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Cathodic Deposition of Triangular Tungsten Clusters from Ionic Liquids: An Explorative Study

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CATHODIC DEPOSITION OF TRIANGULAR TUNGSTEN CLUSTERS FROM IONIC LIQUIDS: AN EXPLORATIVE STUDY

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

By

LINDA N. UBADIGBO
B.S., Chemistry, Central State University, 2009

2012
Wright State University
I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Linda N. Ubadigbo ENTITLED Cathodic Deposition of Triangular Tungsten Clusters from Ionic Liquids: An Explorative Study BE ACCEPTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF Master of Science.

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ABSTRACT

Ubadigbo, Linda N. M.S., Department of Chemistry, Wright State University, 2012. Cathodic Deposition of Triangular Tungsten Clusters from Ionic Liquids: An Explorative Study

In the present work, the triangular tungsten clusters \{[W_3O_2(O_2CCH_3)_6](H_2O)_3\}(CF_3SO_3)_2 and \{[W_3O_2(O_2CCH_2CH_3)_6](H_2O)_3\}(BF_4)_2\cdot5.5H_2O were dissolved in both hydrophobic and hydrophilic ionic liquids (ILs) and subjected to a cathodic potential of roughly 2V. It was proposed that successful deposition of these metal clusters on a platinum electrode would yield Pt-supported anodic catalysts which could be used in ethanol fuel cells (EFCs). Visual examination of the electrode surfaces indicated that a film had been deposited, however, the surface with W_3(CF_3SO_3)_2 quickly oxidized when removed from the IL. Therefore, SEM imaging and EDX analysis of the W_3(BF_4)_2 surface were performed. The data indicated that the film was composed mainly of carbon, oxygen, nitrogen, iron and fluorine with very little tungsten contribution. Electronic spectra taken pre- and post-deposition suggest that structural changes to the W_3O_2 unit occurred with the disintegration of the triangular geometry being a thermodynamically favored route.
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DEDICATION

I dedicate this to my daughter Giana for being the epitome of a “good baby” and bringing a never ending stream of joy into my life. I thank you for being patient with me. I believe your presence has made me a better person and has given me the ultimate motivation to set and achieve goals I would have never thought possible. In your eyes, I am like super woman rescuing you from daycare and shielding you from the “bad snow”. Yet, it is you who imparts me with strength to do it all. So, thank you Gigi.

To my family, especially my Mother and Father, thank you for being supportive through the good and bad times. You guys are truly awesome!
I. INTRODUCTION

According to the Energy Information Administration (EIA), energy consumption is projected to increase from 495 quadrillion Btu in 2007 to 739 quadrillion Btu in 2035 (Fig.1). Energy sources such as fossil fuels along with electric- and water-derived energy all have limited availability. The depletion of natural resources caused by an ever-growing human population with increasing energy demands has forced the price of fossil fuels upward and the integrity of the environment perilously downward. Thus, the need to explore alternative forms of energy that utilize renewable resources is of great precedence.

Figure 1 Projected world energy consumption by source. Courtesy of: U.S. Energy Information Administration (July 2010)
In the past few decades, most research studies focused on the development of direct methanol fuel cells (DMFCs). In recent years, more attention has been given to the improvement of the direct ethanol fuel cell (DEFC). When compared to a DMFC, a DEFC has the potential to produce a higher energy density (8.01 kWh/kg for EtOH versus 6.09kWh/kg for MeOH). Ethanol as a fuel source is more preferable due to its renewability, its low toxicity, and the ability of the biomass from which it is derived to consume CO₂ generated during its oxidation. Some issues with present-day DEFCs and direct alcohol fuel cells (DAFCs) in general are: electro-catalyst poisoning due to adsorbed CO, sensitivity of electro-catalysts to highly acidic media, and lastly, development of novel electro-catalysts that are cheaper than platinum but electro-active enough to break carbon-carbon bonds and completely oxidize ethanol.

**Electrochemical Cells**

There are two types of electrochemical cells: galvanic and electrolytic. Both cells contain electrodes where reduction and oxidation reactions take place at the cathode and anode, respectively. Chemical reactions in a galvanic cell are spontaneous whereas chemical reactions that take place in electrolytic cells are the result of an applied voltage. In electrochemical cells, oxidation occurs as the result of a positive potential being applied and reduction occurs as the result of a negative potential being applied. Thus, the anode is positively charged and attracts anions in the solution. In contrast, the negatively charged anode in a galvanic cell is due to the fact that the spontaneous oxidation reaction steadily floods the anode with electrons that are attracted to the positively charged
cathode (where cations are waiting to be reduced). The voltage difference between the anode and cathode of a galvanic cell is referred to as the cell’s potential or $E_{cell}$. Regardless of the charge on either terminal (anode or cathode), oxidation occurs at the anode and electrons flow toward the cathode in both galvanic and electrolytic cells (Fig. 2). Electrochemical cells of the electrolytic type are generally used for electrolysis and electrophoretic deposition whereas galvanic cells are generally used as batteries and fuel cells.$^7$

![Diagram of galvanic cell and electrolytic cell](image)

**Figure 2** Diagram of a galvanic cell and an electrolytic cell showing the reduction of copper ions occurring spontaneously and then the reverse reaction occurring as the result of an applied voltage.

**Fuel Cells**

Fuel cells generate electricity as a result of electrochemical processes which do not require combustion of the fuel source. The absence of combustion eliminates the production of harmful emissions such as nitrous oxide, mercury or soot.$^5$ Fuel cells require a constant influx of fuel and oxygen in order to operate. There are three additional components of a fuel cell: the anode, cathode and the electrolyte that separates them (Fig.
3). The electrodes (anode and cathode) serve as a junction between an ionic conductor (electrolyte solution) and electronic conductor (external circuit). In essence, it is an interphase in which current changes from being carried by the movement of ions in the electrolyte to being carried by the movement of electrons in the proper electrode. This junction is referred to as an interphase rather than an interface because it is a local instead of a planar phase boundary. The two boundaries are actually adjacent; one region extending out from the electrode into the electrolyte (which is different than the bulk solution) and the other region extending in from the electrode surface (which is different than the bulk of the electrode). Electrodes are usually composed of Noble metals such as platinum, palladium, gold, silver or mercury. The cell electrolyte may consist of an aqueous solution, a complex mixture of salts in solution, a paste, polymer, non-aqueous solutions (ionic liquids) and even gases.

Figure 3. Diagram of a simple fuel cell.
In general, fuel typically enters in on the anodic side where it is oxidized and oxygen typically enters in on the cathodic side where it is reduced to water. During the oxidative process, the hydrogen molecules are split into protons and electrons. The protons pass through the electrolyte/polymer membrane to the cathodic side, while the electrons are forced through an external circuit, thus generating electricity and heat. Once the electrons pass through the external circuit, they recombine with the protons and oxygen in the air to produce water. Fuel cells come in several different forms and are named depending on the type of fuel, and/or the type of electrolyte that is employed. Although there are many types of fuel cells, the foremost ones include: the alkaline fuel cell (AFC), proton exchange membrane (PEM) fuel cell, direct methanol fuel cell (DMFC), molten carbonate fuel cell (MCFC), phosphoric acid fuel cell (PAFC), and solid oxide fuel cells (SOFCs). In recent years, regenerative fuel cells (RFCs), zinc air fuel cells (ZAFCs) and microbial fuel cells (MFCs) have also been explored.

Table 1 Fuel Cell Types

<table>
<thead>
<tr>
<th>Fuel Cell</th>
<th>Fuel Employed</th>
<th>Electrolyte</th>
<th>Catalyst</th>
<th>Operating Temperature (°C)</th>
<th>Efficiency (%)</th>
<th>Commercial Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFC</td>
<td>H₂</td>
<td>KOH/H₂O</td>
<td>Non-precious metal</td>
<td>225-475</td>
<td>60-70%</td>
<td>Aerospace</td>
</tr>
<tr>
<td>PEM</td>
<td>H₂, methanol, ethanol</td>
<td>Solid Polymer</td>
<td>Pt</td>
<td>175-200</td>
<td>40-60%</td>
<td>Automobiles, Transportatio-n</td>
</tr>
<tr>
<td>DMFC</td>
<td>CH₃OH</td>
<td>Solid Polymer</td>
<td>Pt</td>
<td>85-250</td>
<td>&lt;= 40%</td>
<td>cellphones, laptops, battery chargers for consumer electronics</td>
</tr>
<tr>
<td>MCFC</td>
<td>H₂</td>
<td>Na₂/K₂CO₃ in</td>
<td>Non-Pt group</td>
<td>1,200</td>
<td>50-65% (85%)</td>
<td>Large stationary</td>
</tr>
</tbody>
</table>
As seen in Table 1, operating temperatures greatly influence each fuel cell’s application. High temperature fuel cells such as MCFCs, PAFCs and SOFCs are typically used to power large structures such as schools, hospitals and prisons. When used in a combined heat and power (CHP) mode, efficiency is improved by utilizing heat that is generated. Whereas low temperature fuel cells such as DMFCs and MFCs are typically used to power mobile technologies such as consumer electronics or medical devices.\textsuperscript{11}

**Non-aqueous Electrolyte Solutions**

Ionic liquids have become popularized in recent years due to their unique nature and immense physicochemical tuneability. The properties of ionic liquids which make
them favorable are their negligible vapor pressure, electrochemical and thermal stability as well as their recyclability. Although the definition used tends to reflect what field of research they are utilized in, the most universal and widely used definition of an ionic liquid is a salt with a melting point below the boiling point of water.\textsuperscript{12} These liquids consist entirely of positively and negatively charged ions. The cationic component is typically a relatively large organic molecule whereas the anionic component is typically inorganic and relatively small. Figure 4 below shows some commonly used cations and anions.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{Commonly used cations and anions in ionic liquids.}
\end{figure}

It is uncertain exactly where and when the first ionic liquid originated. However, the first documented observation was in the mid-1800s and occurred as the by-product of an AlCl\textsubscript{3} -catalyzed Friedel-Crafts reaction.\textsuperscript{13} The structure of the “red oil” was later
revealed when nuclear magnetic resonance (NMR) spectroscopy became available. This ionic liquid contained an intermediate aromatic cation with a heptachlorodialuminate anion. In 1914 ethylammonium nitrate was discovered by Paul Walden and is believed to be the first room-temperature ionic liquid (RTIL) melting at approximately 120°C.\textsuperscript{13} Decades later, in the early 1980s, one of the first 1,3-dialkylimidazolium-based RTILs was synthesized by mixing 1-ethyl-3-methylimidazolium chloride with various concentrations of aluminum chloride. Although these ionic liquids were highly conductive, their main drawback was their sensitivity to air and moisture.\textsuperscript{13} In 1992, the most notable transformation in the history of ionic liquids occurred when Wilkes and Zaworoto exchanged the chloroaluminate anion in the dialkylimidazolium-based aluminum chloride ILs for tetrafluoroborate and hexafluorophosphate anions.\textsuperscript{14} The resulting RTILs were both air and water stable with the tetrafluoroborate containing ionic liquid being hydrophilic and the hexafluorophosphate anion forming a hydrophobic ionic liquid. With the advent of this method for anion exchange via salt metathesis, research pertaining to ionic liquids increased significantly\textsuperscript{15} (Fig. 5).
First generation ionic liquids consisted of mixtures of N-butylpyridinium chloride and aluminum chloride in varying molar concentrations. They were discovered at the United States Air Force Academy during the exploration to find an alternative electrolyte to use within a thermal battery. The second generation of ionic liquids was both air and moisture stable and gave way to the formulation of the most recent generation of ionic liquids; ionic liquids which can be synthesized in order to modify their physicochemical properties. These ionic liquids have received significant attention due to the number of them which can potentially be synthesized as well as their increasingly variable uses. Given the current, commercially available cations and anions, there are theoretically $10^{18}$ possible ionic liquids that can be achieved through different combinations.
The Effect of Cation and Anion Modification

Previous investigations have shown that alteration of the cation and the anion affects certain intrinsic properties of the ionic liquid. Modification of the cation corresponds to an increase or decrease in conductivity, viscosity and cytotoxicity. Depending on the cations ability to delocalize charge and based on its substituents. For example, elongating the alkyl chain attached to the cation increases its viscosity thus decreasing its conductivity\textsuperscript{17} (Table 2) whereas functionalization of that elongated chain could somewhat reverse the aforementioned physicochemical changes.\textsuperscript{13} In addition, fluorination of the cation increases its lipophilicity which increases its bioavailability by allowing it to permeate across cellular membranes.\textsuperscript{18}

\textbf{Table 2} Select Physicochemical Properties of 1-alkyl-3-imidazolium-based ILs\textsuperscript{19}

<table>
<thead>
<tr>
<th>Chain</th>
<th>Anion</th>
<th>$T_m$\textsuperscript{a}(°C)</th>
<th>$\eta$\textsuperscript{b}(mPa s)</th>
<th>$\rho$\textsuperscript{c}(gcm$^{-3}$)</th>
<th>$\sigma$\textsuperscript{d}(mScm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Et</td>
<td>BF$_4$</td>
<td>13</td>
<td>37</td>
<td>1.28</td>
<td>14</td>
</tr>
<tr>
<td>$^n$Pr</td>
<td>BF$_4$</td>
<td>-17</td>
<td>103</td>
<td>1.24</td>
<td>5.9</td>
</tr>
<tr>
<td>$^n$Bu</td>
<td>BF$_4$</td>
<td>None</td>
<td>180 (233)</td>
<td>1.21</td>
<td>3.5 (8.6)</td>
</tr>
<tr>
<td>$^n$Bu</td>
<td>PF$_6$</td>
<td>10</td>
<td>219 (312)</td>
<td>1.37</td>
<td>1.6 (6.5)</td>
</tr>
<tr>
<td>$^n$Bu</td>
<td>AlCl$_4$</td>
<td>none</td>
<td>(294)</td>
<td>1.23</td>
<td>(24.1)</td>
</tr>
<tr>
<td>$^n$Bu</td>
<td>CF$_3$SO$_3$</td>
<td>16</td>
<td>90</td>
<td>1.22</td>
<td>3.7</td>
</tr>
<tr>
<td>$^n$Bu</td>
<td>TFSI</td>
<td>-4</td>
<td>69</td>
<td>1.43</td>
<td>3.9</td>
</tr>
<tr>
<td>$^n$Bu</td>
<td>CF$_3$CO$_2$</td>
<td>none</td>
<td>73</td>
<td>1.21</td>
<td>3.2</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Melting point, \textsuperscript{b}Viscosity at 25\textdegree C and in parenthesis at 30\textdegree C, \textsuperscript{c}Density at 25\textdegree C, \textsuperscript{d}Conductivity at 25\textdegree C and in parenthesis at 60\textdegree C
Modification of the anion usually affects solvation properties as well as the hydrophobic/hydrophilic nature of the ionic liquid (Table 3). For instance, ionic liquids containing PF$_6$ and TFSI anions tend to be hydrophobic and those which contain BF$_4$ and CF$_3$SO$_3$ anions tend to be hydrophilic; with hydrophobicity increasing as follows BF$_4^{-}$ ≈ CF$_3$SO$_3$ $^{-}$ < PF$_6^{-}$ < TFSI$^{-}$.$^{20}$ The hydrophilic nature of the ionic liquid correlates to the hydrogen bonding ability of the ion pairs. Consequently, the hydrophilic nature of an ionic liquid is directly related to its conductivity. In general, conductivity has an inverse relationship with viscosity because it reduces charge mobility.

**Table 3** Effect of Anion on hydrophobicity in alkylimidazolium-based ILs

<table>
<thead>
<tr>
<th>Anion</th>
<th>Hydrophobicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl$^{-}$</td>
<td>Hydrophilic</td>
</tr>
<tr>
<td>BF$_4^{-}$</td>
<td>Hydrophilic</td>
</tr>
<tr>
<td>CF$_3$SO$_3$ $^{-}$</td>
<td>Hydrophilic</td>
</tr>
<tr>
<td>PF$_6^{-}$</td>
<td>Hydrophobic</td>
</tr>
<tr>
<td>TFSI$^{-}$</td>
<td>Hydrophobic</td>
</tr>
<tr>
<td>BETI$^{-}$</td>
<td>Hydrophobic</td>
</tr>
</tbody>
</table>

**Classic Synthetic Routes**

Ionic liquids can be synthesized in a number of ways; however, all of these methods can be placed within three categories: Direct Combination, Acid/Base Neutralization and Salt Metathesis. In the direct combination method, the cationic component is added directly to the anionic component or vice versa (Scheme 1).
Acid/Base Neutralizations involve the addition of the anion in the form of a Brønsted acid with the cationic component serving as the Brønsted base (Scheme 2). Salt metathesis is typically used secondary to both acid/base neutralization and direct combination in order to exchange the anion (Scheme 3).

**Scheme 1 Direct Combination Method**

![Scheme 1 Direct Combination Method](image)
Properties of 1,3-dialkylimidazolium-based ionic liquids

As stated previously, the size, geometry and composition of the cation and anion in an ionic liquid can influence its physicochemical properties such as melting point, conductivity, density, and transport properties (to list a few).
Melting Point

There are two main principles that govern the melting point of an ionic liquid; the orientation of the cations and anions within a crystal lattice and the degrees of freedom (disordering) allotted.\textsuperscript{21} The crystal packing ability (Figure 6) and lattice energy of an ionic liquid are mainly due to the symmetry of the cation, and coulombic interactions between the cation and anion. The relationship between the lattice energy, the internuclear distance and charge of the ions is known as the Kapustinskii equation:

\[
E_c = \frac{M Z^+ Z^-}{4 \pi \varepsilon \varepsilon_0 r}
\]  

(Equation 1)

Where $M$ is the Madelung constant (packing efficiency), which is unitless and unique to individual ionic compounds, $Z$ is the absolute value of the magnitude of the positive or negative charges on the ions, $\varepsilon_0$ is the permittivity of free space and $r$ is the distance between the nuclei of the ions. According to the Kapustinskii equation, lower melting points are achieved when the charges on the ions are +/- 1 and the internuclear distance is maximized. There are also intermolecular cation-cation, anion-anion and cation-anion interactions that oppose the coulombic attraction between the ions. Decreasing the symmetry of the cation opposes the charge ordering due to the coulombic interactions that normally cause the system to crystallize.\textsuperscript{22} It has been previously shown that the solid structures of imidazolium-based ionic liquids are made up of an extended network of cations and anions that are connected by hydrogen bonds between the aromatic hydrogen atoms attached either directly to the imidazolium ring or indirectly to
the alkyl substituents. The number of anions (or cations) that surround each cation (or anion) can change depending on the size of either ion, but typically each anion is surrounded by at least three cations (and vice-versa). This nanostructural organization of imidazolium crystals is also observed in their liquid phase (Figure 6).  

Figure 6 Generic model of structural packing in ionic solids compared to structural packing in ionic liquids.  

The first neighbor shell of a given ion contains ions with opposite charge (hetero-interactions), the second, by ions with the same charge (homo-interactions) and so on. The imidazolium rings and the adjacent atoms (on the alkyl chain) belong to the polar network (domain), whereas the alkyl chain (where the number of carbons is greater than or equal to four) belong to the nonpolar domain. As the nonpolar domains get larger, the nonpolar domains begin to permeate the tridimensional polar network. However, the tridimensional polar networks still maintain their connectivity (i.e. ion channels) because of the stronger electrostatic force compared to that of the dispersion interactions in the nonpolar region.
Transport Properties

The diffusion of the ions that comprise an ionic liquid is very slow at room temperature. The transport properties of an ionic liquid such as diffusivity, viscosity and ionic conductivity can vary dramatically when subtle structural changes are made to either the anion or cation. For example, the viscosity and ionic conductivity depend on the translational motion of the ions. However, most mobile charge is carried by the cation.\textsuperscript{26} The Stokes-Einstein equation for calculating diffusion is shown below:

$$D = \frac{kT}{6\pi\eta r}$$

(Equation 2)

Where \( k \) is Boltzmann’s constant, \( T \) is absolute temperature, \( c \) is a constant, \( \eta \) is viscosity, and \( r \) is hydrodynamic radius of the species. Both the cationic and anionic components have self-diffusion coefficients which are independent from one another. In the same respect, cation-anion pairs do as well, but do not contribute to the conductivity of an ionic liquid due to their neutrality. Self-diffusivity can only be calculated utilizing molecular dynamic simulation (with/without the use of HNMR).\textsuperscript{26,27} Recent studies have computed this value by calculating the slope of the mean square displacement of the molecules versus time.\textsuperscript{27} Because these molecules tend to diffuse very slowly, data is taken over a relatively long period of time (at least 100ms). On the other hand, simulations can be performed at higher temperatures in a shorter time scale due to the increased dynamics of the system.\textsuperscript{26} A variation in the motions of atoms within different domains (polar and nonpolar) exists. The motion of the atoms in the alkyl chains is faster than that of the ring atoms due to the greater flexibility of the chain and its lower partial charge.
A study by Tsuzuki et al demonstrated that shorter chains resulted in higher self-diffusion coefficients.\textsuperscript{26} Also, ionic liquids composed of aromatic cations tend to have higher self-diffusion coefficients. These self-diffusion coefficients were also influenced by the anion chosen. The following trends were observed: TFSA\textsuperscript{−} > CF\textsubscript{3}CO\textsubscript{2}\textsuperscript{−} ≈ BF\textsubscript{4}\textsuperscript{−} > CF\textsubscript{3}SO\textsubscript{3}\textsuperscript{−} ≈ BETA > PF\textsubscript{6}\textsuperscript{−}. The self-diffusion coefficients of the ions in the TFSA-based ionic liquids are (incongruously) larger than those observed for the smaller BF\textsubscript{4} anion. A positive correlation between the stabilization energy for the formation of ethyl methylimidazolium (EMIM) complex with TFSA\textsuperscript{−} is significantly smaller than the stabilization energy calculated for EMIM\textsuperscript{+} complexes involving BF\textsubscript{4}\textsuperscript{−}. This suggested that the self-diffusion coefficients depend on the extent of anion and cation interaction. The relationship between the self-diffusion coefficients of the ions and the stabilization energies for the ion pairs indicate that at least three factors (size of ions, shape of ions and degree of interaction energy between anion and cation) play important roles in determining the self-diffusion coefficients. Consideration of the different motions which occur in ionic liquids (mainly within the polar and nonpolar domains) is crucial for understanding the transport properties of the ions and solute molecules in the ionic liquids.

**Applications in Research**

Due to the physicochemical and toxicological variability that can be achieved in ionic liquids, they can be utilized in many areas of research. In recent years, they have been used in biotechnological research as both solvents and also directly as
pharmaceutically active agents. In one study, the ionic liquids were polymerized incorporating the amino acid proline. As a result, the ionic liquid polymer was able to bind to a sample of DNA and assist in gene transfection and mediate gene expression without the need of additional reagents. In organic chemistry, ionic liquids have become a widespread alternative to traditional molecular solvents. This is due mainly to their negligible vapor pressure, large liquidus range and thermal stability. Their non-volatility and recyclability leads some to designate them as “green” solvents. There are a number of additional qualities which exemplify the solvent properties of ionic liquids. They can solubilize a wide range of organic and inorganic compounds. Furthermore, they are non-coordinating despite their purely ionic composition which makes them essentially chemically inert. They are immiscible with a number of organic solvents and provide a polar, non-aqueous substitute for two-phase systems. In electrochemistry, the field in which their derivation was established and flourished, the resistivity of the anion towards oxidation and the cation towards reduction gives rise to large electrochemical windows in which the redox chemistry of both organic and inorganic substances can be analyzed. Their wide electrochemical window, thermal stability (in some cases >350°C), and high conductivity allow ionic liquids to serve as excellent non-aqueous solutions in electrochemical systems such as fuel cells, batteries and capacitors and also as a medium in electrochemical processes such as electrodeposition.
Electrodeposition

Electrodeposition is the process by which metal ions in a solution coat the surface of an electrode via an electric field caused by an applied potential. The general set-up for an electrochemical observation that employs a working electrode consists of a cell which contains at least two electrodes (usually three) immersed in an electrolyte containing the analyte of interest (Fig. 7). One of the electrodes is the working electrode, and the other one is a combination of the reference electrode and the auxiliary (although this is not conventional). The potential of the working electrode is varied linearly with time (or remains constant) and serves as the site of metal ion reduction within the cell. The potential of the reference electrode (commonly silver-silver chloride) is kept constant because it is the electrode in which all potential is measured. The resistance of the reference electrode is large enough (>10^{11} ohms) that it draws essentially no current. The auxiliary electrode (counter electrode) is typically composed of platinum wire and is used to conduct electricity from a voltage generator through the solution to the working electrode.  

**Figure 7** General set-up for electrodeposition of metal ions. Where 1) is the cathodic compartment, 2) is the anodic compartment, 3) is the glass frit, 4) the working electrode, 5) the reference electrode 6) the auxiliary electrode and 7) is N_2/Ar inlet
The Working Electrode

The range of potentials in which a working electrode can operate depends on the material it is composed of as well as the type of electrolyte in which it is immersed. Positive potential limits are a result of large currents developing due to the oxidation of water to yield molecular oxygen whereas the cause for the negative limits is due to the reduction of water to molecular hydrogen. The four most common types of working electrodes used are composed of platinum, gold, carbon or mercury. Among these, platinum is the most used because of its favorable electrochemical inertness and ability to be easily molded into a variety of forms. The biggest disadvantage to using platinum electrodes is their high cost and sensitivity to water and acidic media which leads to the reduction of water (or H\(^+\) ions) to molecular hydrogen (which is potentially hazardous). Although gold electrodes behave similarly to platinum, they are inadequate in the positive potential range because their surface becomes oxidized. Carbon electrodes (usually in the glassy carbon form) can achieve a higher cathodic (positive) potential than platinum or gold but fabrication into different forms is very difficult. Like carbon, mercury can achieve very high cathodic potentials and is not as effective in the negative range due to its ease of oxidation. However, it is the only liquid metal at room temperature and thus can serve as a continuously renewed electrode surface. The biggest disadvantage with using mercury electrodes is their toxicity. The limitations of the three other electrode materials in conjunction with the high cost of platinum is the reason that many have chosen alternative electrode materials. Modified electrodes are electrodes produced by chemical modification of various substrates (metals, polymers etc.). These modifications include the irreversible application of functionalized adsorbing substances.
(electrodeposition of alternative metals or metal clusters), covalently bonding substances to the surface, or application of a polymer film (or films of other substances).\textsuperscript{9}

\textbf{Figure 8.} Image of gold, platinum and glassy carbon microelectrodes, respectively.

\textbf{Metal Cluster Compounds}

Metal cluster compounds are a group of at least two metal atoms bonded together via metal-metal bonding. In the last four decades they have attracted a considerable amount of attention due their unique molecular characteristics. These clusters have exhibited behavior that is intermediate between atomic and solid phases thus leading some to constitute them as a new phase of matter.\textsuperscript{31} In these structures, there is a substantial gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). As additional metal atoms are added to the structure, the HOMO-LUMO gap shrinks significantly and causes the energy levels of the cluster to resemble the energy bands of the corresponding solid. The electronic structure of a cluster can dictate whether the cluster acts as metal or a semiconductor. For
example, clusters of metallic elements generally have smaller HOMO-LUMO gaps than that of semiconductor elements. Extensive research has been performed on transition metal clusters. Transition metals are defined as metals which form at least one stable ion in which the $d$-orbitals are incompletely filled (can be applied to individual elements as well). These metals make excellent catalysts due to their ability to change oxidation states and adsorb other substances onto their surfaces resulting in their activation. Metal clusters exhibit similar atomistic properties on their surfaces and their bond lengths are shorter than typical metal compounds. Furthermore, the properties of the clusters can be altered by changing the ligands, cluster configuration (triangular, tetrahedral etc.) and incorporating hetero-nuclear metal atoms. They can also be used as homogeneous catalysts due to their high solubility in a number of solvents. The two key advantages that metal clusters have over mononuclear compounds are: i) the ability to bind many small molecules such as gases and small chain alcohols via multiple metal-ligand bonds and ii) the ability to facilitate multi-electron transfer processes. The transition metals are designated as either early transition metals or late transition metals.

**Metal Clusters: Early Transition Metals**

Early transition metal clusters are electron poor and contain $\pi$-donor ligands (typically oxygen- and nitrogen-based) that contribute extra electrons to the core metals. Ligands can also be sulfur-, halide-, or alkoxy- based as well. Niobium, tantalum, molybdenum, and tungsten tend to have higher formal oxidation states (+3,+4) which help to stabilize the metal cluster unit, by increasing the metal-metal bonding effects. The
highly electropositive nature of the early transition metals forces them to adopt triangular and octahedral metal geometries (Fig. 9).\textsuperscript{35}

![Figure 9](image_url) Examples of early transition metals with a) triangular and b) octahedral geometries

**Figure 9** Examples of early transition metals with a) triangular and b) octahedral geometries

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**Metal Clusters: Late Transition Metals**

The late transition metal clusters are formed by electron-rich transition metals in their low oxidation state (0, +1) and are complexed with $\pi$-acceptor ligands that withdraw electrons from the metals.\textsuperscript{33} These ligands include: phosphine, cyano, nitrosyl and carbonyl groups. The carbonyl ligand is the most popular of the $\pi$-accepting ligands because it occupies terminal, edge-bridging, or face-capping locations in a cluster which helps to balance the metal cluster unit by stabilizing the low oxidation state of individual metal atoms. Typical geometries for these types of metal cluster units are triangular and tetrahedral (Fig. 10).\textsuperscript{33}
Clusters containing three metal atoms (M₃) form the following basic structures:

a) M₃X₆ (without any μ₃-ligand)
b) M₃X₁₃ (containing one μ₃-ligand)
c) M₃X₁₇ (containing two μ₃-ligands)

Metal clusters with the M₃X₆ structure are typically found in complexes containing the [M₃X₆(C₆Me₆)₃]ⁿ⁺ cation (where M=Nb, Ti, Ta and X= Cl, Br). As shown in Figure 11, the metal atoms are bonded together via single bonds, forming a triangular metal unit with two halide atoms creating a bridging bond between neighboring metal atoms (essentially forming a square planar geometry). The three C₆Me₆ molecules coordinate on each of the metal atoms at the axial position. In metal clusters with the M₃X₁₃ structure, compounds have the formula [M₃(μ₃-X)(μ₂-Y)₃L₉]ⁿ⁺ (where M=Ti, Nb, Mo and W). The capping ligands (X) can be Cl⁻, Br⁻, I⁻, O²⁻, S²⁻, and OCH₂CMe₃⁻ whereas the bridging ligands (Y) can be Cl⁻, Br⁻, I⁻, O²⁻ or S²⁻. The terminal ligands (L) can be F⁻, Cl⁻, Br⁻, I⁻, O²⁻, H₂O, OEt⁻, O₂CCMe₃, CN⁻, and a few other acetate based ligands. The structure type M₃X₁₇ is found in compounds with the formula [M₃(μ₃-X)₂(μ₂-O₂Y)₆L₃]ⁿ⁺.
where $M=\text{Mo}$, $W$ and $X=\text{O}^{2-}$, $\text{OEt}^-$. The bidentate bridging ligands $O_2Y$ can be $\text{MeCO}_2$, $\text{EtCO}_2$, and $\text{tBuCO}_2$ whereas the monodentate, terminal ligands ($L$) are typically $\text{H}_2\text{O}$ molecules.\textsuperscript{35}

**Figure 11.** General structure of a) $M_3X_6$, b) $M_3X_{13}$ and c) $M_3X_{17}$ trinuclear clusters.

**Trinuclear Tungsten Clusters**

This study utilizes metal clusters containing the early transition metal tungsten. Due to its low oxidation state, it readily forms trinuclear metal clusters with bond orders ranging from 0.667 to 1. These clusters typically form complexes derived from the $[M_3X_{13}]$ or $[M_3X_{11}]$ structure type and are found in three forms. For example, in the aquo ion $[W_3O_4(H_2O)_9]^{4+}$ the tungsten atoms are bonded in a triangular formation (Fig. 12a). The $M-M$ bonds are capped by a single oxygen atom on one side and three oxygen atoms bridge each pair of metal atoms on the opposite side. The nine water molecules can be
partially or completely replaced by a variety of ligands including: oxalate, EDTA, NCS⁻, and thio derivatives. Preparation of these types of complexes usually involves the reduction of tungsten (VI) or tungsten (V) using sodium borohydride. The trinuclear complexes containing alkoxides have the general formula \([\text{W}_3(\mu_3-X)(\mu_3-\text{OR})(\text{OR})_9]\) where \(X=\text{O}, \text{NH}\) (Fig. 12b). These complexes are bicapped by two \(\mu_3\)-oxygen atoms with single bridges spanning the W-W bonds. The last type of trinuclear tungsten oxo complex is based on the \([\text{M}_3\text{X}_{11}]\) structure and contains the \([\text{W}_3\text{O}_2(\text{O}_2\text{CR})_6(\text{H}_2\text{O})_3]^{2+}\) cation (Fig.12c). The structure also contains the triangular \(\text{W}_3\) unit and is also bilaterally capped by \(\mu_3\)-oxygen atoms. Moreover, each W-W bond is bridged via an acetato- group. This type of cluster is typically synthesized utilizing a one-step process involving tungsten (VI) hexacarbonyl and acetic acid (or any carboxylic acid). 35

![Figure 12](image)

**Figure 12** Representations of metal complexes of a) \([\text{W}_3\text{O}_4(\text{H}_2\text{O})_6]^{4+}\), b) \([\text{W}_3(\mu_3-X)(\mu_3-\text{OR})(\text{OR})_9]\) and c) \([\text{W}_3\text{O}_2(\text{O}_2\text{CR})_6(\text{H}_2\text{O})_3]^{2+}\)

**Aims of this Research Study**

In an effort to alleviate the current issues with DEFCs, the electro-catalytic properties of the previously discovered tungsten trinuclear metal clusters are investigated in a non-aqueous, neutral electrolyte. It is proposed that modification of the platinum
electrode will result in the formation of an electrode with enhanced electrocatalytic properties. In addition, the effects of doping a hydrophobic ionic liquid with a hydrophilic ionic liquid will be explored.
II. EXPERIMENTAL

Materials

Ionic Liquids

N-methylimidazole (99%) was purchased from Sigma Aldrich Chemical Company, Inc. and was redistilled under vacuum at 100mmHg at 80 °C. Lithium bis(trifluoromethanesulfonyl)-imide was purchased from 3M Corporation and used as received. 1-chloroethane gas (99.7%) was purchased from Sigma Aldrich and used without any further purification. Sodium tetrafluoroborate (97%) and Silver tetrafluoroborate (99%) were used as received from Alfa Aesar Co. Ethyl trifluoroacetate (99%) was also purchased from Alfa Aesar Co. and used as received.

Metal Cluster Compounds

Tungsten hexacarbonyl (W(CO)₆), sodium tungstate (Na₂WO₄•2H₂O), and trifluoromethanesulfonic acid (CF₃SO₃H) were purchased from Alfa Aesar Co. Dowex 50x2-100 (H⁺ form) ion exchange resin was purchased from Fisher Scientific Co and used as received. Glacial acetic acid and acetic anhydride were reagent grade and also purchased from Fisher Scientific Co.
Instrumentation and Characterization

Infrared spectra were obtained using a Nicolet 6700 FT-IR. UV-Vis absorption spectra were obtained using a USB 4000 spectrometer which employed an LS-1 tungsten halogen lamp. The software used to interpret spectra was Omnic Ocean Optics Spectra Suite version . NMR spectra were obtained on a Bruker Advance 300 MHz NMR in deuterated acetone and are reported relative to tetramethylsilane as an internal standard. Water determination was performed on a Denver Instruments Coulometric Karl Fischer Titrator, model 260. Water content of ionic liquids was measured in parts per million using Hydranal purchased from Sigma Aldrich as a calibration standard. Concentrations of 1000 ppm and 100ppm were used and sample sizes ranged from 50-100 μL. Injections were done using a glass syringe equipped with a stainless steel needle and Teflon® plunger. Determination of the electrochemical windows of the ionic liquids was performed using EG & G Princeton Applied Research Potentiostat/ Galvanostat (Model 173) equipped with a PAR 175 universal programmer. Analog data were converted to digital data using a MacLab 4 Analog/Digital Instrument Interface. Digital data were recorded by Scope V 3.1 software and eChem V 1.5 software. A platinum microelectrode was used as the working electrode, platinum wire as the auxiliary electrode and HCl treated silver wire was used as the quasi-reference electrode. Scan rates used to determine electrochemical windows were 100 mV/sec. Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy were performed at Wright-Patterson Air Force Base. In addition, organo-metallic molecular models were generated using Spartan ’10.
Synthesis

Synthesis of 1-ethyl-3-methylimidazolium chloride (EMICl)

In a nitrogen-filled glove bag ethyl chloride was slowly condensed into a safety coated pressure bottle manufactured by Ace® Glass Co. that was submerged in a Dewar flask which contained a mixture of liquid nitrogen and ethanol at a temperature of -40°C. When the desired amount of ethyl chloride was obtained, 1-methylimidazole (and magnetic stir bar) was added to the reaction flask so that ethyl chloride was in slight excess (~10%) and the bottle was sealed using a threaded Teflon® stopper. The reaction flask was allowed to warm to room temperature and place in a stirred oil bath at 37°C. The solution became cloudy within twenty-four hours then proceeded to separate into two layers. When a decrease in the volume of the top layer could no longer be observed, the reaction was considered complete (1-2 weeks depending on temperature). The reaction flask was removed from the heat and placed in the freezer to facilitate crystallization. The excess ethyl chloride was decanted and the crystals of EMICl were dissolved in ~20 mL of acetonitrile and recrystallized with ethyl ether. The crystals of EMICl were filtered under vacuum using Schlenk techniques and allowed to vacuum dry for twenty-four hours.

Synthesis of 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIBF₄)

EMIBF₄ was synthesized via a salt metathesis reaction of EMICl and sodium tetrafluoroborate. First, EMICl was dissolved in 100 mL of distilled water. Then an equimolar amount of sodium tetrafluoroborate was dissolved in 100 mL of distilled water. Both solutions were combined into a 250-mL round bottomed flask and allowed to
stir over night. Excess chloride ions were removed via potentiometric titration using silver tetrafluoroborate.

Constructing the Standard Titration Curve

Drops of a dilute (1:1 water) EMICl solution were added to a 125-mL Erlenmeyer flask containing 50 mL of water until potential decreased from 258 mV down to ~60 mV (at which point chloride ions were assumed to be in excess). Under constant stirring, silver tetrafluoroborate was added dropwise and the voltage was recorded until it reached ~450 mV (at which point silver ions were assumed to be in excess. A plot of the potential versus drops of silver tetrafluoroborate showed that the potentiometric equivalence point was 248.5 mV. The working electrode used to monitor the potential during titration was a combination electrode which contained Ag/AgCl and the reference electrode which was Hg/HgSO₄.

Titration of EMIBF₄

EMIBF₄ was diluted with equal parts of distilled water in a 250-mL Erlenmeyer flask. Once the initial reading was determined (38 mV), silver tetrafluoroborate was added dropwise until slightly passed the equivalence point. Precipitated silver chloride was removed via suction filtration using an E-porosity filter. The remaining solution was then roto-evaporated and placed on high vacuum to remove any residual water.
Synthesis of 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide (EMITFSI)

Synthesis of EMITFSI was conducted using the salt metathesis method using EMICl and LiTFSI. Equimolar quantities of EMICl and LiTFSI were dissolved separately in minimal amounts of deionized water. The resulting solutions were then combined in a round bottom flask and allowed to stir for 48 hours. The reaction mixture turned cloudy after 24 hours and as the reaction proceeded, a layer of EMITFSI formed at the bottom of the flask leaving an aqueous layer on top. When the reaction was complete, the aqueous layer was decanted and the mixture was transferred to a separatory funnel. The remaining EMITFSI was washed until the aqueous rinse was free of chloride ions as indicated by reaction with AgNO₃ (about 30 times) and dried under high vacuum for 24 hours to remove residual water.

Synthesis of 1-ethyl-3-methylimidazolium trifluoroacetate (EMITfA)

A modified procedure was used for the preparation of EMITfA. In a nitrogen filled glove bag, 26.15 g (0.272 mol) of 1-methylimidazole was added to a 500 mL round-bottomed flask equipped with a reflux condenser which had two additional outlets and a magnetic stirrer. The methylimidazole was then diluted with 120 mL of 1,1,1-trichloroethane and 69.7 g (0.544 mol) of ethyl trifluoroacetate was added to the flask in one portion. The mixture was refluxed for 3 days and the ionic liquid was decanted, washed twice with 50 ml of trichloroethane and once with 50 ml of tert-butyl methyl ether then dried for 24 hours at 80°C under high vacuum.
Figure 13 Reaction apparatus for EMITfA and metal clusters.

Synthesis of \([\{\text{W}_3\text{O}_2(\text{O}_2\text{CCH}_3)_6\}\text{(H}_2\text{O})_3\}\{\text{CF}_3\text{SO}_3\}_2\)

Using the same setup shown above, W(CO)_6, (2g, 5.6mmol) was refluxed overnight with 200mL of a 1:1 mixture of acetic anhydride and acetic acid using Schlenk techniques. The solution turned a dark green and the yellow precipitate that formed upon cooling was filter off. The solution was diluted with equal parts of deionized water, adsorbed on a cation exchange column (Dowex 50W-x2), and eluted with 2M HCF3SO3. As the solution eluted the column, two bands formed. UV-Vis Spectra confirmed that the last band to elute the column was the desired product. Slow evaporation of the solution
yielded yellow-green crystals. Upon washing the crystals with hexane, some of the green
discoloration was removed.\textsuperscript{37}

**Synthesis of $\{[W_3O_2(O_2CCH_2CH_3)_6](H_2O)_3\}(BF_4)_2 \cdot 5.5H_2O$**

This compound was previously prepared using analogous methods.

**Electrochemical Deposition of Metal Clusters**

Electrochemical deposition of the metal clusters
\{[W_3O_2(O_2CCH_2CH_3)_6](H_2O)_3\}(CF_3SO_3)\textsubscript{2} and \{[W_3O_2(O_2CCH_2CH_3)_6](H_2O)_3\}(BF_4)\textsubscript{2} \cdot 5.5H_2O was performed using a typical cathodic deposition set-up and procedure. Approximately 100mg of the metal clusters were dissolved in 30 mL of EMIBF\textsubscript{4} and EMITFSI under vacuum with constant heating and stirring. The solutions were then transferred to electrodeposition cells shown below in Figure 14.

\textbf{Figure 14} Electrodeposition setup.
The cell potential was set at -1.42V and gradually ramped to -1.80V over the course of five days while the solution was stirred and purged with nitrogen. The progress of the electrodeposition was monitored using cyclic voltammetry. At which time the green electrical lead was disconnected from the platinum foil electrode and connected to the platinum disk electrode.
In this study, the electrochemical properties of the tungsten trinuclear metal clusters \([\{W_2O_3(O_2CCH_3)_6\}(H_2O)_3\}(CF_3SO_3)_2\) and \([\{W_3O_2(O_2CCH_2CH_3)_6\}(H_2O)_3\}(BF_4)_2\cdot 5.5H_2O\) were investigated in EMITFSI, EMIBF4 and EMITFSI doped with EMIBF4 ionic liquids. It was proposed that altering the anionic components on the metal clusters or the ionic liquids would either enhance or reduce the solubility of the metal clusters in the ionic liquid. Hence, decreasing or increasing the number of ions in solution thus decreasing or increasing the amount that would be available for reduction at the electrode surface during the electrochemical deposition process. This would in turn affect the thickness and uniformity of the electroplated surface as well as the overall efficiency of the electrocatalyst.

**Synthesis and Characterization of Tungsten Clusters**

\([\{W_2O_3(O_2CCH_3)_6\}(H_2O)_3\}(CF_3SO_3)_2\)

The tungsten trinuclear cluster with triflate as its anion was synthesized and characterized using UV-Vis, FT-IR and cyclic voltammetry. The reaction proceeded through the controlled oxidation of \(W(CO)_6\) with acetic acid. This process occurs via a series of unspecified reaction steps. The resulting solution was filtered and passed through a cation exchange column and eluted with HCF\(_3\)SO\(_3\). Two separation bands were
observed on the column. In order to distinguish between various products, UV-Vis was employed and the correct band was collected as it eluted the column based on the spectrum which matched previously published spectra.

\[
\left\{\left[\text{W}_3\text{O}_2(\text{O}_2\text{CCH}_2\text{CH}_3)_6\right]\left(\text{H}_2\text{O}\right)_3\right\}(\text{BF}_4)_2\cdot 5.5\text{H}_2\text{O}
\]

This compound was previously synthesized using methods analogous to the synthesis of \(\left[\text{W}_2\text{O}_3(\text{O}_2\text{CCH}_3)_6\right]\left(\text{H}_2\text{O}\right)_3\right\}(\text{CF}_3\text{SO}_3)_2\). However, HBF\(_4\) was used as the eluting solution rather than HCF\(_3\)SO\(_3\).

Figure 15 UV-Vis electronic spectrum of first rinse of trinuclear tungsten clusters that eluted the column.
Figure 16 UV-Vis electronic spectrum of first band to elute the column.

Figure 17 UV Vis electronic spectrum of the desired trinuclear tungsten product.
Synthesis and Characterization of Ionic Liquids

Although the ionic liquids prepared in this study are commercially available, the purchased products contain water and small amounts of chloride ions that render them electrochemically impure and unsuitable for electrochemical applications. The presence of the chloride ions and water limit the electrochemical window of the ionic liquids. Syntheses which require the metathesis of a chloride-containing precursor molten salt, typically result in high residual chloride and water content. However, direct combination methods avoid this issue, yet still present with additional problems due to temperature sensitivity of the N-methylimidazole reagent.

1-Ethyl-3-Methylimidazolium Tetrafluoroborate

EMIBF$_4$ was prepared using N-methylimidazole and ethyl chloride followed by salt metathesis using NaBF$_4$. The synthesis involved the ethylation of N-methylimidazole at the N1 position of the imidazole ring. The next step required the exchange of the chloride anion coordinated to the EMI-cation with the BF$_4$ anion. This was done by combining equimolar amounts of EMICl and NaBF$_4$ in water. Evaporation of the water from the solution resulted in the precipitation of NaCl.
Scheme 4 Synthesis of EMICl

\[
\text{N-Methylimidazole} + \text{ethyl chloride} \rightarrow \text{EMICl}
\]

Scheme 5 Salt metathesis of EMICl with NaBF\(_4\)

\[
\text{EMICl} + \text{NaBF}_4 \rightarrow \text{EMBF}_4 + \text{NaCl}
\]

The pure EMIBF\(_4\) was characterized by IR spectroscopy, H-NMR and cyclic voltammetry. A cyclic voltammogram of pure EMIMBF\(_4\) is shown below indicating an electrochemical window of approximately 3.5 volts which is 0.7 volts lower than what has been reported in the literature. The negative potential limit of -2V corresponds to the reduction potential of the ethyl-methylimidazolium cation whereas the positive potential limit of +1.5V corresponds to the oxidation potential of the BF\(_4\) anion. Although the EMIBF\(_4\) was dried repeatedly for extended amounts of time on high vacuum, it still contained roughly <500 ppm of water as determined by testing with a Karl Fischer titrator.
In some cases, an excess of AgBF$_4$ was added to the ionic liquid resulting in excess Ag$^+$ ions being present in the solution. In addition to Ag$^+$ ions, incomplete filtration results in the presence of AgCl aggregates which also exhibit redox properties. The standard reduction potential for Ag$^+ \rightarrow$ Ag$^0$ is 0.80V whereas the standard reduction potential for AgCl $\rightarrow$ Ag$^+$ Cl$^-$ can be observed at approximately 0.22V. Due to the use of a quasi- silver reference electrode in ionic liquid, these potentials can be shifted. Furthermore, impurities may exist in the ionic liquids which are not derived from any of the starting or intermediate reagents but instead originate from improperly cleaned glassware. It has been shown in previous studies that EMIBF$_4$ readily absorbs moisture.$^{19}$ In this study, cyclic voltammograms were taken every 5 minutes under nitrogen purge to determine whether or not de-aerating the ionic liquid with nitrogen would be beneficial within a certain time frame prior to running cyclic voltammetry. It was found that at approximately five minutes the electrochemical window was 3.20V, at 10 minutes the EC window increased to 3.23V and at 15 minutes it was 3.12V. The results indicate that the
optimum purging time is approximately 5-10 minutes. Beyond 10 minutes, the benefits of
de-aerating the ionic liquid are overshadowed by water adsorption which limits the
potential window. This finding also indicated that EMIBF₄ would still absorb water
during electrodeposition under nitrogenous conditions.

Figure 19 Cyclic voltammogram of EMIBF₄ displaying an EC window of 3.20V after a 5 minute nitrogen
purge.

Figure 20 Cyclic voltammogram of EMIBF₄ purge displaying an EC window of 3.23V after a10 minute of
nitrogen.
Figure 21 Cyclic voltammogram of EMIBF$_4$ displaying an EC window of 3.12V after a 15 minute nitrogen purge.

1-Ethyl-3-Methylimidazolium Bistrifluoromethanesulfonylimide (EMITFSI)

EMITFSI was prepared via the salt metathesis route using EMICl and LiTFSI as described before. The resulting solution was heterogeneous with LiCl dissolved in the aqueous layer on top and the EMITFSI on the bottom layer containing residual LiCl. The aqueous layer was decanted followed by repeated washing (30x) of the IL with distilled water. The washing was complete when the aqueous rinse no longer tested positive for Cl$^-$ as indicated by the addition of AgNO$_3$. The IL was then dried under high vacuum to remove residual water.

Due to the hydrophobic nature of EMITFSI, the majority of the residual water was readily removed and the water content was determined to be <300ppm. In addition, Cl$^-$ was easily extracted and the EC window of the IL was found to be $\sim$4.3V. The
increase in the positive potential limit when equated to EMIBF$_4$, corresponds to the stability of the anionic component of EMITFSI to oxidation. When compared to the BF$_4$ anion specifically, the TFSI anion is more complex and therefore harder to oxidize.

![Cyclic voltammogram of EMITFSI](image)

**Figure 22** Cyclic voltammogram of EMITFSI.

1-Ethyl-3-Methylimidazolium Trifluoroacetate (EMITFA)

EMITFA was prepared via the direct combination method using N-methylimidazole and Ethyl trifluoroacetate dissolved in trichloroethane. The resulting solution consisted of the top organic layer and the bottom layer which contained the IL. Both layers had a yellow coloration however the IL was significantly darker. Upon repeated washing of the IL with trichloroethane and *tert*-butyl methyl ether, some of the yellow coloration was removed. NMR characterization and CV revealed that the IL still contained many impurities. It was found to be electrochemically impure as well when compared to physicochemical properties found in literature.$^{36}$
The H-NMR spectrum shown in Figure 23, clearly defines the hydrogen atoms associated with the imidizolium ring of EMIBF$_4$. Chemical shifts were found at $\delta_H$: 1.54(t, 3H, N-CH$_2$-CH$_3$), 4.25(s, 3H, N-CH$_3$), 4.40(q, 2H, N-CH$_2$-CH$_3$), 7.72(s, 1H, H-5), 7.80(s, 1H, H-4), 9.12(s, 1H, H-2). In comparison to the H-NMR spectra for EMITFA, the spectrum shown in Figure 24 is very convoluted. The high temperatures required to complete the synthesis of EMITFA using the direct combination method resulted in the production of many by products. Even after several washings with trichloroethane and tert-butyl methyl ether, the ionic liquid maintained a yellow hew and the IL could not be electrochemically purified. Under certain conditions, the color and purity of the ionic liquid could be improved.$^{36}$ Although it has been reported that the
electrochemical window of EMITfA is comparable to that of EMIBF$_4$, it was not observed in this research study so further use of this IL was not explored.

**Figure 24** $^1$H-NMR spectrum of EMITfA displaying many impurity peaks.

**Figure 25** Cyclic voltammogram of EMITfA displaying a significantly small potential window due to the presence of impurities.
Scheme 6 Synthesis of EMITfA

Electrochemistry of Metal Clusters in EMIBF₄ and EMITFSI

Cyclic voltammograms of the tungsten metal clusters were performed in both ILs in order to observe the redox chemistry of the metal clusters in a hydrophilic IL (EMIBF₄) and a hydrophobic IL (EMITFSI). The intent was to determine if the amount of the tungsten metal cluster in contact with the electrode surface would be influenced by the nature of the ionic liquid.
The cyclic voltammogram shown in Figure 26 shows a reduction peak at -1.41V which corresponds to the reduction of \( W_3(\text{CF}_3\text{SO}_3)_2 \). The peak at ~0V is due to the presence of \( \text{Fe}^{2+} \) in the ionic liquid. The formation of the reduction peak without a corresponding oxidation peak is indicative of an electron transfer process (E) which results in the formation of a reactant (R). “R” undergoes a chemical reaction faster than it can be converted electrochemically back into the original metal cluster (O). Thus this type of mechanism is referred to as an EC mechanism.

\[
\begin{align*}
E & \quad O + e \leftrightarrow R \\
C & \quad R \xrightarrow{k_{EC}} \text{Product(s)}
\end{align*}
\]
In the CV shown in Figure 27 above, the reduction peak at -1.42V signifies the reduction of the metal cluster $W_3(BF_4)_2$ whereas the peaks at -0.47V and +0.47V indicate reoxidations of electroactive species. These peaks could correspond to the oxidation of reduction degradation byproducts created in the reverse scan. When compared to the CV of $W_3(CF_3SO_3)_2$ in EMIBF$_4$ (Fig. 26), it is evident that the amount of $W_3(CF_3SO_3)_2$ being reduced is greater than that of the $W_3(BF_4)_2$ according to the Randles-Sevcik equation which directly relates the concentration of the dissolved species at the electrode surface to the current produced:

$$i_p = 2.69 \times 10^5 n^{3/2}AD^{1/2}Cv^{1/2}$$  \hspace{1cm} (Equation 3)

Where $i_p$ represents the current maximum, $n$ represents the number of electrons transferred in the process, $A$ is the area of the electrode surface, $D$ is the diffusion coefficient, $C$ is the concentration of the electroactive species, and $v$ is the scan rate.
Furthermore, because the anionic component of both the metal cluster and the ionic liquid are identical, the common ion effect can potentially explain the decreased solubility of the metal cluster in the ionic liquid and thus the decrease in the current generated. In addition, the larger bridging ligands could act as steric hindrances and limit diffusion of the metal cluster cation.

**Figure 28** Cyclic voltammogram of W$_5$(BF$_4$)$_2$ in EMITFSI

**Figure 29** Cyclic voltammogram of W$_5$(CF$_3$SO$_3$)$_2$ in EMITFSI.
When EMIBF$_4$ was added to the solution containing W$_3$(CF$_3$SO$_3$)$_2$ in EMITFSI, a small cathodic current was observed at $\sim$-1.42V. Therefore, it was concluded that addition of a higher conductivity IL (EMIBF$_4$) could serve as a “supporting electrolyte” thus increasing the conductivity of the electrolyte solution. When comparing ILs, it is necessary to take into consideration additional transport and intrinsic properties that affect the nature in which solutes interact with ILs, the way in which they are transported/diffuse through the ILs and thus how they respond to electrochemical stimuli.

**Electrodeposition of Metal Clusters in EMIBF$_4$, EMITFSI and EMIBF$_4$-doped EMITFSI**

Although EMIBF$_4$ absorbs water from the atmosphere even under nitrogenous conditions, its high conductivity ($\sim$14 mS cm$^{-1}$) makes it favorable for many
electrochemical applications. EMITFSI has a conductivity of 3.9 mS cm$^{-1}$; however, it
has a relatively wide electrochemical window which allows for higher working potentials
necessary to fully reduce or oxidize metals (4.5V). It was shown previously in Figure 30
that addition of EMIBF$_4$ to a solution of the W$_3$(CF$_3$SO$_3$)$_2$ cluster in EMITFSI enhanced
the redox properties of the metal cluster. As a result of this finding, it was believed that
carrying out the electrodeposition of the metal clusters in the hydrophobic EMITFSI
would allow for higher working potentials and prevent any intermediate species
generated in situ from being potentially oxidized. The addition of EMIBF$_4$ would
increase the conductivity of the metal cluster/IL solution. Thus, increasing the amount of
metal ions at the electrode interphase and consequently the amount of metal deposited on
the Pt electrode. The figures that follow represent the electrodeposition of the W$_3$(BF$_4$)$_2$
metal cluster. Although W$_3$(CF$_3$SO$_3$)$_2$ was visibly electrodeposited, the electrode surface
oxidized before any spectroscopic data could be obtained (Figure 33b). Therefore only
the results of the W$_3$(BF$_4$)$_2$ analysis will be discussed further.

Figure 31 Cyclic voltammogram taken after 24hr deposition overlaid on the CV taken prior to the
application of a potential.
Figure 31 represents the CV taken after 24 hours of electrolysis. The peak at -0.67V represents the irreversible reduction of the trinuclear tungsten cluster. Because the initial explorative CVs were taken in separate cells using similar but not identical electrodes, the extreme shift from the previously observed reduction peak of -1.42V to -0.67V occurred. The formation of a redox couple between ~0V and +0.5V indicates that an electron transfer (E) occurred followed by a chemical step (C). The product of the chemical step was electrochemically active (E) and thus formed the new product which was easier to reduce than the original metal cluster. This type of process is referred to as an ECE mechanism.

\[
\begin{align*}
  E & \quad O + e \leftrightarrow R \\
  C & \quad R \xrightarrow{k_{CE}} S \\
  E & \quad S + e \leftrightarrow T
\end{align*}
\]

Figure 32 Cyclic voltammogram taken 48 hours after electrodeposition.
After 48 hours of electrolysis, the concentration of the redox couple (discussed previously) increased significantly. In addition, a new irreversible reduction peak appeared at +0.56V as the concentration of the metal cluster decreased which was indicated by the current decreasing from -0.806mv to -0.667mv. It can be noted, that the electrochemical window of the IL decreased significantly as the electrolysis progressed. It has been previously reported that the electrochemical window of imidazolium-based ILs decreases in the presence of water due to the formation of water aggregates at the electrode surface which results in the evolution of hydrogen.\textsuperscript{38} Hydration water, like those of the metal cluster \([\{W_3O_2(O_2CCH_2CH_3)_6(H_2O)_{3}\}(BF_4)_{2} \cdot 5.5H_2O\], are believed to be strongly associated with the metal cluster, therefore, they behave differently than bulk water. Thus the electrochemical window of the IL is governed mainly by the reduction of the metal cluster at the electrode’s surface.

![Cyclic Voltammogram after electrodeposition was complete.](image)

**Figure 33** Cyclic Voltammogram after electrodeposition was complete.

The electrodeposition process was concluded after roughly five days due to the decline in the current generated at the initial reductive potential of -0.67 and the reduced
current drawn by the redox couple between 0-0.5V as seen in Figure 33. A thin film could be observed by the naked eye and is shown in Figure 34 taken under 100x magnification on a microscope equipped with a digital camera.

![Figure 34](image)

**Figure 34** Images of the \( W_3(\text{CF}_3\text{SO}_3)_{2} \) coated electrode (a) prior to oxidation (b) and the electrode deposited with \( W_3(\text{BF}_4)_{2} \).

A study performed by Liu *et al.*, reported the rapid oxidation of a nanocrystalline aluminum deposit due to the presence of decomposed ionic liquid on the surface of the electrode.\(^{39}\) It was shown that completely removing the IL from the deposited surface resulted in air stable, nanocrystalline aluminum deposits.
Scanning Electron Microscopy (SEM) and Energy-Dispersive X-Ray Spectroscopy (EDS)

SEM was used in conjunction with EDS in order to observe the external morphology and chemical composition of the Pt/W$_3$ electrode (Fig. 35 and Tables 4-6, respectively)

**Figure 35** SEMs of W$_3$(BF$_4$)$_2$ coated electrode taken before (a and c) and after (b and d) electrodeposition at 1,000 (a and b) and 50,000 (c and d) times magnification.
When comparing the SEMs of the original Pt foil electrode to the post-electrodeposition SEMs, it is evident that the surface of the Pt electrode has been modified. The surface of the Pt electrode zoomed 50,000 times was relatively smooth and pitted. However, after the deposition, the surface appeared “grainy” and continuous corresponding to a possible increase in roughness and filling of the Pt surface abnormalities. In addition, the metal cluster compound was not electrodeposited uniformly as indicated by EDS data.

**Table 4** EDS Data from Region 1

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>50.74</td>
<td>61.57</td>
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<tr>
<td>O</td>
<td>31.35</td>
<td>28.56</td>
</tr>
<tr>
<td>F</td>
<td>12.29</td>
<td>9.43</td>
</tr>
<tr>
<td>W</td>
<td>5.62</td>
<td>0.45</td>
</tr>
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**Table 5** EDS Data from Region 2

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<th>Atomic %</th>
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</thead>
<tbody>
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<tr>
<td>N</td>
<td>12.29</td>
<td>14.48</td>
</tr>
<tr>
<td>O</td>
<td>25.01</td>
<td>25.80</td>
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<tr>
<td>Fe</td>
<td>20.98</td>
<td>6.20</td>
</tr>
<tr>
<td>W</td>
<td>2.94</td>
<td>0.26</td>
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</table>
Table 6 EDS Data from Region 3

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<tr>
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<th>Weight %</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
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<td>53.94</td>
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<tr>
<td>N</td>
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<tr>
<td>O</td>
<td>23.56</td>
<td>24.39</td>
</tr>
<tr>
<td>Fe</td>
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<td>6.29</td>
</tr>
<tr>
<td>W</td>
<td>3.35</td>
<td>0.30</td>
</tr>
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</table>

Table 7 Atomic Percentages for W₃(BF₄)₂ Metal Cluster

<table>
<thead>
<tr>
<th>Atom</th>
<th>#</th>
<th>Atomic %</th>
<th>Subtotal Mass(%)</th>
<th>Subtotal Mass(g/mol)</th>
</tr>
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<tr>
<td>W</td>
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<td>5.88</td>
<td>43.37</td>
<td>551.52</td>
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<td>O</td>
<td>22</td>
<td>43.14</td>
<td>27.68</td>
<td>351.99</td>
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<tr>
<td>C</td>
<td>18</td>
<td>35.29</td>
<td>17.00</td>
<td>216.18</td>
</tr>
<tr>
<td>F</td>
<td>8</td>
<td>15.69</td>
<td>11.95</td>
<td>151.98</td>
</tr>
</tbody>
</table>

EDS acquisitions were performed on several regions of the modified Pt electrode in order to determine the morphology and elemental composition and to make sure that the data accurately represent the entire surface of the electrode. From these data, it was concluded that the atomic composition varied throughout the electrodedeposited layer. The data indicate that carbon, oxygen, and tungsten were present throughout the bulk layer and that the major atomic species was carbon (>10 wt %) whereas the minor atomic species was tungsten (<10 wt%). However, the bulk of the surface contained iron that
may have originated from the EMIBF₄, nitrogen that may have also been present in EMIBF₄ or the TFSI anion and fluorine from the degradation of the BF₄ anion (of both EMIBF₄ and metal cluster) overtime due to the presence of water. It can be inferred from these data, that initially only carbon, tungsten, oxygen, nitrogen and iron were being electrodeposited onto the Pt foil electrode but as the reductive potential was increased from -1.42V to -1.8V, the amount of the electrochemically generated metal cluster-containing species on the electrode increased. In addition, the amount of the carbon-containing species and fluorine increased as well. The high atomic percent of both carbon and nitrogen in the bulk electrodeposited layer can most likely be attributed to the adsorption of the EMI cation on the surface and possible incorporation of trapped EMI⁺ ions during electrolysis. This same behavior has been observed in the TFSI anion as well. Furthermore, the EMI cation in EMITFSI can decompose (>0.2%) far below its electrochemical limits. This decomposition also influences the morphology and grain size of the deposit. In addition, it has been shown that tungsten clusters adsorb small molecules such as CO and N₂ onto their surfaces. The presence of water in the bulk solution can lead to the formation of OH⁻ which facilitates the degradation of BF₄⁻ resulting in the development of F⁻ ions near the cathode layer.

The high carbon, oxygen and nitrogen content of the deposited layer was of great significance. Previous studies have indicated that the adsorption of ionic liquid ions has a critical influence on the chemistry within the electric double layer. Microscopic investigations have revealed that altering the electrode potential from negative to more positive potentials changes the orientation of alkyl-imidazolium cations at the electrode surface. At more negative potentials, the cations tend to align parallel to the electrode
surface whereas at more positive potentials, the cations tend to align perpendicularly (Fig. 36). Therefore, the cations may sterically hinder large metal cations from diffusing to the electrode surface. In addition, TFSI is a strongly coordinating anion. The multiple coordinating sites coupled with the attraction of the EMI cations could have limited the amount of metal ion present at the electrode.

**Figure 36** Orientation of EMI cations as a result of a) a more negative potential, and b) a less negative potential whereas c) is the proposed orientation of several electroactive species at the electrode surface.

It was proposed in earlier research that the integrity of the tungsten triangular unit was maintained after the electrodeposition process and that Pt bonded to the metal cluster via a lost water molecule at the axial position (shown in Fig. 37). Addition of axial ligands such as water has been shown to lengthen and weaken metal-metal bonds in di-
metallic structures. Axial ligands are also tedious to remove and even so, removal of the ligands does not reverse the elongation of the bond. Furthermore, due to steric effects, the presence of the acetate bridging ligands assists in lengthening the W-W bonds.

Figure 37 Previously proposed Pt-metal cluster complex in a) 2D b) 3D and c) not bonded to Pt electrode in lowest energy conformation

It is believed, however, based on the data acquired in this research study, that \{[W_3O_2(O_2CCH_2CH_3)_6](H_2O)_3\}^{2+} undergoes reductive electrolysis which most likely results in the degradation or alteration of the triangular dioxo-bridged M_3 unit (W_3O_2) and the generation of many stable and unstable electrochemical species. It is unknown whether the water molecules are present in the deposited layer due to the detection limits of SEM. When looking at metal clusters in general (excluding octahedrons), most stable structures contain 18 electrons per metal atom. The 18 electrons correspond to an inert gas configuration i.e. high stability and inertness. In accordance with this accepted
theory, the tungsten atoms in the metal cluster synthesized in this study also contain 18 electrons in their valence shells. Each tungsten atom is coordinated to seven oxygen atoms that donate two electrons, and the remaining four electrons are from the two W-W bonds. Out of those 18 valence electrons, only six electrons contribute to the metal-metal bonding character. Those electrons are located in the 1a$_1$ and 1e molecular orbitals and adopt the electronic configuration of (1a$_1$)$_2$ (1e)$_4$. The remaining molecular orbitals are non-bonding (2e) and anti-bonding (3e and 1a$_2$).$^{46}$

As a consequence, addition of electrons to the metal cluster through cathodic reduction would result in the electrons occupying the lowest unoccupied molecular orbital (LUMO) which is non-bonding. Some tungsten and molybdenum metal clusters have been found to exist with eight and nine electrons (respectively) in their core structures.$^{47}$ However, the core structure and bridging ligands differ dramatically which leads to differing electron delocalization and stabilization. It was found that altering the core from Mo$_3$O$_4$ to Mo$_3$OCl$_3$ substantially lowered the energy of the 2a$_1$ molecular orbital making the electronic configuration of (1a$_1$)$_2$(1e)$_4$(2a$_1$)$_2$ highly favored with the remaining electron occupying a degenerate orbital. The oxidation state of the metal atoms in the nine electron molybdenum moiety is +3.$^{48}$

Bonding in metal cluster atoms can be attributed to three main factors: i) maximization of the cohesive energy of the metal-metal bonds, ii) maximization of the energy of the metal-ligand bonds, and iii) minimization of the steric strain between ligands.$^{49}$ For example, adding ligands to a system may work to stabilize the metal cluster by maximizing metal-ligand bond energy or it can act to destabilize the metal polyhedron by removing electron density from the $d$ orbital thus diminishing metal-metal bonding.
energy. In addition, negative ligand-ligand interactions can evolve. In this present case, it is believed that adding more than two electrons adds to the anti-bonding character of the metal-metal bond which in turn decreases the bond order and lowers the energy of the LUMO thus causing subsequent electron additions to become increasingly favorable in terms of thermodynamics. The result would be disintegration or alteration of the original M₃O₂ unit and therefore fragmentation of the entire metal cluster.

UV-Vis spectra taken pre- and post- electrodeposition indicate that a change to the structure and possibly to the electronic configuration of the metal cluster has occurred. It is evident that the amount of lower energy transitions remains relatively constant whereas the amount of higher energy electron transitions has increased which corresponds to a reduction in delocalization which can correspond to structural changes. In fact, the UV-spectrum shown in Figure 38b closely resembles Figure 38c, suggesting that the cluster could have been reduced to a byproduct found in the original reaction mixture. However, without X-ray photoelectron spectroscopy (XPS), the electronic state, and thus the specific atomic species present on the electrode surface and within the remaining ionic liquid solution cannot be determined.
Figure 38 The electronic spectra of a) metal cluster prior to electrodeposition, b) post-electrodeposition and c) first band to elute during column chromatography
IV. CONCLUSION

This research study has shown that the electrochemical deposition of trinuclear tungsten metal clusters via cathodic reduction results in alteration of the structural components which comprise the W₃O₂ unit and/or the deposition of thin films that are unstable in air. In addition, it was discovered that doping of a hydrophobic ionic liquid with a hydrophilic ionic liquid with a higher conductivity, increases the concentration of electroactive species at the electrode surface which can potentially influence film thickness and morphology. Furthermore, it is evident that adsorption of both cations and anions may have limited the metal ions available for reduction at the cathode. Thus, implicating ionic liquids as not only solvent molecules, but also as electroactive reagents.

Due to the lack of XPS data, the electronic states of the atoms present on the surface of the electrode could not be determined. In future explorations of this research, it would be of great importance to gain knowledge of potential reduction byproducts in order to determine how or why the triangular metal unit disintegrates and the origin of the other major deposited components such as carbon, oxygen, and nitrogen. In addition, it would be beneficial to investigate the electrochemical properties of various triangular trinuclear tungsten clusters in varying ionic liquids in order to determine if there are electronic configurations which favor cathodic reduction, in hopes that the catalytic activity of these clusters towards small chain alcohols such as ethanol can be harnessed and further explored.
V. REFERENCES


44. Woods, C.J. Electrochemical Deposition of Molybdenum and Tungsten from Trinuclear Metal Clusters (M₃O₂(OAc)₆(H₂O)₃(CF₃SO₃)₂ in 1-Ethyl-3-methylimidazolium Tetrafluoroborate. M.S. Thesis. 2010. Wright State University.


