation (Janz, 1988) and extrapolated from binary solution data where necessary, are for temperatures higher than those under discussion here, T < 150ºC (Salanne et al. 2012), and so in supercooled states near ambient temperatures, the Li^+ ion would be at least a factor of 10 more mobile than the quasi-lattice in which it moves and which determines the viscosity. Indeed decoupling indexes of 10⁹ have been determined for LiAlCl₄-LiAlI₄ binary solutions at their glass transition temperature (Angell et al., 2011). Thus Li^+ can evidently escape quite easily from a tetrachloroaluminate environment.
On the other hand, using the viscosity data provided by Fannin et al, where possible to obtain an assessment of the degree of decoupling of conductivity from viscosity in the case of the single IL [EMI][AlCl₄]. The values are plotted in Figure 5.6, which contains also the data discussed for LiAlCl₄. Figure 5.6 shows, firstly, what was already assumed as known, namely, that [EMI][AlCl₄] is a "good" ionic liquid, i.e. the equivalent conductivity is well predicted from the viscosity since the points fall on the ideal Walden line. Secondly, the plot shows that, distinct from LiAlCl₄, there is negligible or even weakly negative decoupling, in the case of the [EMI][AlCl₄] ionic liquid (the upper red point falls distinctly below the line of black triangles for the LiAlCl₄ liquid).

Combining preliminary viscosity data for our own mixed ILs with the conductivity data of Figure 5.4 yields the second pair of large (blue online) points, which lie distinctly below the ideal line. This shows that, in this case, the ions contributing to conductivity are unfavorably coupled, though the effect is quite small.
When the cations are mixed a significant degree of coupling occurs. This can be interpreted as ion pairing or, more specifically, loss of alkali cation mobility due to trapping. To better understand this observation we can turn to the detailed diffusivity studies of solutions of lithium salts in organic cation ionic liquids that have been performed by Price and co-authors (Nakagawa, 2004) and by Greenbaum.
and co-authors (Huang et al., 2007) for the cases of Li\(^+\) in [EMI][BF\(_4\)]:LiBF\(_4\) and in [PR\(_4\)][TFSI]:LiTFSI, respectively. In each case they found that the Li\(^+\) cation is the least mobile species in the ionic liquid. Thus the "trapped alkali cation" model seems to retain some validity.

At this point there needed to be asked if this problem can be fixed by replacing the organic cation by one of the inorganic, or semi-inorganic cation, salts of Figure 5.1, or analog cases. After all, Figure 5.1(b) showed the opposite behavior from that seen in Figure 5.5. The answer is probably, no. This answer is based on the observation that the conductivity of the Figure 5.1(a) tetrachloroaluminates are distinctly lower than that of [EMI][AlCl\(_4\)] probably due to low ionicity, though this remains to be established by appropriate methods. For comparison of Nernst-Einstein equation and Walden plot methods (Miran et al., 2012). Studies of this question using some novel halide transfer ionic liquids, are in progress.

How important is this depression of the ionic liquid conductivity in the sodium case, relative to the Li case? Figure 5.3 shows that even at the composition of maximum depression the conductivity of the ionic liquid is still half a decade higher than the conductivity of any β" alumina separator so decreased conductivity itself should not be the rate-limiting factor in electrochemical device performance. However, when it comes to electrodics (Bockris & Reddy, 1998) the effect on electrodeposition rates might be more serious. Indeed reported (Kim et al., 2005) that unlike lithium, sodium is not electrodeposited from chloroaluminate ionic liquids, perhaps because the separation of the trapped Na\(^+\) from the electrode surface makes the essential electron transfer step improbable. The sodium trapping
can apparently be partially relieved by addition of the volatile molecular liquid
SO$_2$Cl$_2$ (Kim et al., 2005).

5.5 Alternative Approaches

It is obvious from the above discussion, that there are serious impediments to the use of ambient temperature ionic liquids as the transporting medium for alkali cations in electrochemical systems. The problem is more severe for Na$^+$ and larger alkalis. The highest conductivities available are of the order of a single mScm$^{-1}$ at ambient temperature and the alkali species are the least mobile in the mixture. This turns attention back to the type of system in which the alkali cation is the most mobile rather than the least namely those in which the alkali metal is next nearest neighbor to a highly charged Lewis acid species and in which there are no other low-charged cations in the system to encourage the sort of traps that have been discussed above. An apparent problem, here, would be the fact that such systems are invariably crystalline or glassy at ambient temperature, assuming we have excluded molecular or aqueous solutions that engender a quite separate set of problems. But this problem is certainly not insuperable.

There are three classes of solid to be discussed. The first is the much-studied superionic crystal class of solid of which the well-known β"-alumina and NaSICON ceramics are outstanding members. They have the disadvantage of brittleness, but have already served well in hybrid alkali-metal anode/ aqueous cathode batteries (Zhou et al., 2010: Lu et al., 2011), i.e. low temperature systems, as well as in the famous ZEBRA cells at higher temperatures.
The second is the glassy solid or glass-ceramic type of solid that is under intense study in the laboratories of Tatsumisago-Hayashi in Japan (Hayashi et al., 2011) and Martin in the USA (Christensen et al., 2013; Bischoff et al., 2014). A disadvantage is the dependence, so far, on sulfide anionic media for the highest conductivities. Working batteries using mobile sodium ions in sodium thiophosphate glass-ceramics, have been described. The single ion Na\(^+\) conductivity can be above 0.1 mS/cm. Lithium ion equivalents have recently reached 17 mS/cm (Seino et al., 2014) exceeding the best commercial molecular liquid solvent cases and they are free of fire hazards and side reactions.

Finally, there is the alkali metal rotator solid class, the study of which is in its infancy (Klein et al., 2014), but could be transformative if successful. It depends on the generation of alkali salts of very large unpolarizable anions with relatively free rotational degrees of freedom at ambient temperature. Like the glasses, the mobile crystalline states are generally metastable with respect to ordered immobile solids and kinetic preservation of the mobile state is a problem to be mastered. Examples of soft solids with lithium ion resonances of only a few hertz broad implying high alkali-ion mobility, are on record (Klein et al., 2014).

Remarks. The present conductivity study has confirmed and elucidated the presence of an alkali cation trapping phenomenon as a problem when the alkali cation is mixed with weaker field ionic liquid cations, even in a system with the least basic anions commonly available, e.g. tetrachloroaluminates. Physical models for the effect suggest it should be a general problem regardless of whether the large
cations are organic, inorganic, or hybrid. Some alternatives that avoid the alkali cation-trapping problem have been briefly considered.

6 INORGANIC VS. ORGANIC CATIONS OF IONIC LIQUIDS AND THEIR SOLUTIONS WITH ALKALI-METAL CONTAINING ELECTROLYTES

6.1 Introduction

Although many low-melting inorganic salts are known, and have been studied for various applications ranging from heat treatment quenching baths and molten carbonate fuel cells (Kolb, 2008), the number of cases that are actually liquid below 100°C is quite small. Mixtures of lithium haloaluminates can be molten as low as 60°C (Angell et al., 2011), and introduction of some thiocyanate anions can render them fully non-crystallizing (Liu et al., 1996). Hussey and coworkers (Wang & Hussey, 2013) have recently provided an example of an inorganic ionic liquid by mixing the cations as well as the anions. Derivatives of hydrazine that are low viscosity ionic liquids, have been used in producing hypergolic ionic liquids that ignite spontaneously on contact with appropriate oxidizing liquids (Zhang & Shreeve, 2011).

Hydrazinium salts formed by proton transfer from acids to hydrazine, melting well below 100°C (Sutter et al., 1971), and their mixtures with small amounts of water have been used in the production of liquid propellants for use in artillery and rocketry. In electrochemical applications, mixtures of ammonium salts with melting points well below 100°C, have been used as fuel cell electrolytes,
thanks to the proton-carrying ability of the ammonium cation (Belieres & Angell, 2007). Finally, batteries with voltages as high as 4 V have been constructed using the melt of the crystallizable salt [SCl₃][AlCl₄] as the anolyte (Hvistendahl & Mamantov, 1984). A similar chloride transfer process was used to make "quasi-salts" (Xu et al., 1996) with tetrachloroaluminate anions for possible applications in lithium battery technology due to the high conductivities that could be obtained in their solutions with LiAlCl₄.

The success experienced in the latter type of study lead us to wonder whether the use of similar chloride transfer salts might serve to replace the organic cations in ambient temperature electrolytes that were studied by us recently in efforts to characterize ionic liquids that might be useful in the search for electrolytes for low temperature sodium batteries (Tucker & Angell, 2014). That study produced graphic examples of the loss of conductivity that usually can accompany the mixing of alkali salts with their organic cation counterparts. Although this problem can be overcome in systems running at intermediate temperatures of 100–180°C, (Xue et al., 2014) the low conductivities at ambient temperature have severely restricted the use of ionic liquids with alkali cations in any applications that require high currents.

While the arguments advanced to explain the low conductivities of the mixed ionic liquids plus alkali salt electrolytes would seem likely to apply to the inorganic chloride salt cases as well, it was felt that the study of additional inorganic cation systems deserved some attention in view of the apparent success in the case of lithium ion electrolytes (Xue et al., 2014). Since AlBr₃ is considered by many to be a more powerful Lewis acid than AlCl₃, and since PBr₅ is a more crowded (bromides possess larger ionic radii) species than PCl₅ hence it was chosen for the investigation.
of the binary PbBr$_5$ + AlBr$_3$, and its mixtures with an alkali-metal analog, to carry out an exploratory study. Such an investigation requires a characterization of the components of any mixture of interest and it is perhaps in the components of the mixtures that the most fascinating results of this study have been encountered.

6.2 Experimental Section:

Materials. The AlBr$_3$, of stated purity 99.5%, was purchased from in anhydrous form in ampoules from Alfa Aesar and Stern Chemicals. PbBr$_5$, of 95% purity also in the anhydrous form was purchased from Aldrich. NaCl, was previously stored in the lab from Sigma-Aldrich. All chemicals were stored under inert conditions before and after synthesis.

6.2.1 Synthesis

All preparations were made in a low dewpoint drybox using freshly opened ampoules of AlBr$_3$, PbBr$_5$, and vacuum-dried NaCl. The glassware was freshly cleansed in a NaOH base bath, washed with deionized water, then dried over a period of days and powders were placed in the Argon filled glove box. The stoichiometric amounts of the white powders were weighed inside the glove box then put in a glass weighing bottle. The respective powders were manually stirred together with a glass rod then gently capped with a lip for a ground-glass seal. The samples were heated on a hotplate up to 160-190°C for 3hrs then allowed to cool back to room temp overnight inside the glove box. If samples were necessarily transferred outside the glove box then they were stored in a rubber sealed desiccator.
containing MgClO$_4$; never exposed to the air of the laboratory. The glass sample bottles and vials were wrapped with foil as these bromo-halides are apparently susceptible to photochemical redox reactions from a light source (Jotner et al., 1964).

6.2.2 Phase Stability from Differential Thermal Analysis

Small amounts of the prepared samples were pipetted into sealed Pyrex glass tubes (5mm o.d. x 3mm i.d.) under an inert atmosphere. Another smaller diameter thin-walled capillary tube was inserted then immersed in the sample but not quite touching the bottom of the outer capillary tube. A k-type thermocouple was inserted into the inner hollow capillary for the most precise temperature measurements as possible. The thermocouple wired was connected to a NI detector where the signal was recorded on LabView software. The sample tube was wrapped with Teflon to keep moisture out then inserted deeply into an aluminum block for a snug fit. The sample control was dried Al$_2$O$_3$ packed and wrapped in the exact manner as the test sample. The aluminum block was heated at ~12 K/min with a heating cartridge attached to a 120V Staco Energy transformer.

6.2.3 Ionic Conductivities

The prepared electrolytes were pipetted into the small glass vials under an inert atmosphere then the platinum electrodes immersed then sealed. The exact aluminum holding apparatus with lid accommodated with fiber glass insulation was utilized except the dip cell versus the capillary cell as for the prior EIS measurements. A dip cell was adequate for the preciseness of ionic conductivity
measurements as these phosphorus-bromo samples were an order of magnitude lower in conductivity than the ionic liquid benchmark of [EMI]AlCl$_4$ from Wilkes and co-workers (Wilkes et al., 1982; Fannin et al., 1984). The dip cell used was an improved version of the earlier versions in which the previous plastic cap was replaced with a Teflon lid and seal held in place by a newly machined aluminum cap and Viton seal. The aluminum lid was needed to tolerate the higher temperatures up to 265°C during the slowly paced heating ramp of 1 K/min. The Viton seal was thicker, more thermally durable, and provided a much snugger fit beneath lid at the glass vial screw junction hence creating a fully closed system. This was vital upon testing as a function of high temperatures to attain exceptional conductivities all the while the stoichiometry of the chemical composition remaining the same due to the Viton sealing, which is evident by the measurements upon the cooling departure.

6.2.4 Viscosity

The prepared electrolytes were placed in an aluminum container specifically designed for spindle spun viscosity measurements by a Brookfield LV1 viscometer. The electrolytic samples were preheated by a special transformer with a sleeved slot for the provided cylindrical container. The temperatures were ramped and stabilized within a 90 min period prior to testing with a Barnett temperature controller. The sample area was covered with a glass dome with a tube inlet for N$_2$g and narrow inlet for the spindle neck for required rotations by the viscometer. The N$_2$g at low flow provided an inert atmospheric blanket beneath the glass dome above the exposed surface sample.
Density. The density was measured utilizing a special 1 ml volume flask, where some of the sample was placed inside then capped. The flask was heated to the necessary temperatures then sample pipetted off until the meniscus equaled 1 ml then immediately weighed to record the volumetric densities as a function of temperature as required for the Walden plot.

6.2.5 Structural Characterization from NMR Spectroscopy

To obtain structural information relevant to interpreting the interesting behavior of the liquid and crystal samples of this study, NMR chemical shifts for the nuclei $^{23}$Na, $^{27}$Al, and $^{31}$P, were obtained, using a Bruker 400 MHz spectrometer. Spectra were taken in the range 25°C to 100°C on samples that had been flame-sealed under an inert atmosphere in standard NMR tubes.

6.2.6 X-Ray Diffraction for Crystals

X-ray powder diffraction patterns were obtained using a Siemens D5000 diffractometer with Cu Kα radiation. The sample on a standard glass slide was covered with a transparent film to protect against atmospheric water. Background scattering from the glass slide and film were subtracted from the initial pattern.
6.3 Results:

6.3.1 Binary System: NaBr-AlBr₃

As in the NaCl-AlCl₃ system, there are two binary crystalline compounds, NaAlBr₄ and NaAl₂Br₇, the second of which is of special interest to this investigation. The X-ray diffraction patterns at 25°C for each, after background subtraction are shown below in Figure 6.1 and show close similarity to those of the corresponding chloride compounds. According to the DTA thermograms, the crystal of NaAlBr₄ melted sharply at 196°C to a liquid of high conductivity, 300 mScm⁻¹.

Figure 6.1 X-ray scattering patterns at 25°C for the two binary compounds in the system NaBr-AlBr₃ system.
The dc conductivity and the DTA thermogram data for NaAlBr$_4$ from room temperature to above the melting point are shown superimposed in the Figure 6.2. Noted that there was a high conductivity in the solid state preceding the actual fusion. Evidently the alkali cations move fairly free in the crystalline lattice as the melting point was approached, even though the ambient temperature crystal structure showed little sign of disorder.

Figure 6.2 Superposition in temperature of the DTA thermogram and dc conductivity data for the composition NaAlBr$_4$. The conductivity is quite high in the crystalline state, but jumps another two orders of magnitude on melting. The conductivity of two ceramic separator materials, β-β" alumina and NaSICON from Ceramatec Corp. are shown for comparison.
This behavior takes a more dramatic form the case of NaAl₂Br₇, for which the corresponding data are shown in Figure 6.3. It is clear that some dramatic structural change must take place at 63ºC, which was suggested in the NMR data shown further below here:

![Graph showing dc conductivity data and DTA thermogram for NaAl₂Br₇. The higher temperature transition at 94ºC is the melting transition, and the major transition at 62ºC occurs in the solid state. The conductivity of this crystalline solid increases by five orders of magnitude to a remarkable 10 mScm⁻¹ at 65ºC, higher than that of the well known Na⁺ β-β" alumina mixed phase and comparable to that of the most Na⁺ conductive solid phase known to date is the NaSICON of Ceramatec Corp. (Coors et al., 2010). The data for the latter are included as dashed lines in the figure onset of the anion rotation.](image-url)
The high conductivity will then reflect the facilitation of the Na\(^+\) translation by the anion rotation: a sort of "paddlewheel" motion like that suggested long ago for the case of the superionic crystal Li\(_2\)SO\(_4\) at T > 600\(^\circ\)C (Borgesson). The progression from the ordered crystalline state through to the rotator phase then finally to liquid is well illustrated by the NMR spectra that will be shown in the Discussion section.

6.3.2 Binary System: PBr\(_5\)-AlCl\(_3\)

Two compounds form in this system at the equimolar composition there is a well-defined compound with a high melting point, which is not of interest to this study of the ionic liquid state. More interesting, is a much lower melting material of stoichiometry PBr\(_5\) + 2 AlCl\(_3\). In view of the high conductivity measured for this latter composition referred to it as [PBr\(_4\)]\([\text{AlBr}_7]^{-}\), introducing the brackets to clarify the presentation as is common in the description of organic cation-based ionic liquids. The conductivity data for this composition are presented along with data for mixtures with NaAl\(_2\)Br\(_7\), shown in Figure 6.4. The ionicity of this liquid is one of the questions to be addressed in our discussion section.

6.3.3 Ternary System: NaBr-PBr\(_5\)-AlBr\(_3\)

A constant AlBr\(_3\) line of the ternary system NaBr-PBr\(_5\)-AlBr\(_3\), i.e. the mixed cation system NaAl\(_2\)Br\(_7\) + [PBr\(_4\)]\([\text{AlBr}_7]^{-}\). In this section we see the results for the intended inorganic cation equivalent of the mixed cation system studied in the recent journal article (Tucker & Angell, 2014) that stimulated the undertaking of the present project. This investigation refers to the study of the mixed
tetrachloroaluminate system of ethylmethylimidazolium tetrachloroaluminate plus sodium tetrachloroaluminate, written more simply as [EMI]+[AlCl4]+ NaAlCl4. It was obliged to choose the [Al2Br7] stoichiometry because of the high melting points of the tetrachloroaluminate compounds. Figure 6.4 presents the Arrhenius plots of five separate compositions across the binary cut, which will be used to produce the isotherms in the Discussion section.

Figure 6.4 Arrhenius plot of three mixtures in the pseudo-binary system NaAl2Br7 + [PBr4+]2[Al2Br7] together with data for the liquid states of the neat members. Filled symbols are for data acquired during heating while open symbols are for cooling runs to confirm stability over the temperature range.
Finally in this section, reported is the viscosity data that are needed to assess the behavior of the conductivities seen above in Figure 6.4. These are shown in Figure 6.5 in the same Arrhenius plot form used for the conductivities. It is striking that although the conductivity of the alkali salt was the highest measured as seen in Figure 6.4, but its viscosity rather than being the lowest is actually the highest implying that the strong decoupling seen in the crystal state is remembered in the liquid state.

![Arrhenius plots of the viscosities of the end members of the binary system NaAl\textsubscript{2}Br\textsubscript{7} + [PBr\textsubscript{4}]\textsubscript{4}[Al\textsubscript{2}Br\textsubscript{7}] and one mixture together with viscosity data for [EMI][AlCl\textsubscript{4}] and its mixture with NaAlCl\textsubscript{4} studied previously.](image)

Figure 6.5 Arrhenius plots of the viscosities of the end members of the binary system NaAl\textsubscript{2}Br\textsubscript{7} + [PBr\textsubscript{4}]\textsubscript{4}[Al\textsubscript{2}Br\textsubscript{7}] and one mixture together with viscosity data for [EMI][AlCl\textsubscript{4}] and its mixture with NaAlCl\textsubscript{4} studied previously.
6.4 Discussion:

6.4.1 Rotator Phase of NaAl₂Br₇

The conductivity of NaAl₂Br₇ between the first order transition temperature at 60°C and the melting point at 94°C is among the highest conductivities ever measured for sodium ions in a solid-state material. As Figure 6.3 makes clear, the sodium ion is almost as mobile in the plastic crystal state as it is in the liquid. The progression from low temperature ordered phase, to a plastic crystal, to a liquid, is well characterized by NMR spectroscopy, particularly for the ²⁷Al nucleus. Spectra are shown in Figure 6.6(a) for ²⁷Al and in Figure 6.6(b) for ²³Na.

![NMR spectra](image)

(a) NMR spectra for ²⁷Al in NaAl₂Br₇ part (a) for ²³Na in part (b) at temperatures between 25°C and the liquid state at 100°C. The loss of structure on passing through the first phase transition at 62°C (refer to Figure 6.3) is obvious as reflected in the generation of liquid-like motional narrowing in the spectrum of ²³Na.
What is not seen in the $^{27}$Al NMR spectra, is any indication of how much of this freedom of alkali cation motion remains above the melting point, when the crystal lattice provided by the anions had collapsed. The answer is hinted at by the viscosity data for this liquid seen in Figure 6.5, but is only clearly seen when the data are presented in the combined form of the Walden plot presented in the next section.

6.4.2 Mixed Cation System: $[\text{Na}^+][\text{Al}_2\text{Br}_7]+[\text{PBr}_4^+][\text{Al}_2\text{Br}_7]$  

The first observation to be made in discussing the results for the present mixed inorganic cation system is that the form of the binary conductivity isotherms is different from that of the previously studied system containing the organic cation $[\text{EMI}^+][\text{AlCl}_4] + \text{NaAlCl}_4$. At first sight this might indicate the banishing of the alkali cation trap that frustrated the realization of high conductivities in the mixed alkali + organic cation system. Unfortunately, it seems that the reason for the smoothly increasing conductivity with alkali content is a more complicated reason related to the intrinsically low conductivity of the inorganic liquid.

In Figure 6.7 we compare the results for the two systems where it is seen that at $25^\circ$C the non-alkali member towards the end is more than two orders of magnitude less conductive in the case of the inorganic cation. To show that this is due to low ionicity rather than the overcoming of the alkali cation trapping we turn to the Walden plot, Figure 6.8 below, which examines the conductivity per mole of ions assuming full conversion to ions as a function of the liquid fluidity, which is the reciprocal of the viscosity (poise, P).

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Figure 6.7 Comparison of 25°C, 65°C, and 100°C conductivity isotherms of the system [EMI⁺][AlCl₄⁻]+[Na⁺][AlCl₄⁻] with those of the all-inorganic system [PBr₄⁺][Al₂Br₇⁻]+[Na⁺][Al₂Br₇⁻]. As will be seen in the further Discussion section, the above formulation of the system cannot be well supported.
Figure 6.8 Walden plot depicting the equivalent conductivity as a function of inverse viscosity. The diagonal is the ideal behavior line, where the ionic mobility is strictly controlled by the fluidity of the medium in which the ions are moving. For the sodium heptabromodialuminate, the conductivity was found to be much higher than predicted from the viscosity, which implies almost free sodium-ion motion.

Except for the behavior of sodium heptabromodialuminate, the deviations from the ideal Walden line found for the solutions of this study are not much greater than those seen for a typical collection of ionic liquids in the literature for known
electrolytes. The former shows a greater freedom of motion for the alkali cations that have been seen for any other ionic liquid in our experience.

For the remaining mixtures the deviation from ideal behavior is less than an order of magnitude, which at first sight is not of great concern. It was surprising; therefore, this investigation veered to the NMR spectra for confirmation. It was found that the system being studied was far from being ideally dissociated; though not more so than some tetraalkyl ammonium ions of tetrafluoroborate anions (Angell et al., 2012). The $^{31}$P resonances observed in this system were extraordinarily diverse in frequency, see below Figure 6.9. They covered the range from $+230$ ppm down to $-80$ ppm. Since the areas of the resonance spectra are quantitatively related to the number of participating nuclei, they were very revealing in the information they give about speciation in the liquid. There were three resonances in evidence, one at $+227$ ppm, which was to be attributed to the $\text{PBr}_4^+$ cation (Aubauer, 2001) accounted for only 9% of the $^{31}$P nuclei in the system. The resonances were so separated in frequency that exchange of bromides between species was probably not obscuring the quantitative nature of the speciation. Based on the cationic data of Dillon et al: this was attributed on the weaker of the other two resonances to $\text{PBr}_4^+$ while the stronger peak, $21$ ppm downfield from $\text{PBr}_4^+$ in literature reports, is assigned to $\text{PBr}_3$ unchanged molecular species.

The spectra established directly what was seen only indirectly in the Walden plot: namely, that the intended bromide transfer was only weakly accomplished in this system, and that the system must be described as a "poor" ionic liquid. Usually "poor" implies the presence of a high concentration of ion pairs, but in the present
case it is more appropriate to consider it as indicating simply a small fraction of transferred bromide ions. Less than 10% of the PBr$_5$ molecules have lost a Br$^-$ anion to the Lewis acid AlBr$_3$ to form Al$_2$Br$_7$. The fraction of phosphorus atoms incorporated in cationic structures barely changes as the temperature increases.

Figure 6.9 NMR spectra of $^{31}$P in the liquid states of the inorganic liquid, showing that is evidently not well represented by the formula [PBr$_4$][Al$_2$Br$_7$]. The considerable conductivity of the liquid at ambient temperature seen in Figure 6.4, 87% of the $^{31}$P nuclei are in the structure with a resonance at -82 ppm, which is that of molecular PbBr$_5$. Only 9% were found in the structure with resonance at +229 ppm assigned to the PBr$_4^+$ cation. Note: The species with the sharp resonance at -62 ppm is unidentifiable at the moment.
Furthermore, the fraction of phosphorus atoms incorporated in the cationic structures diminished as the temperature increased. This has the fascinating consequence that there is no longer the same basis for an alkali cation trapping effect since the molecular species, PBr₅, were behaving more like inert solvent molecules, i.e. PBr₅ than less likely PBr₄⁺ cations. In this case most of the sodium ions are probably retaining the high mobility that is indicated by the Walden plot for the single component conductor NaAl₂Br₇. This positive Na⁺ ions contribution to the equivalent conductivity is being outweighed by the effect of depressing the smaller number of PBr₄⁺ ions (included in the calculation of equivalent conductivity) are not actually being there, hence not contributing to the ionic conductivity. Therefore the deviation from the Walden plot lies in the subionic domain. Halogen transfer salts of much higher conductivity than that observed in Figure 6.4, are known, e.g. the liquid [CH₃C=O⁺][AlCl₄⁻] exemplifying a high conductivity at 25°C (Xu et al., 1996) equal to that of [EMI⁺][AlCl₄⁻] well over 10 mS/cm², but this can no longer can be regarded as an inorganic ionic liquid.

Remarks. This project has revealed some interesting phenomenology concerning the possible degrees of freedom of motion for sodium ions in inorganic ionic liquids and their crystalline phases; though it has evidently missed its original objective of providing a simple inorganic cation alternative to the EMI⁺ cation of an earlier alkali cation trapping study performed by this lab group (Tucker & Angell, 2014). Although the crystalline materials are known where the molecular species, PBr₄⁺ can be identified; it now seems that inorganic cations based on covalent
bonded molecular cations, e.g. NH$_4^+$, would make a better choice for studies that seek inorganic/organic cation comparisons of systems encountering the alkali trapping effect as previously reported. The number of small single-charged cations available is not a large quantity.
7 HIGHLY ENERGY EFFICIENT NA-Fe (REDOX) BATTERY BASED ON AN IONIC LIQUID CATHODE

7.1 Introduction

Energy storage is widely recognized as one of the key problems in need of solution in our modern society. It is central to the functioning of our cell phones, laptops, automobiles and now increasingly to the support of our energy grid. With the increasingly serious environmental consequences of fossil fuels usage now forcing themselves upon society, e.g. the recent huge methane explosions in Siberia. The exploitation of environmentally responsible alternative sources for both energy generation and storage has become a critically important demand for everyday living additionally our research and technological capabilities. Green technologies such as wind and solar are currently decreasing in cost, but can be considered as intermittent solutions yet can only fully develop in tandem with energy storage systems that can serve the load-leveling function.

While lithium ion batteries have established a firm hold on the portable electronics market, and have been proposed for broader purposes, they are not necessarily the best choice for large-scale energy storage and load-leveling applications. A relevant observation is that of Winfried Wilke, IBM nanoscience and
technology director and former proponent of the lithium-air battery present owner of a *Tesla Model S* (van Noorden, 2014). Yet while content with the 400-km (248-mi) range that the Tesla lithium ion battery already provides and stressing that the real problem is cost as battery packs for electric cars cost more than $500 kW/h, where the same observation applies to the grid energy storage problem. Wilke stated,

> "What’s holding back the mass acceptance of electric cars

*is really the price rather than the energy density."*

Considering the abundance and low cost of sodium, along with its very suitable redox potential ($E = -2.71$V in standard aqueous reduction potential tables) sodium-based batteries are regarded as a possible preference for large-scale energy storage. A variety of sodium batteries were already under study almost 50 years ago. The most promising so far have been the molten salt batteries or so-called "liquid sodium" batteries that utilized liquid sodium as the anode. The most-known cases are the Na-S (Kummer et al., 1968; Tokoi et al., 1991) and Na-NiCl$_2$ (ZEBRA) (Coetzer, 1986; Sudworth, 1994) batteries. They have been intensively studied for the powering of electric vehicles and most recently for energy storage and load-leveling of environment-dependent power plants (solar, wind, etc.). However due to the high operating temperatures, >300°C, needed to maintain good kinetics in the solid electrolyte and solid cathode (NiCl$_2$) materials, they have been known to encounter problems of thermal management and some safety issues, and also impose stringent requirements on the rest of the battery components. Since the melting point of sodium is only 98 °C, sodium-based batteries may in principle operate in the
moderate temperature range of 100-180°C. But for this purpose, new solid
electrolyte separators and cathode materials would be required.

As an alternative to the Na-β″-Al₂O₃ that is widely used as a robust solid
electrolyte for Na-S and Na-NiCl₂ batteries, a special type of NaSICON sodium-ion
ceramic conductor (Coors et al., 2010) is being examined. NaSICON has the general
formula Na₁⁺ₓZr₂SiₓP₃₋ₓO₁₂, 0 < x < 3. The NaSICON from Ceramatec (Gordon et al.,
2010) exhibits a conductivity that is an order of magnitude higher than that of
mixed polycrystalline Na-β″-Al₂O₃ in the moderate temperature range with
conductivities on the order of 10⁻² S cm⁻¹ at 120°C while claimed to be stable in direct
contact with molten sodium at elevated temperatures (Eccleston, et al., 2012)
notwithstanding earlier reports to the contrary except when phosphorus-free
(Kreuer, 1986). While mechanical robustness remains a problem to deal with, the
higher conductivity and lower production cost of NaSICON provided an important
step towards low to moderate temperature sodium-based batteries.

For the cathode materials and electrolytes, ionic liquids (ILs), which are
completely ionic materials that remain liquid at or near room temperature (Wilkes,
2003; Seddon, 1997) provide a route to high conductivity catholytes that can serve at
intermediate temperature (MacFarlane, 2014). ILs also have many properties of
interest for, environmentally friendly batteries, non-volatility, and being relatively
safe such as non-flammability being prime amongst them.

Studies of ILs that contain enough sodium ions to create sodium-ion battery
electrolytes, are at an early stage of development and are known to be problematic
in some cases (Kim et al., 2003). In the past few decades, many researchers also
studied the electrochemical properties of different ionic liquid redox couples and mentioned their potential for use as cathodic materials. For example there have been discussions of such systems as Fe^{II/III} dissolved in either EMIAc (Ac = acetate), EMITFA (TFA = trifluoroacetate), or EMITf (Tf = trifilate) (Ueno, 2012), in a EMICl–FeCl₃ system (Katayama, 2002), EMICl–AlCl₃–FeCl₃ (Lipsztajn et al., 1985), EMICl–CuCl (Chen et al., 1999), or EMIDCA–CuCl (Leong et al., 2008), but so far there have been no reports of practical batteries using such ionic liquids as cathodes. One of the reasons is probably the low mobility of Na⁺ ions in the ambient temperature ionic liquid, which has been the subject of recent investigations (Angell & Tucker, 2014) in particularly by isothermic ionic conductivity, viscosity, and NMR diffusivity studies for the equivalent case of lithium electrolytes (Nakagawa et al., 2004; Ye et al., 2007).

However the low alkali ion mobility problem is largely overcome at moderate temperatures (> 100°C) so that redox couples and Na⁻ ions where the cathode homogeneously mixed with the electrolyte are called catholyte in this presented in this paper; which can work well at temperatures not much above the melting point of sodium. Here we report our findings that the EMIFeCl₄ ionic liquid can dissolve considerable NaAlCl₄ at room temperature then using the EMIFeCl₄·NaAlCl₄ catholyte, the intermediate temperature liquid sodium battery becomes a reality.

There are some fundamental aspects of redox electrolytes to be discussed here. In a recent study of the redox couple Fe^{II/III} in ionic liquids it was noted that the potential (referenced to Ag/Ag⁺ in a silver-silver chloride cell) could be widely varied, depending on the basicity of the medium in which the redox couple was
dissolved. From this study it was possible to see that a cell in which an appropriate redox couple could be maintained in the liquid state in the cathode half cell, would have a high voltage when coupled to a Na/Na\(^+\) anode. Given that the potential difference between the Na/Na\(^+\) and Ag/Ag\(^+\) potentials in standard aqueous solutions is 3.5 V; as depicted in their Figure 3 reported by Angell and co-workers (Ueno et al, 2012) suggests that a Na/Fe\(^{III}/^{II}\) cell in which the cathode medium was an acidic melt of high Lewis acid character (e.g. triflate ionic liquids), could have a cell potential of ~3.8 V, comparable to that of the popular Li-LiFePO\(_4\) cell.

The solubility of iron triflates in such ionic liquid media is, however, very low and this would discourage the exploration of an acidic ionic liquid media for redox cathodes. On the other hand, tetrachloroferrates of ionic liquid cations are not only rich in ferric ions but are also low-melting and of exceptional conductivity (Xu et al., 2003). While some lowering of the above cell potential must be expected when the near neighbors of the redox-active species are bound chloride ions such as in FeCl\(_4^-\), rather than bound oxides as in triflates. The Lewis acidity of FeCl\(_3\) can be expected to provide a good compromise. Thus we have been encouraged to test the electrochemical possibilities of sodium-ion battery cells of the class represented by the overall cell reaction:

\[
Na + Fe^{III} \xrightarrow{\text{discharge}} Na^+ + Fe^{II} \xleftarrow{\text{charge}}
\]

Equation 7.1

In the ionic liquid medium of EMIALCl\(_4\) + NaFeCl\(_4\) at temperatures where the sodium is in the homogenous liquid state. Similar to EMIALCl\(_4\) + NaAlCl\(_4\) recently studied system for low ion mobility behavior at relatively low temperatures (Tucker
et al. 2014). This combination has wide composition ranges that were liquid at room temperature, which provided for easy manipulation of the cell during assembly.

There are many possible versions of this type of cell, depending on the initial electrolytic constituents as both are illustrated in the Eqn 7.2 and Eqn 7.3. The essential difference between the two is the production of solid NaCl in Eqn 7.2 compared with its maintainability in solution in Eqn 7.3.

In view of our greater experience with the simple 1:1 class of halometallates (Xu et al., 2003) it was the case of Eqn 7.2 that we had explored first, and report on herein the electrolytic reaction:

$$\text{Na} + \text{EMIFeCl}_4 \xrightarrow{\text{charge}} \text{[EMI}^+\text{][FeCl}_3^-\text{]} + \text{NaCl}$$ 

Equation 7.2

In applying Eqn 7.2 chemistry, we added in slight excess EMIFeCl$_4$ to compensate for the higher melting trichloroferrate species that is generated during discharge, in order to maintain the electrolyte in the liquid state except for the precipitated NaCl. Note that FeCl$_3^-$ is not a trigonal anion, but a catenated tetrahedron chain species. At the moment a phase diagram for this ternary system has yet to be generated. The second case to consider is the acidic version of the electrolytic reaction:

$$\text{Na} + \text{EMIFe}_2\text{Cl}_7 \xrightarrow{\text{charge}} \text{[EMI}^+\text{][FeCl}_3^-\text{]} + \text{NaFeCl}_4$$ 

Equation 7.3

Unless there are additional technical problems to solve, it will probably be necessary to replace the EMI cation with a cationic species, organic or inorganic, that is more stable against Lewis acid attack; in view of the much higher Lewis acid
activity once the tetrahalomettallate stoichiometry is surpassed. The Eqn 7.3 case should not only have a higher cell potential due to the increased acidity of the Fe₂Cl₇ anion, but should also have a considerably enhanced capacity based on Fe as the limiting species. There will also be less requirement for inactive EMIALCl₄ to maintain the liquid state of the electrolyte, which will be the next focus of investigation.

The cell capacities (expressed in mAhg⁻¹) will depend on the composition of the catholyte that is needed (i) to maintain the liquidus temperatures below operating temperatures, and (ii) to optimize conductivities. For the choice made in the cell reported herein, the electrolyte had the simple molar composition EMICl, FeCl₃, NaCl, and AlCl₃ in mole ratio 1:1:1:1, which is the same as [EMI][AlCl₄]₀.₅[EMI][FeCl₄]₀.₅. In light of experience this is surely not the optimum composition for our electrolyte for full Fe(III) to Fe(II) reduction. Ternary compositions, to be described by [EMI][FeCl₄]ₓ[EMI][AlCl₄]ₙ[NaFeCl₄]ₖ, (x+y+z = 1.0) that should have the ability to better maintain high conductivity during discharge that are the subject of an ongoing investigation. A full phase diagram for this ternary system has yet to be generated.

For the cell reaction Eqn 7.2, the theoretical capacity based on complete oxidation conversion of Fe(II) to Fe(III), is 87 mAhg⁻¹ using the molecular weight of EMIFeCl₄. Surprisingly, it was been able to obtain 74% of this theoretical capacity in the first attempt, described in the following.
7.2 Experimental Protocol:

7.2.1 Battery Materials and Electrolyte Preparation

Anhydrous 1-ethyl-3-methylimidazolium chloride (EMICl), FeCl₃, AlCl₃, NaCl, and FeCl₂ were all purchased from Sigma–Aldrich. NASICON was supplied by the Ceramatec corporation and general beta” alumina discs by Ionotec, Ltd. All materials were stored and used in an argon gas atmosphere glovebox. The preparation of the ionic liquid catholyte is very simple; just by mixing the anhydrous EMICl, FeCl₃, NaCl, and AlCl₃ by a molar ratio of 1:1:1:1, where the optimum molar ratio of EMIFeCl₄ and NaAlCl₄ is the subject of ongoing investigation. EMICl and FeCl₃ spontaneously fused to an ambient temperature ionic liquid. The AlCl₃ and NaCl were then added, but slower to dissolve yielding a homogeneous solution after briefly heating for about 30 min at ~200°C.

If the temperature is raised above 160°C on unprotected samples, the color of the melt darkens orangish-brown, probably due to the effect of temperature on the Fe-Cl charge transfer band. However, the cell performance seems unaffected up to 200°C. Control of AlCl₃ activity by the buffering strategies (Koronaios, 1999) might be useful to extend the temperature range of the battery.

7.2.2 Cell Setup and Electrochemical Characterization

(i) Conductivity determinations. Conductivities of transition metal-containing ionic liquid electrolytes of interest were surveyed using twin platinum wire dip-type electrodes sealed into a stainless steel threaded caps that were screwed onto glass vials containing the samples loaded under argon gas in a drybox.
The Viton gasket sealed cells were weighed before and after measurements to check on sample integrity during study. Data were taken using a PAR VMP2 potentiostat in the frequency range 0.1-100K Hz, during slow heating from ambient to 155°C and also during cooling to confirm that ramp rates were slow enough to yield equilibrium data and ensure that no sample decomposition or crystallization occurred in the temperature range of study. Frequency independent conductivity values were obtained from Nyquist plots following the precautions were previously discussed.

(ii) Cyclic voltammetry. The electrochemical properties of the catholyte were investigated by cyclic voltammetry (CV) using a potentiostat/galvanostat (Princeton Applied Research, VMP2). A three-electrode cell was employed with platinum as the working, and counter electrodes, as well as the reference electrode. All the scans were made at 180 °C with a scan rate of 10 mVs⁻¹.

(iii) Demountable battery design and assembly. The test cell used in the in depth evaluation of our catholyte is a planar design utilizing flat Viton gaskets to seal the anode compartment during an initial sodium wetting procedure at temperatures up to 300°C, and subsequently, following a partial disassembly, to attach and seal in, the cathode compartment. The assembled cell is shown in Figure 7.1(a) and the cell schematic shown in Figure 1(b). For machining convenience, the cathode compartment was made from stainless steel, but this needs protection from reaction with the Fe(III) of the catholyte. For the present testing this was achieved with platinum foil. A future generation version would use a quite different design with ceramic casing, stress-free separator, and upper copper cap with seal.
While it is common battery practice to generate liquid sodium in the anode chamber in situ during charging, although alternatively chosen to introduce sodium metal into the anode chamber in an initial stage to take advantage of a ceramic-wetting procedure described below, it was found providing better anode performance for our early stage of battery development. Copper wool was used the as the current collector. The open structure allowed for the volume of sodium to expand and contract during operation. Liquid $\text{EMIFeCl}_4 \cdot \text{NaAlCl}_4$ (50 mol% $\text{NaAlCl}_4$), together with additional $\text{EMIAICl}_4$ maintained the liquid state during generation of the higher melting $\text{EMIFeCl}_3$, which was absorbed in the carbon felt that served as the current collector and it also provided a wicking effect that ensured effective catholyte contact with the NaSICON separator.

**(iv) NaSICON separator preparation and wettability testing.** A sessile drop technique (Reed et al., 2013) was used to test the wettability of NASICON of sodium, with and without ITO-coating (ITO = indium tin oxide). Complete wetting of a liquid on a solid surface means that the contact angle is zero or close to zero such that the liquid spreads over the surface easily hence optimizing interfacial surface area. Contact angles greater than $90^\circ$ allowed the liquid to bead where it could
easily roll off the solid surface. Solid sodium pieces were placed on the NaSICON discs heated on a hot plate in an argon gas glovebox under exemplary dry conditions at H₂O and O₂ contents both below <0.1 ppm. Where the hotplate temperature was raised and lowered in the sequence indicated below here seen in Figure 7.2.

![Figure 7.2 Tests of liquid sodium wetting of NaSICON in untreated state (LHS) and in ITO-coated state (RHS) for comparison. The test was carried out with the two discs side by side so that the time-temperature conditions were identical. It can be seen that the spreading of the sodium in the ITO coated case was permanent.](image)

More complete wetting can be obtained using a precursor thin film of tin (Reed, et al., 2013), but in our case an incomplete coverage was the preferred option. There are evidently a variety of strategies that can be used to optimize the coverage of the separator considered optimal for a particular cell design.
7.3 Results

The conductivities of the several candidate ionic liquids and mixtures are plotted as Arrhenius functions of temperature in Figure 7.3. The data for EMIAICl$_4$ and its 1:1 mixture with NaAlCl$_4$ are taken from well-known work (Wilkes, 1994). It is notable that essentially identical results are obtained when Al is replaced by Fe in the same oxidation state which means as expected the alkali-cation trapping problem (Tucker et al., 2014) is common to both solutions. Likewise, most of the conductivity deficit due to the alkali ion trapping, is eliminated by raising the temperature to above 140ºC, as in our battery operations. Comparisons with the two common Na$^+$ conducting ceramics separators, β'-β" alumina and NaSICON, are included in Figure 7.3.
Figure 7.3 Specific conductivities of several ionic liquids and their mixtures with Na analogs where filled and open markers are measurements conducted upon heating and cooling, respectively. For neat EMIFeCl$_4$, data from three consecutive runs coincided within measurement of uncertainty. The conductivities for this IL superimpose on those for EMIAICl$_4$ from Angell and co-worker (Tucker et al., 2014). The mixtures with alkali salts show the same lower conductivities and larger temperature dependences discussed recently in terms of alkali cation trapping phenomena. Comparison is made with the conductivity of the two common sodium ion conducting ceramics, Na mixed and sintered β-β$''$ alumina, and NaSICON. Note: filled and open markers are data points collected upon heating and cooling of the electrolytes, respectively.

The electrochemical behavior of the chosen catholyte liquid EMIFeCl$_4$:NaAlCl$_4$, is displayed in the cyclic voltammogram displayed in Figure 7.4.
In part (a) the scan covers the potential range that includes the reduction to metallic iron at the negative extreme and the oxidation of chloride ion to chlorine gas at the positive extreme. The oxidation of metallic iron deposited at -1.2V is only weakly manifested at -1.1V probably due to passivation and this may be the source of the third oxidation peak at +0.5V for which no other explanation is obvious. When the potential range is limited to avoid the latter process, the redox process for the Fe(II)/(III) couple is simple and reversible as seen in Figure 7.4(b).

![Figure 7.4](image)

**Figure 7.4** Cyclic voltammograms of EMIFeCl₄·NaAlCl₄ catholyte, for varying voltage ranges, (a) -1.3~1.3 V; (b) -0.4~0.05 V. (Pt as reference electrode, scan rate 10 mV/s, T= 180 °C). Processes associated with different peaks, or displacements, are indicated on the plots. The second oxidation peak is not identified though presumably relates to the irreversible (due to passivation) deposition of metallic iron seen at the leftmost part of the CV. This process was avoided in the more restrictive CV seen in part (b) where only the range of the Fe(II) to Fe(III) oxidation process and its converse, were selected for study.

This reversible process can also be seen in the assembled battery context, now by reference to the anode process Na/Na⁺. Voltammograms in the range 3.0-
3.5V from scans at different scan rates from the cell, ranging from 0.01-0.20 mVs$^{-1}$, are shown in Figure 7.5.

![Cyclic voltammograms at 180°C with Na$^+$/Na reference electrode for the assembled cell, taken at different scan rates in the range 0.01 to 0.20 mVs$^{-1}$ while in the voltage range 3.0-3.5 V. Where the cathode redox process is occurring in order to establish the most appropriate range for testing the charge-discharge function of the cell. It can be seen that at slow rates there are two steps in the redox process while, at higher rates, the major process begins at the same potential during oxidation as it does on reduction thus implying a high order of reversibility in this process. The cell voltage, 3.25 ±0.05V, taken from these onset points, is considerably higher than those of either of the common liquid sodium-ion batteries, Na-S (2.0 V) or Na-NiCl$_2$ (2.58 V), as anticipated from the considerations outlined prior here.](image)
Most important of course, and also most promising, is the cell performance in its charge and discharge functions. As is commonly recommended, the cell was conditioned by an initial charge/discharge cycle conducted at very slow rates, 0.02C over 10 hours. Following such conditioning, the cell was cycled using a slower charging rate than discharge rate because of the need to redissolve the precipitated NaCl. Where such asymmetric kinetics are also seen in the cases of Na-S (Ellis, 2012) and Na-NiCl₂ cells (Li et al., 2013). The voltage versus capacity behavior during the first 50 cycles is depicted in Figure 7.6. While the cell cycles well near its reversible potential there is clearly a source of capacity loss of 23% after 20 cycles and decreasing with increasing cycling, in which the source of which will need further discussion.

More importantly, believed is the 96.2% energy efficiency, calculated from the ratio of the product [cell capacity (to cell cutoff point) x midpoint voltage] in successive charge-discharge cycles:

\[
\text{Energy efficiency} \% = \frac{V_{\text{mid discharge}} \times Q_{\text{discharge}}}{V_{\text{mid discharge}} \times Q_{\text{discharge}}} \times \frac{V_{\text{mid charge}} \times Q_{\text{charge}}}{V_{\text{mid charge}} \times Q_{\text{charge}}} \times \text{Coulombic efficiency}
\]

Equation 7.4

This quantity is related to, but must be smaller than the Coulombic efficiency, which is also shown in Figure 7.6(b). For energy storage purposes, high-energy efficiency, which requires a highly reversible electrochemical system, is vital for performance longevity. The Coulombic efficiency at 98.2% is also high, though it certainly needs to be higher and neither demonstrates any adverse trend with cycle
number. It might be expected to improve both in future cells with improvements in cell design and electrolyte optimization.

By the 50th cycle the cell had lost 50% of its capacity and the run was terminated and the battery cell was opened for inspection. A stress crack was found in the ceramic separator. However, apart from the capacity loss, the performance metrics were very encouraging, and the cell clearly warrants much further investigation.

Figure 7.6 (a) Charge/discharge curves for different cycles of the Na-Fe battery at 180°C, the discharge rate is 0.1C and charge rate is 0.05C. Before the cycling, a conditioning process has been done by charging/discharging at a low rate of 0.02C for 8 hours. (b) Coulombic and energy efficiencies as a function of cycle number.

7.4 Discussion

Energy efficiencies of 96% are rather unusual especially for new battery systems in their initial exploration stages such as in this case. They tell immediately that there is little dissipation of energy in overcoming potential barriers at the electrolyte-electrode interfacial surfaces and no adverse side
reactions; even at the moderately high temperatures of the present study. They also shed insight that the IR losses (current-resistance of Ohm’s law, $V = IR$) involved in the passage of Na$^+$ ions across the ceramic separator and within the electrolyte are not a serious source of energy inefficiency.

The major concerns at the moment are the source of capacity loss seen in Figure 7.6(a), and the origin of the separator crack. They may be related as each of them being a consequence of the fragility of the ceramic separator. This method of sealing the cell involves application of some extremely mild compressive stress, and if there is any bending component to the compression, the low elasticity of the membrane can lead to cracking and cell leaking, resulting in permanent loss of iron to the metallic state. There is a very positive, crucial aspect to this finding; however, which is the crack found on disassembly was significant. There were no signs of an induced thermal runaway reaction nor fire hazard. This apparent "safe failure" feature has since been tested by pouring the active catholyte liquid directly onto shiny molten sodium in a container in a dry box, and the total absence of any hazardous response has been the spectacular, an extremely favorable observation. Therefore, the sodium is slowly darkened as it reduces the iron in the catholyte. Evidently the fire hazard from internal shorts in this battery system is minimal (Dustmann, 2004).

The possibility of utilizing the more robust $\beta'\beta''$ alumina separator was eliminated in preliminary investigations which showed smaller cell capacity and more serious polarization. This suggests another possible source of capacity loss during repeated charge-discharge cycles. Although higher melting phases formed during discharge (the trichloroferrite and NaCl phases) should be restored to
original conditions during recharge, a slow segregation of insoluble material during the cycling could lead to capacity loss. This could be obviated by a more informed choice of ternary electrolyte composition that would avoid any trichloroferrite crystallization.

Investigations of the sources of capacity loss will be carried out in more detail after the more pertinent question of improved voltage and capacity performance using the Eqn 7.3 chemistry has been investigated. For these future studies, a new cell design aimed at removing stress from the separator will be employed; in the hope of obtaining more extended data than has proven possible in the present study.

Finally discussed here briefly are some of the potential advantages of, variations on and applications of, the present energy storage system. Noted again that the catholyte when correctly formulated is freely flowing liquid an ambient temperature. It is not difficult then to imagine its potential to serve in a flow battery system; and even in a "gas fuel station" facility in which the spent catholyte is drained out then replaced with a fully oxidized catholyte of low sodium content, since Na\(^+\) ions are generated on discharge still within the cell. This would require the battery system to carry excess sodium metal and the number of such "rapid recharges" would be limited by this sodium supply. Replenishment of the sodium supply could only be accomplished by a typical electrochemical recharging process.

Remarks. A major advantage of the present system, apart from its high output voltage, low operating temperature and affordable materials costs, is its evident immunity to internal shorts as displayed here, hence abated fire hazard. Should the alternative catholyte of Equation 7.3 prove to work as well as the present
Equation 7.2 version then the increase of cell capacity would essentially be another major advantage.

While the Fe$^{II/III}$ redox couple is the obvious first choice for this type of liquid sodium cell, it is not the only one. The Mn$^{II/III}$ does not have the advantage of the high Lewis acidity of the FeCl$_3$ of the present cell and would presumably require a higher operating temperature, but would relish the advantage of an extra +0.3V of output voltage. An alternative system based on Cu$^{I/II}$ as an active cathode material has been tested in this laboratory and in the facilities of the co-PI, Martin, and co-workers shows promise (Liu et al., 2014). The chemistry in this case is closer to that of the ZEBRA cell technology, but will run at much lower temperature with a higher output voltage and a less expensive transition metal. Given the stability of NaSICON to aqueous solutions, the copper chemistry can be applied using known high-boiling, concentrated saline solutions in the cathode compartment.

Overall, it is believed that here has been demonstrated the feasibility of an interesting new class of medium temperature liquid sodium cells that warrant further attention from the energy storage technology community.
8 A NOVEL, EASILY SYNTHESIZED, ANHYDROUS DERIVATIVE OF PHOSPHORIC ACID FOR USE IN ELECTROLYTE WITH PHOSPHORIC ACID-BASED FUEL CELLS

8.1 Introduction

The phosphoric acid fuel cell is known as one of most researched, and commercially most advanced types of fuel cell (Srinivasan et al., 1999; Kreuer, 2001). Initially developed as a liquid electrolyte device, prone to leaking and ionic shorts, it is now being refined, by incorporation of $\text{H}_3\text{PO}_4$ in polymeric materials (Yang, 2001) such as polybenzimidazole (PBI), into a very promising and cost-competitive alternative (Li et al., 2010) to the Nafion fuel cell (Kwak, 2003; Asano 2006). An advantage it holds over its Nafion rival is the higher temperature range of operation permitted by the electrolyte. It can be used up to 160°C before water loss, to form pyro-phosphoric acid ($\text{H}_4\text{P}_2\text{O}_7$), leads to reduced conductivity and poorer performance. The range may be extended by elaborate humidification and pressurization provisions, which of course also increase the expense and failure-probability of the system. The water management problem remains a barrier to the full commercialization of this type of fuel cell. Any modification of the electrolyte that could extend its operating temperature range and reduce its dependence on the presence of some water, without reducing its other favorable characteristics would be of great interest.
Here is described an inexpensive, easily synthesized, modification of H$_3$PO$_4$ (presumed to be a binary solution with a new more complex acid) that extends the temperature range of the phosphoric acid fuel cell to 250°C, while improving its operating fuel efficiency considerably. To prior knowledge, the current efficiency ($\equiv \frac{i}{i_{\text{theoretical}}} = \frac{i}{i_{\text{current}}}$) obtained with the electrolyte described here, is higher than that of any other type of fuel cell operating at 1 atm pressure. Its voltage efficiency is also comparable to somewhat better than that of the reported phosphoric acid based fuel cells. Only describing the first stage of this development, viz., the liquid electrolyte and its fuel cell performance, leaving the important second stage of development of a membrane based on proper incorporation of the liquid into a robust polymer host to future reports.

8.2 Cell Chemistry

The additive is a derivative of phosphoric acid in which phosphoric acid is combined with silicon to form a silicophosphoric acid which probably has multiple molecular forms, yet to be fully resolved. Initially it was thought to be a substantial component of the electrolyte, but later work suggests that is a minor but temperature dependent component that stabilizes the phosphoric acid against loss of more than a small amount of water. Its possible molecular form will be discussed briefly below. It is the subject of continuing investigation.

The electrolyte is prepared by reacting SiCl$_4$ with anhydrous phosphoric acid obtained by fusion of the dry crystalline form ($T_m = 42^\circ$C). The reaction is carried out under mild conditions, under gentle flow of nitrogen gas, initially 45°C ($T_b$ of SiCl$_4$ is
57°C) and continuing with gradually rising temperature (reaching 100°C) for three hours until the liquid is saturated with reaction products (becoming creamy in color due to a fine precipitate of solid material), followed by gradually increase of temperature to 270°C over one hour that establishes an equilibrium content of H$_3$P$_2$O$_7$. The H$_3$PO$_4$-insoluble components can be increased in quantity by extending the reaction time. The fuel cell performance has been evaluated in the presence of the stable suspension of solid silicophosphate, which is believed to be essential for maintaining electrolyte properties. The solid is of highly disordered character according to X-ray diffraction patterns to be discussed elsewhere (Ansari et al., 2012).

Both the liquid, and the stable-suspended solid are strongly acidic in character. The solid material contains Si in six-coordination. It has interesting properties including the ability, on solution in water and extended evaporation, to produce clear deformable polymeric solid possessing stability up to 140°C at 1 atm and conductivity in excess of that of pressurized Nafion. This rubbery solid or gel-like material will be described in more detail elsewhere. The conductivity is included in Figure 8.1.
Figure 8.1 Ionic conductivities of the new SiPOH-stabilized electrolytes compared with various fuel cell electrolytes, including Nafion. Data from the present work are in solid symbols for heating runs and small open symbols for cooling runs, to show reproducibility. The conductivity of the protic ionic liquid DEMA triflate, used in a recent fuel cell membrane (Lee et al. 2010; Lee et al., 2010), shown as a dashed line.

8.3 Results:

8.3.1 Conductivity

The presence of SiPOH and an equilibrium content of $H_3P_2O_7$ in the phosphoric acid, leads to an increase in electrolyte viscosity. However, as shown in Figure 8.1, the electrolytic conductivity, determined using a twin electrode dip-type cell of cell constant 1.83 cm$^{-1}$, is superior above 150ºC, presumably due to a superior "free" proton contribution. The conductivity is reversible up to 285ºC. Tested at a
constant 250°C, the conductivity remained invariant within the temperature control fluctuations, over a 24-hr period. Over a 48-hr period at 230°C, so loss of water has been greatly diminished, and in an operating fuel cell (producing water) would not be of consequence.

In Figure 8.1, comparison is made with anhydrous H₃PO₄, Nafion, and with the rubbery polymer obtained by hydrating the solid products of the reaction (to be described separately). The diethylmethylammonium triflate [DEMA⁺][OTf⁻] (Nakamoto et al., 2007) data used in a recent protic ionic liquid fuel cell (Lee et al. 2010; Lee et al., 2010) are shown as a dashed line. Even at 25°C, the conductivity is still as good as that of the best ambient temperature protic ionic liquid fuel cell electrolyte.

8.3.2 Fuel Cell Performance

The performance of our modified H₃PO₄ liquid electrolyte, studied in the same Teflon sandwich cell with E-Tek gas diffusion electrodes, described in previous publications (Belieres et al., 2006), as shown in Figure 8.2. Note that testing was able to operate smoothly at temperatures as high as 226°C, and could go higher if not for the materials limits on tubular design and machined components of the cell. Upon using non-humidified gases, enabled drawing of currents of 1 Amp/cm², with open circuit voltages (OCV) of nearly 1.0 V. This OCV is only 0.12 V below the thermodynamic value for that temperature, and is somewhat higher than that obtained with the standard 85 wt% phosphoric acid electrolyte; shown here below:
Figure 8.2 Tafel plots (IR corrected) for fuel cell performance, using the new SiPOH-stabilized phosphoric acid, compared with performance using the commercial standard, 85% $\text{H}_3\text{PO}_4$. The experiments used identical Teflon fuel cell blocks with identical E-Tek electrodes, and the same flow rates of $\text{H}_2$ and $\text{O}_2$ for each electrolyte at each temperature (see Table 8.1 for details). Flow rate for $\text{O}_2 = 2\text{-}3x$ flow rate for $\text{H}_2$. Note: the high OCV, and $\sim$1 amp/cm$^2$ current, obtained at 226ºC and the voltage efficiency is also presented in Table 8.1, using two alternative definitions.
Figure 8.3 Polarization curves (linear current and not IR corrected), and the corresponding power densities, for SiPOH-stabilized anhydrous H$_3$PO$_4$, and H$_3$PO$_4$ (85 wt%), electrolytes at different temperatures up to 226ºC.

The power outputs for the SiPOH-stabilized electrolyte at the two temperatures of Figure 8.2 are shown in Figure 8.3. The currents, both at (i) maximum power and (ii) where cell voltage vanishes in the uncorrected polarization curve, are shown, along with open circuit voltage, voltage at maximum power, and other performance characteristics in Table 8.1.

An important aspect of the fuel cell performance with the present electrolyte is the fuel usage efficiency. This is a feature that is discussed in the literature less than one might expect. It is monitored by the hydrogen flow rate at maximum
current. Most workers adjust the fuel flow rates to maximize the current, and then often report this flow rate, typically 10-50 ml/min (Srinivasan et al., 1999) without discussing the relation of fuel supplied to the current obtained. This was understandable as it is usually not an encouraging number. However in the present case, the cell was consuming nearly all the fuel supplied. Provided in Table 8.1 is the current efficiency [defined as (1/2 the moles H$_2$ supplied per sec)/(Faradays of electricity flowing per sec)], both at the peak power condition. A second value based on the current flowing when the cell voltage (without IR correction) vanished, was sometimes made, and in the case of these cells may approach 100%, but the first metric is the more relevant.

Included in Table 8.1 the current efficiencies reported by various workers for different types of fuel cells, and also calculate it in cases where both hydrogen flow rate, and current at maximum power, were reported but no current efficiency calculation was made. The current efficiency, when the standard 85% H$_3$PO$_4$ electrolyte was used in our cell, was high, consistent with experience of the favored electrolyte. Indeed, at 121°C, it was as high as with the SiPOH-stabilized electrolyte. However a major difference arose when the higher temperature range was explored, the SiPOH-stabilized electrolyte reaching 1 amp/cm$^2$ without any sacrifice in cell voltage. The power output at this temperature, shown in Figure 8.3, reached a very favorable 184 mW/cm$^2$, and this number could clearly be improved upon with more attention to cell design as to more closely approach the ideal rectangular polarization curve (Atkins & De Paula, 2006).

The voltage efficiency is also presented in Table 8.1, using two alternative definitions. The first is simply the [OCV/theoretical emf] x100 at the temperature of
measurement, while the second (and more relevant one) is that based on the voltage at the power maximum - obviously a much smaller number. Again, the SiPOH-stabilized electrolyte is yielding favorable numbers relative to other cells for which the data are available. Again, the advantage of high temperature operation is to be stressed.

Table 8.1 Fuel cell performance conditions and metrics:

<table>
<thead>
<tr>
<th></th>
<th>Operating</th>
<th>H₂ flow rate</th>
<th>Max. Current dens</th>
<th>Current dens</th>
<th>Current Effic.</th>
<th>Voltage</th>
<th>Voltage Effic.</th>
<th>Reference</th>
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<tbody>
<tr>
<td></td>
<td>Temp (°C)</td>
<td>(m/min)</td>
<td>(mA/cm²)</td>
<td>(mA/cm²)</td>
<td>% at P&lt;sub&gt;max&lt;/sub&gt;</td>
<td>Effic. % (OCP)</td>
<td>% at P&lt;sub&gt;max&lt;/sub&gt;</td>
<td></td>
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<tr>
<td>Nafton 115</td>
<td>70:30</td>
<td>22.0</td>
<td>100.0</td>
<td>700.0</td>
<td>-</td>
<td>5.3</td>
<td>-</td>
<td>57.2</td>
</tr>
<tr>
<td>Nation/morganic composite (R7:30 weight ratio)</td>
<td></td>
<td>120.0</td>
<td>&gt;270</td>
<td>580.0</td>
<td>432.6</td>
<td>1.7</td>
<td>1.2</td>
<td>81.8</td>
</tr>
<tr>
<td>Pristine Nation membrane</td>
<td></td>
<td>80.0</td>
<td>300.0</td>
<td>1000.0</td>
<td>1200.5</td>
<td>4.6</td>
<td>3.1</td>
<td>79.4</td>
</tr>
<tr>
<td>Molten carbonate fuel cell (fluidized bed electrode)</td>
<td></td>
<td>650.0</td>
<td>10 (O₂)</td>
<td>115.6</td>
<td>-</td>
<td>8.8</td>
<td>-</td>
<td>29.1</td>
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It should be recognized that favorable voltage efficiencies, which would further improve with cell designs that produce a slower crossover to mass transport control, might be enhanced by the fact that the electrolyte thickness (3mm to permit exchange of liquid electrolyte without change of any other parameters) is greater than that of the common membrane (>1mm). This would inhibit fuel crossover effects that diminish cell voltage. This might invalidate comparisons with some
membranes. The cell was designed so that, by simple exchange of liquid electrolyte, multiple comparisons of the current flowing and the voltage, where both open circuit and that at the power maximum could be made for different protic ionic liquids, though this feature could not be utilized in the present study because of the importance of the solid SiPOH suspension to the function of the system.

The challenge now is to incorporate this electrolyte in a polymer membrane without low temperature aqueous processing which evidently produces chemical modifications (witness the hydrated polymer with extraordinary conductivity shown in Figure 8.1; the fuel cell performance of which will be described in separate publications). Because it is of more acid character than hydrated H₃PO₄, the SiPOH-stabilized electrolyte should be more firmly retained in a polybenzimidazole membrane than H₃PO₄ (due to the larger proton transfer energy to the basic nitrogen) (Belieres et al., 2007; Angell et al., 2012), so this type of membrane is an obvious first choice. Like the structural characterization of the SiPOH molecule(s), we defer such membrane evaluations to subsequent papers.

8.4 Discussion

Phosphorus-silicon-oxygen combinations incorporating H₃PO₄, have been used previously to produce proton-conducting electrolytes for fuel cell applications (Matsuda et al., 2002); have described phosphosilicate gel powders and H₃PO₄-impregnated porous silica gel powders that have moderately high conductivity and stability at elevated temperatures, but they are made by sol-gel processes and must have chemical constitutions that are quite different from that of the present fully
anhydrous system. A more closely related, but partly organic formulation (Niida et al., 2002; Jänighen et al., 2012), in which dimethyl dichlorosilane was reacted with phosphoric acid, which was prepared as a precursor material for low-melting glass formulations.

These active compounds are evidently of less complex character, resulting in an H$_3$PO$_4$-soluble material, probably of temperature-variable form, that strongly influences the properties of the H$_3$PO$_4$-based electrolyte. One possible form, which high level electronic structure calculations (ORCA program package - DFT using B3LYP/G (Becke, three-parameter, Lee-Yang-Parr) functional) show to be stable and of stronger acid character than H$_3$PO$_4$ itself, is Si(PO$_4$H)$_2$, with Si coordinated as in Figure 8.1. Calculations were done in parallel mode using a cluster of 8 nodes; and are comparable to though somewhat more quantitative than those of Schaeffer and co-workers (Morris et al., 1997) on H$_3$PO$_4$.

Si(PO$_4$H)$_2$ is a relatively small molecule, consistent with the high conductivity of the liquid at 280ºC. Such species are not known in the solid state, however, and are likely to be present only as a consequence of temperature-induced coordination number changes from the six-coordinated state known for most solid forms of silicophosphates (Lejeune et al., 2007), and also identified in NMR studies of the solid that forms as a component of the equilibrium described below. The known solid silicophosphate forms are of complex structure (Jänighen et al., 2012) and it would be surprising if they were to be more than marginally soluble in phosphoric acid.
Figure 8.4 One of the possible structures of siphoric acid monomer shown in Sticks (left) and Balls and Cylinders (right) formats. Silicon (green), Hydrogen (white), Oxygen (red), and Phosphorous (yellow).

The double edge-sharing, fourfold coordination, would constitute an unusual silicon coordination, made possible by the intense oxygen polarization by P(V). Other possibilities involving corner-linked phosphates and edge-shared phosphate octahedra, are noted below and will be considered elsewhere. The white solids, that form a suspension when the reaction that produces the SiPOH electrolyte is continued, have silicon in six-fold coordination presumably with phosphate oxygen. The ambient temperature liquid state does not contain detectable $^{29}$Si, so the constitution of the high temperature solution, which need not be known for the present report, is uncertain at this time and is the subject of continuing study.

One of a variety of possible equilibria between solid and liquid forms could be that depicted in the following scheme, the right hand side being favored by higher temperatures.

$$\text{Si(PO}_4\text{H)}_{2\ast}(\text{H}_3\text{PO}_4)_2 \ (6\text{-coord.}) = \text{Si(PO}_4\text{H}_2)_4 \ (4\text{-coord.})$$

$$= \text{Si(PO}_4\text{H)}_2 + 2\text{H}_3\text{PO}_4 \quad \text{Equation 8.1}$$

These forms are related by the redistribution of protons and tilting of the orthophosphate groups such an equilibrium would involve minimal changes in
density; thus accounting for the stability of the suspension, which can only be
separated by prolonged centrifugation. The molecular level characterization of the
silicophosphoric acid, which being called SiPOH for convenience, is not needed to
appreciate the fuel cell performance so will be left for later articles to be published
by Huang and co-workers.

Remarks. Here we describe briefly the preparation, electrical conductivity,
and fuel cell performance of the SiPOH-containing electrolyte. It is assumed that
the good performance of the present electrolyte is partly a consequence of the higher
temperatures that can be reached, but partly also a consequence of some favorable
modification of the surface tension that improves the complex kinetics at the three-
phase boundary (gas/catalyst/electrolyte). This is a subject for future investigations,
in which comparative surface tension measurements will be included.

Note: Adapted with permission from Ansari, Y. Tucker T.G., and Angell C.A.
A Novel, Easily Synthesized, Anhydrous Derivative of Phosphoric Acid for Use in
Electrolyte with Phosphoric Acid-based Fuel Cells. J. Power Sources 237 (2013) 47-
9 A FLEXIBLE INERT PHOSPHORIC ACID SILICA-SUPPORTED GEL WITH CONDUCTIVITY ABOVE NAFION AND DURABLE FUEL CELL (PEMFC) OPERATION AT 150ºC

9.1 Introduction

Proton exchange membrane fuel cells (PEMFCs) are under intense development as non-polluting power sources that in principle are the most efficient means of converting chemical energy to electrical energy and thence mechanical work. However, practical realization of this efficiency, even in the simple H₂/O₂ fuel cell case, proves to be fraught with difficulties. Nafion fuel cells (Peighambardoust et al. 2010) based on sulfonated polytetrafluoroethylene (PTFE) proton-conducting membranes, are favored for their high conductivities (Kreuer, 2001), but are limited to temperatures below 100ºC because of loss, at higher temperatures, of the water needed for high conductivity (Lou et al., 2010; Kwak et al., 2003). This means that the fuel cell is susceptible to catalyst poisoning by carbon monoxide impurities in the gas, which therefore must be super-pure. The Nafion-based cells also suffer from acute water crossover, hence water management problems.

Attempts have been made to increase the operating temperature of the Nafion membrane cell by (Ghassemzadeh et al. 2010) operating the cell under pressure (Asano et al., 2006; Endoh et al., 2004) doping phosphoric acid solutions
into Nafion-based composite membranes (Zhai et al., 2007; Aili et al. 2011, Ma et al. 2012), indeed both methods give results that are favorable as alternatives to the pristine Nafion membrane cell. However, Nafion and other perfluorinated polymer electrolytes (i.e., Flemion and Aciplex) are seriously limited in commercial applications because of the high materials costs, coupled with the reduced performance at high temperatures (Yee et al., 2012). Therefore, a search for new polymer electrolyte membranes of lower cost and higher temperature viability is urgent.

Solid silicophosphate electrolytes produced by sol-gel processes can have high conductivities (10^{-2} S/cm at 20°C) and have been seen as a viable alternative to Nafion membranes on both cost and temperature range counts (Park et al., 2000; Tsvetkova et al., 2008). They have the advantage that organic molecules and solid acids may be incorporated into the inorganic networks to vary the properties. However, these membranes suffer from the onset of mechanical fragility during the fabrication process; becoming laced with cracks during escape of the water that is released in the curing process (Park et al., 2000; Matsuda et al., 2002). The conductivity of their sol-gel derived glassy material reached 10^{-2} S cm^{-1} without the need to add highly hydrated and temperature-sensitive solid acids (Tsevetkova et al., 2008). Unfortunately, of the many studies of such phosphate-derivatized electrolytes, favored for their stability against reduction by hydrogen, we find very few reports of their actual incorporation into and testing of fuel cells. In this respect, the present contribution is unusual. In the comprehensive review (Zhang & Shen, 2012), little attention is given to phosphate or silicophosphate membranes, though a complex sulfonate-derivatized ceramic membrane described by Peled and
co-workers (Zhang & Shen, 2012) is recognized as promising - indeed these latter workers did report fuel cell tests, in addition to favorable conductivities. Despite open circuit voltages (OCVs) that were only 0.8 V, the maximum power outputs obtained were comparable with those reported here. Many hybrid inorganic (siloxane) - organic phosphininc acid derivatized polymer membranes (Kato et al., 2007), but these never achieve the conductivity levels that are needed and, again, fuel cell tests are rare - perhaps because good fuel cell performance is rare. The advantages of both the above membrane types, Nafion-like polymers and >100°C stable silicophosphate compositions, may be combined if the silicophosphate or siloxy links are introduced in a different manner, viz., starting from the quasi-solid product of the synthetic process used to make the "SiPOH" suspension whose outstanding performance, as a liquid electrolyte, described in a recent contribution (Ansari et al., 2013). In the present contribution we provide conductivity data for this new material, and more importantly, show how the new material can serve as the membrane in simple H2/O2 fuel cells that can produce currents in excess of 1 amp/cm² at temperatures up to 150°C as described below.

9.2 Preparation and Description of New Polymer (Gel) Membrane

When the stable milky suspension as the liquid electrolyte was centrifuged for a long period, a thick paste, described as SiPOH, from which most of the unaltered phosphoric acid has been separated is obtained. The exact composition of SiPOH is still unknown. It contains silicon in a six coordinated state, according to 29Si NMR spectroscopy (see below) and the X-ray diffractogram (seen later) indicates
high disorder. According to ICP analysis of the material after washing with an unreactive solvent (pentafluoropropanol), it has an Si:P ratio of 1:4. When this paste is reacted with water (in which it dissolves completely), a floppy gel was formed upon standing. An example would be the solution of 1.63g of paste in 3g of distilled water from which the gel forms in 90 min or less. The initial gel was a mechanically frail material that shrinks away from a Teflon container and strengthens into a rubbery button as shown in Figure 9.1(b) as water was removed by vacuum oven drying at 40ºC. A modified version of the SiPOH paste preparation (Ansari et al., 2012) in which the liberated HCl is collected in a novel internal chemical trap.

![Figure 9.1](image)

(a) Drying curve showing the loss of 90% of the initial gel mass (obtained by dissolution of siphoric acid in water), during vacuum drying with periodic weight recording. Constant mass is reached after about 15-hr, as vapor pressure approaches zero. (b) button of rubbery polymer (called here SiPOHgel) obtained by the described procedure. (c) preparation of the fiber glass reinforced disc for fuel cell membrane. 1" fiber glass filter disc is immersed in initial pre-gel solution and incorporated in the polymer as the water is evaporated off (vial shown upside down after partial drying). (d) Disc impregnated with polymer is removed, and chosen diameter disc punched out (shown held by tweezers).

The weight loss versus time function for the gel formed from the initial solution of SiPOH, is shown in Figure 9.1(a). It is seen to be rapid at first, but then
to reach a constant mass. In the process, some 90 wt% of the initial water content is lost. This rubbery material contains little or no free water because heating at 300°C was accompanied by a mass loss of only 10 wt% - and the weight of the dry (now crystalline, but hygroscopic) powdery material remained almost unchanged when the temperature was raised to 600°C. As an additional measure of its stability, the gel-like material seemed to be quite invariant with temperature up to 150°C see below in Figure 9.2. It had a yellowy color as seen in Figure 8.1(b), but was colorless in other preparations. It was translucent rather than transparent, so must had some heterogeneity at the microscopic level. The calcined powder had an XRD pattern (see Discussion section) that cannot be indexed to any known structure; and is distinct from any of the structures seen to result from calcination of the original SiPOH. The Si:P ratio must remain the same as that of the solid acid viz. 1:4 except for any excess H₃PO₄ retained in the unwashed SiPOH paste. The possible structures will be considered in the discussion section. Firstly, this investigation took advantage of the rubbery character to test its potential as a fuel cell membrane material.

9.3 Results:

9.3.1 Ionic Conductivity, Fuel Cell Commissioning & Testing

The conductivity of the SiPOHgel material of Figure 9.1(b) was measured on a sample cut from the flexible button. The conductivity was determined using a piston type cell with stainless steel electrodes and mild spring compression for good electrode contact. The results are shown in Figure 9.2, in which comparison is made
with data from three separate reports on Nafion membranes measured under different conditions of hydration and pressure. The stability of the present sample at temperatures up to 150°C is shown by the agreement of data obtained during heating with data taken during subsequent cooling. The conductivity of the SiPOHgel is seen to exceed the conductivity of all other samples at any temperature above 60°C. The closest competition comes from a very wet Nafion membrane containing 16 water molecules per sulfonyl group. The most impressive comparison is that with 100% H₃PO₄ a well-known Grotthuss-type proton conductor. Noted between ambient and 150°C, the conductivity increased almost one half of the way (on the log scale) to the theoretical, infrared limit for ionic conductivity of 10 S cm⁻² (Angell et al., 1990).

An important advantage of our flexible solid electrolyte over Nafion is the low water content. It is the low water content that permits it to serve to so much higher temperatures. The specific conductivity of Nafion is strongly influenced by the number of water molecules surrounding the hydronium ion that charge-compensates the pendant sulfonyl group (Kreuer, 2001).
The conductivity of SiPOHgel at temperatures up to 150ºC compared with those of Nafion samples from different authors (identified in the legend), using high hydration, pressure and humidification. Solid circles are for points obtained during heating; small open circles are obtained during cooling, and confirm high temperature stability. Data for H$_3$PO$_4$ 100% are included for comparison.

As is well known, water is transported across the membrane during operation, causing flooding. Consequently water-management becomes a crucial problem (Bernardi, 1992; Mosdale et al., 1995; Okada et al., St-Pierre, 2000; Zhang et al. 2008; Ji et al., 2009). This problem should not arise in the present membrane due to the low water content and the higher operating temperature that was permitted.
A second slice from the button of pristine SiPOHgel was tested as a membrane in a sandwich fuel cell of the type used in previous studies, for which details are here provided. The cell is illustrated, in exploded view, in Figure 9.3.

Figure 9.3 Exploded view of the Teflon sandwich type fuel cell for testing. Not included in the diagram are gaskets between membrane and E-Tek electrode.

Data obtained from this crude initial test exceeded our expectations for current density, but showed unsatisfactory OCV values of ~0.8V probably due to fuel crossover effects caused by membrane imperfections. A better membrane preparation procedure, incorporating a fiberglass wool filter membrane [Cole-Palmer item QR-200 (Toyo Roshi Kaisha Ltd, Japan) ~2 mm thick initially] as supporting matrix was developed as detailed in Figure 9.1(b) and Figure 9.1(c). The improved membrane was placed in the Figure 9.3 cell assembly between two standard E-Tek electrodes (LT140E-W; 0.5 Pt mg/cm²). To achieve a better interfacial contact between the electrode and the electrolyte, the assembled cell was left in a desiccator overnight, prior to testing. During the testing, the cell was left 2-3 hours at each temperature to ensure thermal equilibrium. The temperature of the cell was tracked.
relative to the oven atmosphere temperature during the test, for any indication of direct hydrogen gas consumption by fuel crossover.

Figure 9.4 Tafel plots (IR corrected) for fuel cell performance using the pristine SiPOHgel (lower curves with poor OCV) and the fiberglass-reinforced and dimensionally regular SiPOHgel membrane (upper curves). The experiments used identical Teflon fuel cell blocks with identical E-Tek electrodes. Different gaskets allowed for active areas of 0.5cm$^2$ and 0.8cm$^2$. Flow rates of H$_2$ for each electrolyte at each temperature are included in legends. Flow rate for O$_2$ = 2 x flow rate for H$_2$. The dotted lines at the top of the diagram are the thermodynamic OCV’s for the temperatures indicated.

The very pleasing polarization curves obtained using the improved MEA are displayed in Figure 8.4. The OCV has regained the values obtained with the liquid electrolyte cell (Ansari et al., 2013) and the maximum current now slightly exceeds
the 1000 mAcm$^{-2}$ value reported previously for the higher temperature of 226°C. The difference is attributed to the superior conductivity of the present MEA.

Figure 9.5 Polarization curves (linear current, not IR corrected), and corresponding power densities, for the pristine SiPOHgel membrane (at 152°C) and the fiberglass reinforced SiPOHgel membrane (at 124°C and 154°C). Note: the power maximum of 202 mWcm$^{-2}$ obtained at 0.4 V for the fiberglass-reinforced membrane at 154°C.

Although the OCV for the cell is above 1V as seen here in Figure 9.5. The Tafel slope is significant and it is clear that the major problem of the oxygen electrode polarization is not solved by this otherwise quite impressive new PEM cell (Barclay, 2006). Much development will be needed to reduce oxygen reduction inefficiency, and concomitantly the slope of the Figure 9.5 plot so that maximum
power can be obtained at a higher potential. The power output at maximum power is, however, a very respectable 200 mWcm$^{-2}$; which we hope to increase with improved cell design such as thinner membranes being an obvious starting point. It is likely that the very low "free" water content of the membrane, refer back to Figure 9.1(a), will be accompanied by a reduction in the rate of platinum catalyst corrosion.

9.3.2 Potentiometric Scans

To address the question of membrane endurance under load (usually referred to as a degradation rate) we prepared a new membrane using a modified, more controlled route than in the initial SiPOH preparation. The gel appeared less robust than in the earlier preparation, perhaps as a consequence of less effective drying. It was again prepared in a glass wool fiber support, refer back to Figure 9.1. Used in the same cell, review Figure 9.3, but with a smaller cross section active area, maximum power was reached at 187 mAcm$^{-2}$, lower than previously, but quite sufficient for the purpose of endurance testing.

The cell with this membrane was submitted to constant current (potentiometric) tests of 24-hr duration (the maximum setting on the PAR 2273) at current densities of 50 mAcm$^{-2}$ at 120°C in order to compare with an earlier study (Thomson, 2010) using the same cell and the same E-Tek electrodes, but carried out using 85% phosphoric acid as the liquid electrolyte. The potential at 50 mAcm$^{-2}$ in our cell exceeded, by 20%, that of the earlier study, and remained quite constant over the entire run.
Figure 9.6 Degradation testing of the SiPOHgel membrane at 120°C and 50mAcm$^{-2}$, and at the current of maximum power at 150°C. Comparison is made with an earlier study (Thomson, 2010) made using the same cell with the same E-Tek electrodes, but with liquid 85 wt% phosphoric acid.

A further, and more severe, test was conducted at 151°C at the current of maximum power, 187.5 mAcm$^{-2}$. In this case, a noticeable downward drift was detectable after about 12-hr, amounting to 1-2 mV or 2-4% decrease over the 24-hr period, where the data are presented in Figure 9.6. They compare very favorably with data for Nafion (Hang et al., 2007) from the Tang laboratory, as follows:
Table 9.1 Degradation rate values of SiPOHgel compared to Nafion versions over 24-hr periods (Jiang & Chu, 2001).

<table>
<thead>
<tr>
<th>Fuel cell membrane:</th>
<th>Nafion 112</th>
<th>Nafion-SiO₂ stabilized</th>
<th>SiPOHgel, K version</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell current:</td>
<td>600 mA/cm²</td>
<td>600 mA/cm²</td>
<td>187.5 mA/cm²</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(maximum power)</td>
</tr>
<tr>
<td>Degradation rate:</td>
<td>2.33 mV/min</td>
<td>0.12 mV/min</td>
<td>0.0087 mV/min</td>
</tr>
</tbody>
</table>

9.4 Discussion

The extraordinary conductivity of this membrane material demands a structural interpretation. Obviously a precise structure cannot be provided for an amorphous material but some principal features can be deduced. While arrived to conclusions systematically below; wishing to stress here that there will prove to be nothing extraordinary to understand or interpret in terms of conductivity mechanisms, beyond what is abundant in the literature on phosphoric acid itself. The reason will be obvious once we have reasoned our way to the conclusion that SiPOHgel is no more than a very successful way of sequestering phosphoric acid in gel form in a flexible nano-permeated network of pure silica.

The most helpful diagnostic tool in seeking this understanding is NMR spectroscopy because all three elements have good NMR nuclei, two of them (¹H and ³¹P) in natural abundance. X-ray diffraction studies of calcined products, on the other hand, offer only puzzles at this time, because of the bewildering variety of possible Si-P-O and Si-P-O-H structures that are known (Krawietz et al., 1998; Elisa et al., 2010; Jähnigen et al., 2012) and the fact that the crystalline product of calcination of the rubbery solid of Figure 9.1(b) has a powder diffraction pattern that is distinct from that of any previously recorded crystal powder pattern. All that can
be said at this time is that the structure of the nearest crystal is characterized by a complex and extended medium range order of very low symmetry (see below) and may not be relevant to the SiPOHgel structure, as we show below.

9.4.1 NMR Spectra

Most instructive, and immediately informative, of the NMR spectra of SiPOHgel are the $^1$H and $^{31}$P spectra, taken jointly plus shown in Figure 9.7. The sharp spectral lines of the spectra for $^1$H and $^{31}$P resonances indicate liquid-like mobility in this solid rubbery material. The fact that the resonances in both the $^1$H and $^{31}$P NMR spectra are essentially those of phosphoric acid, $\text{H}_3\text{PO}_4$, strongly indicates that the preparation procedure has caused a total reorganization of the original "SiPOH" solid acid, (with six-fold silicon coordination, see Figure 9.7 here below) to produce a phosphoric acid gel for which the supporting structure must be a silicate or silicophosphate porous net. The latter can be excluded by the solid state NMR spectra discussed below. However, the fact that the Si:P ratio must remain at the original value of 1:4, implies that the gel must be a very "tight" one. The length scales for silicate and $\text{H}_3\text{PO}_4$ components must remain comparable to maintain the 1:4 composition ratio.
Figure 9.7 The $^1$H and $^{31}$P spectra of the rubbery gel of Fig. 1b showing sharp resonances at 9.5 ppm relative to TMS, and at 0.0 relative to H$_3$PO$_4$. The liquid-like sharpness of the lines, despite measurement in a standard liquid state spectrometer, is consistent with the observation of liquid-like conductivities in Figure 9.2.

A structure, in which the P content is realized in H$_3$PO$_4$ molecular form, would be consistent with the finding of Figure 9.2 that the thermal stability limit for high conductivity is around 150ºC, the same as that attributed to phosphoric acid. That the supporting structure contains silicon in its normal 4-coordinated state (as opposed to the 6-coordinated state of ambient temperature SiPOH), is shown by the MAS (magic angle spinning) solid state NMR spectrum for Si (in its natural abundance) in Figure 9.7. The resonance is found at -115 ppm referenced to the
standard TMS, but using in situ solid tetrakis(trimethylsilyl)silane (TTSS) as secondary reference (TTSS -9.8 ppm). A chemical shift of -115 ppm is in the downfield extreme chemical shift range for SiO₄ groups, past the average for the Q₄ grouping given for silicate minerals by Magi et al (Jähnigen et al., 2012). This implies that the Si in SiPO₄gel belongs to a completely connected siloxy network. Since, by preparation, there are 4 P for every Si, and since the number of the H₃PO₄ molecules grows as the cube of the dimension of any nanodomain, the dispersion of H₃PO₄ in the silica network must be nanoscopic, or at least highly ramified.

When we combine the above observations with the fact that the solid state NMR spectrum of ³¹P (not shown here) produced no important new lines; a barely detectable resonance at -11 ppm is not considered significant. We may conclude that there has been an almost total segregation of P from Si as molecular H₃PO₄. The segregation has then left a purely silicate network as the supporting structure. Obviously, to account for the almost undiminished conductivity from that of pure H₃PO₄, the H₃PO₄ domains must be interconnected, or the proton hopping between H₃PO₄ domains must be very free. ³¹P diffusivity measurements still to be performed should provide clarity on this issue.
Figure 9.8  Solid-state MAS $^{29}$Si NMR of (a) the siphoric acid (SiPOH) precursor to the formation of the polymer gel of Fig. 1b, showing a sharp resonance at -210 ppm that establishes the presence of silicon in six-coordination in SiPOH, and (b) the SiPOHgel material of the present contribution, showing a resonance at around -115 ppm that is typical of silicon when four-coordinated to bridging oxygens in tetrahedral silicate networks.

9.4.2  XRD of Calcined and Amorphous Structural Patterns

Figure 9.8 shows the x-ray powder patterns obtained for the products of SiPOHgel after heating at 300°C for 5 hours, during which a weight loss of 10% occurs. The spectrum is distinct from any of those obtained for SiPOH after treatments to remove any remaining liquid material by washing in perfluoropentanol (PFP). The principal difference lies in the splitting of the SiPOH peak at $2\theta = 13^\circ$, and the virtual absence of the strong line at $2\theta = 23^\circ$. These structures are not found in the registry of crystalline compounds indexed by their three strongest XRD lines.
The weight loss during the calcination of SiPOHgel to give the XRD of Figure 9.8, lower pattern, may be associated with the same process that reduces the conductivity above 150°C; probably the loss of a mole of water per mole of phosphorus and the reincorporation of the pyrophosphoric acid into complex silicophosphate structures.

Figure 9.9 X-ray powder pattern for SiPOHgel after heating at a temperature of 300°C, sufficient to calcine the gel. Comparison is made with the products of calcination (at 300°C and 600°C) of SiPOH that has been "treated" i.e. freed of any liquid phase by washing in pentafluoropentanol (PFP). None of these structures are known. The uppermost trace with sharp peak at 2θ = 10° is the XRD of SiPOH washed free of excess H₃PO₄ and H₄P₂O₇ using PFP. The sharp peak, with otherwise amorphous features in the XRD, is typical of an orientationally disordered phase.
While these patterns, in principle, can lead to precise information on atomic and molecular positions in a SiPOHgel-derived structure, they probably all involve some sort of structural rearrangement from the target structure used in the experiments on conductivity and fuel cell operation. They are therefore likely to be less useful in understanding the nature of the membrane material than the simple amorphous state XRD of the gel itself.

The XRD of SiPOHgel, shown in Figure 9.9 is simple yet somewhat unambiguous. The similarity to the XRD of powdered silica gel taken on the same diffraction equipment, is striking. It is different and less complex than that of hydrated silica gel. This leaves little doubt that the material we are investigating is a dense amorphous silica network, with sufficient network defects that the structure remains flexible. Within the gel there is evidently a uniform distribution of essentially pure phosphoric acid.
Figure 9.10  Comparison of the XRD pattern of the SiPOHgel with that of conventional anhydrous silica gel. The pattern is much simpler than that of hydrated silica gel. The comparison suggests that the present material is a homogeneous network of siloxy units that might be slightly more correlated than in silica gel, yet loosely enough connected that the structure remains floppy and easily, but elastically, deformable.

While this sort of structure probably does not bind the $\text{H}_3\text{PO}_4$ any more strongly than does the polybenzimidazole-based membrane materials that have been under intense study in recent years, (Li et al., 2010; Li et al., 2008) it should not lose $\text{H}_3\text{PO}_4$ any more rapidly than do these post-formation-doped membranes. The very
low rates of H$_3$PO$_4$ depletion recorded by Linares et al (Linares et al., 2012) under gas flow at temperatures up to 190°C, give little cause for concern.

It might be asked, why not simply absorb H$_3$PO$_4$ into dry silica gel and use that material as the electrolyte? But this has already been attempted in the work of Matsuda and co-workers cited in the introduction, and then abandoned by their laboratory. These researchers found that the conductivity of the aqueous H$_3$PO$_4$-soaked sililica gel faded rapidly to below $10^{-4}$ S cm$^{-1}$ on standing at 130°C. Phosphosilicate powders compressed to disc form, with P/Si ratios near unity behaved better, retaining their $10^{-2}$ S cm$^{-1}$ conductivities over longer periods of time at the same temperature (Matsuda et al., 2002), but this is still far below the SiPOHgel conductivity at the same temperature seen back above in Figure 9.2. Their study clearly has features in common with the present study, but they evidently did not find the aqueous route to the rubbery solid product that seems to have the unique properties needed for fuel cell applications, as illustrated in Figure 9.4 and Figure 9.5.

**Remarks.** We have so far only prepared and tested SiPOHgels obtained by relatively low-temperature dehydration procedures. We surmise that a more aggressive dehydration might produce a gelled form of the >200°C-stable liquid electrolyte on which reported here recently. While the present formulation is desirable for processes operating in the range not far above 100°C, an extension of the temperature range would have advantages for some purposes and will be the subject of future investigations.
While we are not aware of other acid gels that form by self-assembly in situ via the present process, it seems quite likely that there are analogous cases, based on the hydration of other silico-oxy acids (Tang et al., 2007) waiting to be made. It will be interesting to determine the maximum acidity material that can be prepared in this semi-solid form by the procedure we have described. Although phosphates are preferred over sulfates for fuel cell purposes because of their stability against reduction by hydrogen, there will be other purposes for which the benign confinement of a stronger acid might be very desirable.
10.1 Electrochemical Devices for the Near-Future:

10.1.1 Alkali-Metal Battery Systems

In conclusion, alkali-metal batteries as energy storage and delivery devices would sustainably alleviate the power fluctuations during the regular nocturnal periods, unforeseen cloudy weather conditions, and everyday energy peak hour spikes. When an electrical grid overload would occur in certain high demand locales then the required electricity would be regulated by compensation of increased power from the stationary batteries and excess diverted to other areas if needed on the grid or stored in the batteries for later times.

Specifically, sodium-ion batteries would make for excellent electrochemical devices utilized by an electrical grid. Fuel cells are also electrochemical devices that could generate electricity on demand from a fuel source potentially produced solely by the renewable energies. Also eradicating the humidification process and membrane pressurization for the limited low temperature operation: hence lower cost and higher efficiency overall. An ideal electrical grid system would be powered primarily by renewable energies such as wind and solar devices. Thus, increasing efficiency and conserving the environment from further fossil fuel depletion. The
integral factors of this thesis were proposed then tested as these electrolytes for electrochemical devices of alkali-metal batteries and non-humidified fuel cells were: 1) attained exceptional conductivities for increased energy densities, 2) completely inorganic systems of lower cost materials, 3) thermally stable against decomposition, and 4) less sensitive to atmospheric water degradation nor requiring moisture for cell operation.

When synthesized then characterized the electrolyte sample: phosphorusbromide heptabromodialuminate (PBr$_4$Al$_2$Br$_7$) exemplified favorable physical characteristics of an inorganic ionic liquid (IIL) as a molar ratio of 1:3 with sodium heptabromodialuminate (NaAl$_2$Br$_7$) to an ionic conductivity of $10^{-1.75}$ S/cm. This ionic conductivity was lower than the well-studied sample of 1-ethyl-3-methylimidazolium tetrachloroaluminate to sodium tetrachloroaluminate ([EMI]AlCl$_4$:NaAlCl$_4$ 1:3) by a difference of 40 degrees, but was reclaimed at exactly 100°C and well above. The optimal molar percentage of aluminum bromide for low temp homogenous mixing ranges from 0.333% (n = 1 mol) up to 0.667% (n = 2 mols) or higher temperatures is required for this type of melt. The aluminum bromide complexes have similar Lewis Acidity stemming from being slightly less in strength for the Al·Br bond rated at 430 kJ/mol than the Al·Cl rated at 511 kJ/mol (Mitra, DePue, Parkin, & Atwood, 2006).

Thus far, eliminating the “alkali cation-trapping effect” with 50% molar fraction or higher of the respective alkali-metal halide aluminate, PBr$_4$Al$_2$Br$_7$: NaAl$_2$Br$_7$ 1:3. There have been many suggestions to the understanding of this ion-trapping phenomena yet still this day remains not thoroughly explained for
[EMI]AlCl$_4$:NaAlCl$_4$ 1:1 (> 50 mol% of NaAlCl$_4$) under 140°C, yet illumination was shed of the subject as best in this thesis (Tucker & Angell, 2014).

The new IIL here had a larger electrochemical window of ~5V than the 4V of the known, semi-organic [EMI]AlCl$_4$:NaAlCl$_4$. The ability of the inorganic cation to withstand higher temperature ranges hence avoiding decomposition as being a completely inorganic system. The cation and anion of the ionic liquid electrolyte coalesce once more where the physical and electrochemical properties are recovered. The higher temperature regime against decomposition of this material applied as a liquid electrolyte in the cathode operating at a low to moderate temperature range of 100-180°C would be an advantage for sodium-ion battery usage for the sodium-ion transfer yet still well below the standard range 250-350°C of ZEBRA and NaS-type batteries.

The constituent electrolyte of the IIL sample was PBr$_4$Al$_2$Br$_7$ exhibited almost 10mS/cm ($10^{-2}$ S/cm) conductivity at 150°C, which was an order of magnitude appreciably less in conductivity as compared to NaAl$_2$Br$_7$. The ionic conductivity testing commenced at room temperature when the electrolyte was in the solid state; where the initial measurement was below $10^{-5}$ S/cm and increased sharply to the inhomogeneous liquid state upon initially melting increasing up to $10^{-3}$ S/cm. The liquid electrolyte equilibrated after the solid-liquid phase transition at $T_m = 102°C$ and remained thermally stable upon the heating ramp up to 220°C. This feature specifically of these inorganic ionic liquids is very desirable for a sodium-ion battery system as to increase the temperature range of operation; which if necessary to proceed into a high temperature regime avoiding permanent decomposition of the electrolyte, typically due to the organic cationic component (Stuff, 1989).
This allowed for ionic conductivity measurements of the NaAl$_2$Br$_7$ electrolyte during the unique solid-solid phase transition for a significant two orders of magnitude increase in ionic conductivity at around 67°C (Kendall et al., 1923) then to the solid-liquid phase transition as thereafter the ionic conductivity was uniformly above $10^{-1}$ S/cm upon heating to around 105°C. These solid-solid then solid-liquid phase transition temperatures were also evident in thermograms in direct correlation with the $\sigma_{dc}$ measurements, which are all of this work here. The electrolyte remained thermally stable and well behaved within this 100-260°C regime where as upon natural cooling the measurements demonstrated the reversibility of the sample as a closed system; these aluminates sublime as purer single component substances and have a tendency to have high vapor pressures even as compounds (Xu et al., 2003).

This inorganic electrolyte, NaAl$_2$Br$_7$, remained around an order of magnitude higher in conductivity well above 100mS/cm than a previous alkali-metal cation oxy-anion electrolyte, CsHSO$_4$, mainly utilized for H$_2$/O$_2$ fuel cell purposes had exhibited a similar increase in conductivity of $\log 10^{-2.3}$ S/cm when reaching the threshold temperature of around 141°C as demonstrated by Haile and co-workers (C. Chisholm & Haile, 2000). Now the super-protonic conduction is short-lived for an organic or even semi-organic system after reaching this state as the compound begins decomposition at ~140°C (175°C when described elsewhere (Boysen & Haile, 2003)), hence development of these thermally stable, inorganic electrolytes. Accordingly, the novel, anhydrous silico-phosphorus electrolyte for the non-humidified fuel cell was based on being an inorganic system.
10.1.2 Non-Humidified Fuel Cell Systems

The performance was increased for a single fuel cell under ambient conditions. The ideal temperature of 120°C is well above the boiling point of water and near the optimum thermodynamical temperature for optimal performance and reduced CO (carbon monoxide) catalysis poisoning. This fuel cell operated at 121°C procuring current and power densities of 731 mA/cm² and 345 mW/cm² (IR corrected), respectively; which can be compared to a lab benchmark of unmodified 85% orthophosphoric acid solution in the plot (Ansari, Tucker, & Angell, 2013). The temperature was also low enough to design materials for mobile devices and reduced safety issues. The current and power densities at 226°C rose to 966 mA/cm² and 238.5 mW/cm² (IR corrected), respectively. The testing benchmark was again, the standard solution of phosphoric acid at 226°C under the same conditions, was measured at 303 mA/cm² and 115 mW/cm² for the current and power densities, respectively. Any higher in temperature then the ortho-structure of 1 mole H₃PO₄ dehydrates and morphs into the pyro-structure of H₄P₂O₇; that is 2 moles of H₃PO₄ minus one mole of H₂O, hence degrading the fuel cell performance significantly. This novel silico-phospho-oxy based gel membrane was able to endure a 6-day stress testing above 120°C of constant current tests over 24-periods demonstrating higher at 50mA/cm² when contrasted to the percentage and a very low degradation rate of 8.7⋅10⁻³ at max power of 187.5 mA/cm² as compared to enhanced versions of Nafion 112.

As aforementioned the enhanced performance due to more rapid phosphate rotation for the proton conduction via the specialized Grotthuss mechanism has
another beneficial effect. The operating current efficiency rose from 36.4% to 38.4% and from 14.4% to 44.3% at 121°C and 226°C, respectively. This benefit was a quicker recovery time of the novel electrolyte when load tested as a H₂/O₂ fuel cell under ambient conditions. The higher proton utilization is optimized the proton conduction (Grotthuss-type mechanism) for redox properties increased the energy density of the fuel cell to where benefitting from minimized fuel crossover, therefore reduced wasted heat energy into the fuel cell block due to thermodynamic expulsion. Of all these great benefits mentioned, one of the better enhancements was the significant reduction of hydrogen gas consumption at the anode chamber. The fuel cell with the modified silicophosphate electrolyte consumed only 3.1 and 4.1 ml/min of hydrogen gas at the 121°C and 226°C, respectively compared to typical consumption ranging widely from 12-80 ml/min. The rapid proton conduction and speedier recovery period due to the quicker rotation ability due to the degrees of freedom and for more geometrical structural space rearrangement of phos-oxy groups centered on silicon had a structural platform initializing more active hydrogen atoms that had spurred even more cell efficiency making this a more sustainable electrochemical device and a lesser fed amount of hydrogen gas, hence cheaper in cost for the already established commercial PAFC applications.
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APPENDIX I

ARRHENIUS PLOTS OF NOVEL & KNOWN IONIC CONDUCTIVITIES
ADDITIONAL DATA COLLECTED
APPENDIX II

CYCLIC VOLTAMMOGRAMS OF MOLTEN SALTS & IONIC LIQUIDS
ADDITIONAL DATA COLLECTED
Telpriore Gregory Tucker, Ph.D.

Telpriore “Greg” Tucker (U.S. citizen) was a doctoral student in the Department of Chemistry & Biochemistry at Arizona State University. There as a research assistant he earned the PhD in Chemistry graduating in fall 2014, where he pursued an emphasis in electrochemistry for renewable energy applications. The research towards his dissertation was the utilizations of ionic liquids as the internal chemical components of low-temperature alkali-metal type batteries for energy storage and non-humidified fuel cells for energy generation; projects primarily funded by Sandia National Labs, Army Research Office, U.S. Department of Defense (DoD) and the U.S. Department of Energy (DoE). Greg was the founding president of the Central Arizona Graduate Chapter of The Electrochemical Society (ECS) for fellow doctoral students, which was recently awarded the ECS Chapter of Excellence for 2013-14. Including, being founding director of The Electric Battery Bike Organization (TeBBBo) in the summer of 2013, establishing the first dedicated student registered club for the promotion of electric bicycles (ebikes) and an affiliate of the new Bicycle Advisory Committee both located at ASU in Tempe, AZ. As a doctoral student in an era of sustainability, Telpriore began an entrepreneurial venture by providing ebikes for green mobility to his local community plus Phoenix Metro Valley through his small business, The Southwest Battery Bike Company located in downtown Phoenix off 11th St & Washington St at Co+Hoots. Outside of his graduate career, Dr. Tucker is a life-coach with The Ironmen Network, the vice president of the Eastlake Park Neighborhood Association (EPNA) and lastly, an active member of the Eastlake-Garfield Steering Committee (EGSC) for the Reinvent Program by the City of Phoenix. For more info please contact him at emails: tgtucker@asu.edu and tucker@thebatterybike.com or call: 1.602.753.8825