Electrochemical Oxidation of Ethanol in Ionic Liquids and Its Possible Use in Fuel Cells

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ELECTROCHEMICAL OXIDATION OF ETHANOL IN IONIC LIQUIDS AND ITS POSSIBLE USE IN FUEL CELLS

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

By

ASHLEY M. TOPPER
B.S. Wright State University, 2006

2010
Wright State University
March 16, 2010

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Ashley M. Mason ENTITLED Electrochemical Oxidation of Ethanol In Ionic Liquids and Its Possible Use In Fuel Cells BE ACCEPTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF Master of Science

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Abstract

Mason, Ashley. M.S., Department of Chemistry, Wright State University, 2010.

Electrochemical oxidation of ethanol in ionic liquid and its possible use in fuel cells.

Electrochemical properties of EtOH in EMImBF$_4$ ionic liquid were investigated and compared to the electrochemical properties of EtOH in 0.1M HClO$_4$/H$_2$O.

As was shown earlier, oxidation of EtOH in HClO$_4$/H$_2$O involves formation of PtO on the electrode surface, which makes the electrode poisoned. We have found that the best procedure for removal of PtO from the Pt electrode is heating the electrode in concentrated H$_2$SO$_4$. Cyclic voltammograms obtained after cleaning several Pt electrodes conforms that this treatment gives clean Pt electrodes without any PtO. Electrochemical oxidation of EtOH in EMImBF$_4$ ionic liquid show that is poisoning of Pt electrode by formation of PtO occurs even at high EtOH concentration (1mA).

A commercial phosphoric acid fuel cell (PACF) with EMImBF$_4$ electrolyte instead of H$_3$PO$_4$ concentrate was used. A polarization curve at 30 °C gives the open cell voltage of 0.25 V. For comparison the source cell with EMImBF$_4$ and H$_2$ fuel generates an open cell voltage of 0.70 V at 30 °C.
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Dedication

To my family, friends, and Dr. Katovic for not letting me quit even when it took me 4 years to finish my masters. And to my husband who supported me in every step I take. Woohoo finally finished.
I. Introduction

Molten Salts

Molten salts are liquids obtained by melting inorganic salts usually at relatively high temperatures. They have been known for hundreds of years but their practical application as solvents, began some 100 years ago when they were used as the solvent in electrochemical reduction of alkali metals and other transition metals. Molten salts are liquids composed entirely of ions. They are formed when the solid form of the salt is heated past its melting point. The terms “molten salts” and “fused salts” were the term used to describe inorganic salts in their liquid state. Some examples of molten salts would be LiCl, KCl, and NaCl whose melting points are 610°C, 776°C, and 801 °C respectively.3

Molten salts were used in electrochemical synthesis because they have a number of favorable physical and chemical properties. Although using molten salts as solvents have several advantages they also have a number of disadvantages. Molten salts have high ionic conductivity and are thermally stable at relatively high temperatures.2 They also have low or negligible vapor pressure. Most redox couples show reversible redox behavior in molten salts because of high associated temperature which speeds up the charge-transfer rate.2 They also have low densities and low dielectric constant. These liquids are non-aqueous in nature. The disadvantages of
molten salts are that they are corrosive and hygroscopic. Also, their high operating temperatures increases the necessity for safety precautions when working with these liquids. In addition, molten salts usually have a narrow electrochemical window because they contain halide anion. Most of these systems are moisture sensitive so extra care must be taken for their preparation.

There was a study done by the Dupont Company in 1930’s to try to decrease the temperatures needed to work with molten salts. Different melts were discovered that lowered the melting point of the molten salts to make them safer. Low temperature melts are obtained by combinations of different salts that when combined have a lower melting point than any of the original salts. Four different classifications of molten salts systems are given in Table 1. The most common mixture is known as the Hitec. Hitec is a mixture of KNO$_3$ + NaNO$_2$ + NaNO$_3$ and it has a melting point of 142 °C. The weight ratio of the Hitec mixture is 53:40:7 respectively. The reason why this mixture is so commonly used is because it has excellent thermal stability range up to 482 °C.$^6$

**Table 1. Classification of Ionic Molten Salt Systems**

<table>
<thead>
<tr>
<th>Type</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single</td>
<td>LiCl; NaNO$_3$; K$_2$CO$_3$</td>
</tr>
<tr>
<td>(cation + one anion)</td>
<td></td>
</tr>
<tr>
<td>Binary mixture (two cation + same anion)</td>
<td>LiCl + KCl; Na$_2$SO$_4$ + K$_2$SO$_4$</td>
</tr>
<tr>
<td>Tertiary mixture (three cations + same anion)</td>
<td>LiNO$_3$ + NaNO$_3$ + KNO$_3$</td>
</tr>
<tr>
<td>Quaternary mixture (four cations + same anion)</td>
<td>NaCl + KCl + MgCl$_2$ + CaCl$_2$</td>
</tr>
<tr>
<td>Reciprocal (different anions and cation)</td>
<td>LiNO$_3$ + NH$_4$NO$_3$ + NH$_4$Cl</td>
</tr>
</tbody>
</table>
Molten slat systems may be composed of various salts containing different anions like carbonates, halides, hydroxides, nitrates, thiocyanates, and sulfates. Depending on the required application, the appropriate molten salt system may be selected.

Carbonate melts are important because of their potential use for technological applications, for example for fuel cells or energy storage applications.\textsuperscript{2} Binary and ternary melts commonly use carbonate melts for use of electrochemical studies. These melts usually contain impurities such as hydroxide and oxide which result from dissociation and hydrolysis reactions.

\[
\text{M}_2\text{CO}_3 \rightarrow \text{M}_2\text{O} + \text{CO}_2
\]

\[
\text{M}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow 2\text{MOH} + \text{CO}_2
\]

**Ionic Liquids**

The term ionic liquid and molten salt have been used interchangeably in the past, but it is becoming more common to use the term ionic liquid to refer to salts that are liquids at ambient temperatures.\textsuperscript{7} Ionic liquids are salts that have a melting point below 100 °C. They consist entirely of ions which are usually composed of a large bulky organic cation and a small inorganic anion. By changing the cation and the anion, or both, their properties will change, such as: density, melting point, viscosity, and hydrophobicity. Their properties can be tailored to fit any requirements of a particular process that is why they are referred to as “designer solvents”.\textsuperscript{12}
most common that the cation accounts for the low melting point and the anion determines the chemical properties of the salts.⁸

The most common cations used in the formation of ionic liquids include (a) alkylsulfonium, b) alkylphosphonium, c) alkylammonium, d) N,N’-alkylimidazolium, and e) N-alkylpyridinium cations.⁸,¹¹

a) \([S_{x}R_{3-x}]^{+}\) b) \([P_{x}R_{4-x}]^{+}\) c) \([N_{x}R_{4-x}]^{+}\)

d) [Image of alkylimidazolium cation]
e) [Image of N-alkylpyridinium cation]

By changing anion or alkyl chain length different properties of ionic liquids are changed.¹⁴ Similarly, a large variety of ionic liquids can be produced just by varying an anion such as: BF₄⁻, CF₃CO₂⁻, CF₃SO₄⁻, and PF₆⁻. These anions are water and air insensitive and possess high thermal stability. Choosing the right anion, the ionic liquids properties such as air and water stability can be optimized.

Ionic liquids have strong ion-ion interaction, not often found in the high temperature molten salts. The strong interaction allows for many useful properties to be displayed by ionic liquids.
They are also thermally stable up to 400 °C. They have large electrochemical windows, and are electrochemically stable. The difference between the anodic and cathodic decomposition potential is greater than 4 V. They are relatively inexpensive and easy to synthesize. Ionic liquids have beneficial properties that allow them to be used as solvents in a wide range of chemical applications. These properties included high electrical conductivity, non-corrosive and non-toxic by nature, non-volatility with insignificant vapor pressure, immiscibility with a number of organic solvents, and the ions of the salts do not coordinates to transition metals.\textsuperscript{4, 8-11}

The term “Green Solvent” is often used to describe room temperature ionic liquids. These ionic liquids are used to replace organic solvents for synthetic chemistry and extraction techniques. The overall non-volatile, non-flammable, and thermally stable solvents are very promising replacements for the traditional volatile organic compounds (VOCs).\textsuperscript{13}
Table 2. Different properties of ionic liquids, including possible use as solvents.\textsuperscript{25}

<table>
<thead>
<tr>
<th>Properties</th>
<th>Possible Use as a Solvent</th>
</tr>
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<tr>
<td>- viscous liquid</td>
<td>- they do not evaporate like other solvents</td>
</tr>
<tr>
<td>- no measurable vapor pressure</td>
<td>- can be used in chemical synthesis, particularly catalysis</td>
</tr>
<tr>
<td>- non-explosive, non-oxidizing</td>
<td>- they have potential to make synthetic processes more efficient</td>
</tr>
<tr>
<td>- air and water stable</td>
<td>- can be used in separation technology</td>
</tr>
<tr>
<td>- able to solvate wide range of species: organic, inorganic and organometallic compounds</td>
<td>- highly polar noncoordinating solvents</td>
</tr>
<tr>
<td>- composed of poorly coordinating cations</td>
<td>- provide a nonaqueous, polar alternative for two-phase systems</td>
</tr>
<tr>
<td>- immiscible with a number of organic solvents</td>
<td></td>
</tr>
<tr>
<td>- the melting points are in the range +80$^\circ$C to –96$^\circ$C</td>
<td></td>
</tr>
<tr>
<td>- they have flexibility of structure (change of cation and anion)</td>
<td></td>
</tr>
<tr>
<td>- cheap and easy to synthesize</td>
<td></td>
</tr>
<tr>
<td>- high conductivity</td>
<td>-unique solvents for electrochemical investigation, especially for transition metal complexes, which might be unstable in other media</td>
</tr>
<tr>
<td>- a wide electrochemical window</td>
<td>- as an electrolyte in batteries and solar cells</td>
</tr>
</tbody>
</table>
Applications of Ionic Liquids

In 1914 room temperature ionic liquids were first discovered by Walden\textsuperscript{15}, but their potential applications was not realized till about twenty years ago as a result of a Star Wars research project on battery electrolytes.\textsuperscript{15-17} The very first ionic liquid that was recorded in literature was ethyl ammonium nitrate ([EtNH\textsubscript{3}][NO\textsubscript{3}]).\textsuperscript{11,15} There have been some new specific application for room temperature ionic liquids, such as solvents for use in solar cells, recovery of biofuels, and energy storage devices.

Because ionic liquids are not volatile and have no significant vapor pressure they have been used as a replacement to some the more volatile or toxic organic solvents. The Montreal Protocol of 1989 banned the use of volatile organic solvents, so ionic liquids would be a great substitution.\textsuperscript{14} Ionic liquids have also replaced volatile organic solvents in large scale industrial and pharmaceutical synthesis. In addition of being nonvolatile, they have potential to dissolve variety of organic, organometallic and inorganic compounds, making the synthesis more efficient. By varying either the chain length or the alky substituent can alter the lipophilicity of ionic liquids which then gives the ionic liquids with range of being either completely miscible or immiscible in organic species can be obtained. The ionic liquids that are immiscible with specific organic solvents provide a polar alternative for a two phase system and are non-aqueous. Ionic liquids are often composed of poorly coordinating ions, making them non-coordinating solvents with high polarity.
**Electrochemical Cell**

There are two types of electrochemical cells galvanic and electrolytic. In a galvanic cell chemical energy is spontaneously converted into electrical energy. In an electrolytic cell electrical energy from an external source is converted into chemical energy.

The Zn, Cu galvanic cell is shown in figure 1. The right half cell contains a Cu electrode universal in CuSO₄ solution, while the left half cell contains a Zn electrode in ZnSO₄ solution. The electrolyte bridge contains Na₂SO₄ solution and connected both solutions, allowing the migration of ions.

![Figure 1. Galvanic cell](image)

**Figure 1.** Galvanic cell
Cathode: $\text{Cu}^{2+} + 2 \text{e}^- = \text{Cu}$

Cu$^{2+}$ is reduced to Cu

Anode: $\text{Zn} = \text{Zn}^{2+} + 2 \text{e}^-$. 

Zn is oxidized to Zn$^{2+}$

A schematic representation of the cell is shown below:

$\text{Zn} \mid \text{Zn}^{2+} \parallel \text{Cu}^{2+} \mid \text{Cu}$

Two vertical lines between $\text{Zn} \mid \text{Zn}^{2+}$ and $\text{Cu}^{2+} \mid \text{Cu}$ represent phase interchanging (solid to liquid) while the two vertical lines in the middle represent the liquid interface between bridge and cathodic and anodic solutions.

The half cell, where reduction takes place, is called a cathode while the half cell where oxidation takes place is called anode. On the anode Zn is oxidize to Zn$^{2+}$ releasing two electrons.

$\text{Zn} = \text{Zn}^{2+} + 2 \text{e}^-$. 

On the cathode Cu$^{2+}$ is reduced by two electrons gives Cu metal.

$\text{Cu}^{2+} + 2 \text{e}^- = \text{Cu}$

The cell potential is calculated from the equation:
\[ E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} \]

\[ \Delta G = -nFE \]

If the cell potential is positive the \( \Delta G \) is negative i.e. the cell is galvanic.

An electrode is an electron conductor (metal or graphite) in contact with solution containing a redox couple. The galvanic cell chemical change is spontaneous \( (\Delta G = -) \). In an electrolytic cell nonspontaneous electrochemical reaction are forced to take place by applying potential.

**Electrochemical methods**

Electrochemical methods include a group of quantitative analytical methods that are based upon measurements of the electrical properties of a solution of the analyte in an electrochemical cell. There are three types of electrochemical methods:

1. **voltammetry** - methods that measure the relationship between the concentration and an electrical parameter such as potential, current, resistance (or conductivity), capacitance or quantity of electricity. The correlation between applied potential and resulting current is measured.

2. **potentiometry** – methods that measure potential of the cell are functions of concentration of electro active process.

3. **coulometric methods** – methods in which the amount of analyte is determined by measuring the amount of electricity \( (C) \) during the electrolysis in an electrolytic cell.
The most common electrochemical technique used for the study of variety of inorganic and organic species are cyclic voltammetry controlled potential coulometry, and spectroelectrochemistry.

Voltammetry

Voltammetric methods are a group of electrochemical methods in which information about the analyte is obtained from current vs. voltage curves (plots of current as a function of applied potential). Normally, the working electrode that is used in this type of analysis has a small surface area (few square millimeters) and is called mini electrodes.

The shape and amplitude of the applied potentials can be different giving rise to different voltammetric methods such as linear sweep voltammetry (LSV) with a linear change of potential, cyclic voltammetry (CV) and pulse voltammetry (PV). In 1938, Matheson and Nichols discovered CV and LSV \(^{21}\). In linear sweep voltammetry the potential of an electrode, which is immersed in an unsaturated solvent is linearly increased and the resulting current is measured. Randles \(^{22}\) and Sevcik \(^{23}\) did the theoretical treatment of current vs. potential. They found that current reaches a maximum value at a potential which is 28.5 mV more negative then \(E^\circ\):

\[
E = E^\circ - 0.0285/n \text{ V} \quad \text{for cathodic process}
\]
\[
E = E^\circ + 0.0285/n \text{ V} \quad \text{for anodic process}
\]

The change in current as a function of the applied potential is called voltammogram, and is shown below on figure 2. Voltammograms show the change in reduction/oxidation currents as a
function of the applied potential. For the reaction \( O_x + n\text{e}^- \leftrightarrow R \) the concentration of R increases (O decreases).

As an outcome the cathodic current increases and reaches a maximum. The maximum is obtained when all of \( O_x \) in the proximity of the electrode is reduced to give R. If now (in the case of cyclic voltammetry) the potential is reversed in a positive direction, the reaction then goes in the opposite direction and oxidation occurs (\( R \rightarrow O_x \)), the cathodic current decreases and the anodic increases and reaches a maximum when \( E = E^\circ + 0.0285/n \).

Peak potential is obtained when:

\[
E_p = E_{1/2} - 28.5/z \text{ mV} \quad \text{at 25°C}
\]
For an electrochemically reversible process the peak potential separation, $\Delta E_p$, is independent of the concentration of electroactive species and independent of the scan rate. It is characteristic of the electroactive species in a given solvent. Peak current ($I_p$) at 25°C is given by the Randles-Sevcik equation \(^{22,23}\) which correlates the current as a function of $A$, $c_0$ and applied potential:

\[
I_p = 2.69 \times 10^5 \text{C/molV}^{1/2} \cdot n^{3/2} \cdot A \cdot D_0^{1/2} \cdot v^{1/2} \cdot c_0
\]

$A$=surface area of electrode (cm$^2$)

$n$=number of electrons

$c_0$=concentration of oxidized species (mol/cm$^3$)

$D_0$=diffusion coefficient (mol/cm$^3$)

\[
a = z \cdot F \cdot v / RT
\]

$v$=scan rate (V/s)

$\tau$=time (s)

$I_p$ has unit Ampers.

**Cyclic voltammetry**

A cyclic voltammetry cell employs three electrode systems: the working, the reference, and the counter or auxiliary. The current between the working and the counter electrode is measured as a function of applied potential. Figure 3. shows a typical cyclic voltammogram (CV), for a reduction process $O_x + ne^- \rightarrow R$. The applied potential is scanned first in a negative direction, and then reversed back to the initial potential.
In the forward negative sweep the electroactive species is reduced $O_x + ne^- \rightarrow R$. At the potential which is about 0.2V more negative than the peak potential, predominant species at the surface of the electrode is $R$. On the reverse positive sweep, the $R$ is reoxidized back to the initial species $O_x$, $R-ne^- \rightarrow O_x$, giving the anodic current with a peak at $E_{p,a} = E_{f/2} + 0.0285/n \text{ V}$. Characteristic parameters of cyclic voltammograms are the cathodic peak potential ($E_{p,c}$), the anodic peak potential ($E_{p,a}$), the cathodic peak current ($I_{p,c}$) and the anodic peak current ($I_{p,a}$). The parameters are shown in Figure 3. The formal reduction potential $E^\circ$ for an electrochemically reversible process is:

$$E^\circ = E_{p,c} + (E_{p,a}/2)$$
The peak potential separation $\Delta E_p$, gives the number of electrons, $n$, involved in the redox reaction:

$$\Delta E_p = E_{p,c} - E_{p,a} = 0.059/n$$

The peak current is given by the Randles-Sevcik equation:

$$I_p = 2.69 \times 10^5 C/molV^{1/2}\cdot n^{3/2}\cdot A\cdot D_o^{1/2}\cdot v^{1/2}\cdot c_o$$

For a simple electrochemically reversible reaction when both Ox and R are stable

$$I_{p,c} = I_{p,a} \quad (or \quad I_{p,c}/I_{p,a} = 1)$$

The standard rate constant, $k^o$, for the electron transfer process can be determined using the peak potential separation, obtained from a different scan rate. The peak potential separation increases with the scan rate when the standard rate constant, $k^o$, is small in comparison to the scan rate.

$$I_{p,c} / I_{p,a} < 1$$

When the ratio $I_{p,c}/I_{p,a}$ is less than 1, which means the chemically unstable reaction product has undergone further chemistry the following chemical step can be obtained for the $I_{p,c}/I_{p,a}$ ratio and the scan rate, $v$:

$$O_x + ne^- \rightarrow R \rightarrow Z$$

In the case of an electrochemically irreversible reaction, there will be no current on the reverse sweep as well as a shift in the peak potential of 30 mV/α n as well as a 10 fold increase in scan rate ($v$).

Table 3 shows different CV characteristics for reversible quasireversible, and irreversible processes. The different processes can be distinguished by the rate of the electron transfer process. Reversible and quasireversible voltammograms are shown in Figure 4.
Table 3. Properties of reversible, quasireversible and irreversible electrode processes.\textsuperscript{25}

<table>
<thead>
<tr>
<th>Type of process</th>
<th>$E_{p,c}, E_{p,a}$</th>
<th>$E_{p,c} - E_{p,a}$</th>
<th>$I_{p,c}/I_{p,a}$</th>
<th>$I_p/\sqrt{V}$</th>
<th>$I_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reversible</td>
<td>- do not depend on $\nu$</td>
<td>$= 57/n$ mV independent of $\nu$</td>
<td>$= 1$ independent of $\nu$</td>
<td>$= \text{constant}$ independent of $\nu$</td>
<td></td>
</tr>
<tr>
<td>Quasireversible</td>
<td>- both cathodic and anodic peaks are drawn, but their shape and height depends on $\alpha$, $k^o$, $D_0,D_R$</td>
<td>- is higher than for reversible process and it depends on $\nu$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Irreversible</td>
<td>- depends on $\nu$</td>
<td>- there is no current on the reverse sweep</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$\nu$ = 57/n mV independent of $\nu$; $I_p$ = constant independent of $\nu$; $I_p/\sqrt{V}$ depends on $\alpha$, $k^o$, $D_0,D_R$ independent of $\nu$. 
The standard rate constant of the electron transfer ($k^0$) and the scan rate ($\nu$) are the kinetic parameters of the electrode reaction upon which the electrochemical reversibility of a voltammetric curve depends. The following limiting values given by H. Matsuda and Y. Ayabe can be used to determine whether the process is reversible. If $\alpha=0.5$, $D_o=D_R$, at 25°C the voltammogram will be:

a. reversible if $k^0/\nu^{1/2} \geq 0.3 \text{ cm/s}$

b. quasireversible if $0.3 \text{ cm/s} \geq k^0/\nu^{1/2} \geq 2 \cdot 10^{-5} \text{ cm/s}$

c. irreversible if $k^0/\nu^{1/2} \geq 2 \cdot 10^{-5} \text{ cm/s}$. 
Figure 4. Example of A. reversible, B. quasireversible cyclic voltammograms.
Figure 5. Cyclic voltammetry of Fe (CN)$_6^{3-}$.
(b-d) cathodic current increases
(d-f) cathodic current decays
(i-j) anodic current increases
(j,k) anodic current decays
I,p,a anodic current peak
I,p,c cathodic peak current [max]
E,p,a anodic peak potential
E,p,c cathodic peak potential [at max]

Cyclic voltammetry has become a very useful and simple technique to study a redox chemistry of a system. For that reason cyclic voltammetry has often been referred as an electrochemical equivalent of spectroscopy. In addition to obtaining the characteristic voltammogram (spectrum), information pertaining on the rate of electron transfer step to the stability of the reduction product as well as the chemistry of the chemical reaction(s) that follow the electrochemical step is also obtained.\textsuperscript{25}

**Fuel Cell**

Fuel cells are devices that convert chemical energy directly into electrical energy. It is foreseen that fuels cells will be the favored energy source as fossils fuels runs out. Hydrogen will be the preferred fuel, and will become the world leading fuel and energy resource. Solar cell will be used to electrolyze water and generate the hydrogen. Ethanol will be the other useable energy resource because it is obtained from biomass fermentation.\textsuperscript{45} This will greatly impact
both the large and small application such as vehicles, portable computer, mobile telephones, and military equipment. A fuel cells range of application exceeds all other types of energy converters. This is shown in the following figure.²⁷

There are disadvantages when it comes to fuel cells, the main one being that when comparing to classical generation of power at the present time, are the overall costs ($/KW). Attempts are underway to make fuel cell prices lower. On the other hand the overall efficiency of the fuel cell is better than a combustion engine. ²⁷ Fuel cells are simple and durable long lasting systems because there are very few moving parts. Fuel cells don’t make very much noise so that makes them applicable for portable power applications. The low pollutants, the water by-product, are the fuel cells main advantage.⁴⁵

**Ethanol Fuel Cell**

Recently ethanol has been considered to be used to replace methanol in fuel cell application. Ethanol is very similar to methanol it’s a good hydrogen carrier but it is not nearly as poisonous. Another advantage of ethanol is that it is readily produced in large quantities from biomass, primarily by fermenting corn or sugar cane. When comparing the oxidation potential of ethanol and methanol, the potential difference is approximately 70 mV. The complete oxidation of ethanol to carbon dioxide is more difficult because ethanol requires a larger activation energy for breaking the carbon-carbon bond.²⁸ The electrochemistry of ethanol in 0.1M HClO₄ could produce acetaldehyde, acetic acid, or carbon dioxide. Acetaldehyde or acetic acid both has a high commercial value. ²⁸
The electrochemistry of ethanol in aqueous acidic solution has been studied extensively. A cyclic voltammogram of 0.1 M solution of EtOH in 0.1M HClO₄ using a Pt electrode is shown later in Figure 10.

On the initial positive sweep the voltammogram displays an irreversible oxidation peak at 0.6V followed by a second oxidation peak at Epa = -1.1V. On the reverse sweep the voltamogram does not display cathodic current. The first oxidation peak involves the oxidation of CH₃CH₂OH to CH₃CHO.

\[ \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CHO} + 2\text{H}^+ + 2e^- \]

The mechanism involves a one-electron oxidation of EtOH with the formation of alpha carbon – Pt bond.

\[ \begin{align*}
* \\
1. \text{CH}_3\text{CH}_2\text{OH} &\rightarrow \text{CH}_3\text{CHOH} + \text{H}^+ + e^- \\
&\quad \text{Pt}
\end{align*} \]

The second step involves further one-electron oxidation of absorbed CH₃CHOH to aldehyde.

\[ \begin{align*}
* \\
2. \text{CH}_3\text{CHOH} &\rightarrow \text{CH}_3\text{CHO} + \text{H}^+ + e^- \\
&\quad \text{Pt}
\end{align*} \]

At the same potential a surface oxidation of Pt takes place with the formation of PtO.

3. \[ \text{Pt} + \text{H}_2\text{O} \rightarrow \text{Pt(OH)} + \text{H}^+ + e^- \]
4. \[ \text{Pt(OH)} \rightarrow \text{Pt(O)} + \text{H}^+ + e^- \]

This reaction causes the formation of PtO films on the surface of the Pt electrode.

**II. The second oxidation peak**

This is at E = 1.1V involve the oxidation of CH₃CH₂OH to CH₃CHO via the formation of platinum oxide.

5. \[ \text{Pt} + \text{EtOH} \rightarrow \text{Pt(OEt)} + \text{H}^+ + e^- \]
6a. \[ \text{H}_2\text{O} + \text{Pt-OEt} \rightarrow \text{Pt(O)} + \text{CH}_3\text{CH}_2\text{OH} + \text{H}^+ \]
Pt(OEt) can also disproportionate and form Pt and CH₃CHO.

6b. Pt-OEt → Pt + CH₃CHO⁺

The reaction 6b causes the poisoning of the Pt electrode by formation of Pt(O). However, the reaction 6b is faster than 6a, and then poisoning of the electrode will not occur.

**III Activation peak 3**

The oxidation peak at E= 1.1V is observed only on the reverse scan. It involves the reduction of Pt(O), formed on the initial positive scan, by EtOH and the formation of Pt(OH).

7. CH₃CH₂OH + Pt(O) → CH₃CHO + Pt(OH)

At the same potential Pt(OH) will be oxidized to Pt(O).

8. Pt(OH) → Pt(O) + H⁺ + e⁻

Above 0.8V the reaction 7 will not proceed, i.e Pt(O) will not be reduced to Pt(OH) by CH₃CH₂OH. Below 0.6V the oxidation of Pt(OH) to Pt(O) will not proceed.

The ethanol oxidation was also studied by in situ IR technique and by MS spectroscopy. It was found that the main product of bulk electro oxidation of CH₃CH₂OH is CH₃CHO. However, it was found that CH₃COOH and CO₂ are also obtained.

![Oxidation Reaction Scheme](image-url)

**Figure 6. Oxidation Reaction Scheme**
It was postulated that the second oxygen in CH$_3$COOH and CO$_2$ was obtained from absorbed Pt-OH. At lower, EtOH concentration CO$_2$, CH$_3$CHO and CH$_3$COOH are the major oxidation products. At the higher EtOH concentration CH$_3$CHO is the main oxidation product. The catalytic properties of the electrode material is key to controlling the formations of absorbed intermediates and thus avoiding the formation of poisoning species, which can then be deleterious for fuel cell operation.$^{29}$

If it is possible to avoid poisoning effect then the complete oxidation will occur. This would make ethanol more favorable fuel than methanol, because ethanol would produce twelve electrons per molecule of ethanol.

\[ \text{CH}_3\text{CH}_2\text{OH} + 3\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^- \]

By either altering the electrode or the electrolyte is a way in which the poisoning of the electrode could be avoided and the complete of EtOH can occur. Many studies have been done by altering the electrode by using bi and tri-metallic catalyst.$^{30, 31, 32, 33, 34, 35, 36}$ These articles have shown that a decrease the poisoning effect does occur but the overall effect cannot be avoided. The different electrolytes that have been studied are: acidic, alkaline and carbonate.$^{27, 29, 37}$ Each electrolytes have their positive and negative sides. The acidic solution gave the best overall power performance. FTIR and DEMS have also been used to determine the amounts of intermediates formed during the oxidation of ethanol.$^{27, 31, 34, 38, 39, 40, 41, 42, 43, 44}$
There are several types of fuel cells:

1. Alkaline Fuel Cell (AFC)
2. Phosphoric Acid Fuel Cell (PAFC)
3. Solid Polymer Electrolyte Fuel Cell (SPEFC)
4. Molten Carbonate Fuel Cell (MCFC)
5. Solid Oxide Fuel Cell (SOFC)
6. Direct Methanol Fuel Cell (DMFC)

**Phosphoric Acid Fuel Cell (PAFC)**

A commercial phosphoric acid fuel cell uses a proton-conductivity solid electrolyte, silicon carbide soaked in 85-100 wt% H₃PO₄. The fuel is in H₂ gas. The following reactions occur on the anode and cathode.

**Anode:**

\[ \text{H}_2 - 2\text{e}^- \rightarrow 2\text{H}^+ \]

**Cathode:**

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

The electrodes are made of Pt or Pt alloys dispersed on carbon black. The electrolyte is concentrated H₃PO₄ (100%) which will conduct protons at elevated temperatures (~200°C)
II. Experimental

Materials

N-Methlimidazole (99% and 95.5% redistilled grades) was purchased from Aldrich Chemical Company. The N-Methylimidazole (99.5%) was used as received, and the N-Methylimidazole (99%) was distilled at 100 ºC under vacuum (30 mmHg). Ethyl Chloride, ethanol, perchloric acid were also obtained from the Aldrich chemical Company and used as received.

Sodium Tetrafluoroborate (99%) and Silver Tetrafluoroborate were purchased from the Alfa Aesar Chemical Company. The glacial acetic acid, acetone, and acetonitrile (HPLC grade) was obtained from the Fisher Scientific Chemical Company. High purity, 18 MOhm, water was used when necessary.
Instrumentation

The amount of water in all samples of ionic liquids was determined by using a Denver Instrument Coulometric Karl Fisher Titrator, Model 260. The samples (50-100 µL) were injected by using a glass syringe with stainless steel needles. The syringes are kept in the oven so they are dry before use. USB 4000 Fiber optic spectrometer was used to obtain UV/Vis spectra of ionic liquid.

When synthesizing ionic liquid it is important to remove all the chloride ions out of the solution. This is done by adding the AgBF₄ solution until the equivalence point of AgCl was obtained. The Extech 651 Digital pH / mV / temp meter was used to generate AgCl titration curve. The Ag and Hg/Hg₂SO₄ electrodes were used. The equivalent potential of AgCl was determined by titration of Cl⁻ with Ag⁺ solution in H₂O. A plot of the titration curve (E vs AgBF₄) is shown in the Figure 7. From this figure the equivalence potential was determined to be .274 V.

![E vs AgBF₄](image)

**Figure 7.** Titration curve
Cyclic voltammetry was done using either EG&G Princeton Applied Research potentiostat/galvanostat model 173 or model 273. Model 173 was also used for controlled potential electrolysis. The potentiostat model 173 was interface to a Houston Omnigraphic 2000 x-y recorder. Model 273 x,y output were connected to Mac Lab 4 interface to (e-corder 201 interface) and the CV’s were recorded on a Mac laptop computer that had the software Scope 4.0 (eDAQ).

Cyclic voltammogram were obtained using a small three-electrode cell. The volume of the solution was between 0.1 to 2.0 mL. The cell is shown in the figure 8 below:

**Figure 8.** Electrochemical cells used for (A) cyclic voltammetry and (B) for constant potential electrolysis
The working electrode was either glassy carbon, gold, or platinum. The small working platinum electrode was 1mm$^2$ (Cypress Systems, Inc., Lawrence, KS). Ag/AgCl in IL was used as a reference electrode. In some cases, a silver wire was used as quasi reference electrode. Platinum wire served as the counter electrode.

Figure 9. Large volume electrochemical cell
The large volume cell contained a CaF$_2$ crystal sealed on the bottom of the cell by water resistant epoxy. 7 mm polycrystalline platinum disc in Teflon, from Pine Electrodes, was used as working electrodes. Platinum wire served as the counter electrode and Ag/AgCl electrode (Microelectrodes, Inc.) was the reference electrode.

**Activating Platinum working Electrodes**

The platinum working electrodes when obtaining CV’s tend to get poisoned and they need to be reactivated. Activating the electrode is done by two different methods. The first one is to soak the working electrode in concentrated sulfuric acid overnight. If the electrode still isn’t activated then the working electrode is placed a small beaker with deionized water in it. The beaker with the electrodes is placed in the E/MC Ultrasonic Cleaner for a few hours. The working electrode should then be reactivated.

**Cleaning Ionic Liquid**

Ionic liquid (IL) should be colorless but sometimes it contains small amount of brown or dark yellow impurities. To remove the impurities a 1:1 solution of IL CH$_3$CN was stirred with active alumina overnight. The Al$_2$O$_3$ was filtered and CH$_3$CN was removed by vacuum distillation. If impurities were not removed completely then the process needs to be repeated.
Preparation of 1-Ethyl-3-Metylimidazolium Chloride

Standard literature methods were modified to prepare 1-Ethyl-3-Metylimidazolium Chloride (EMImCl). An \( I^2 R \) glove bag was filled with nitrogen gas, N-methylimidazole (n-MeIm) was weighed into an ACE glassware reinforced pressure bottle. The pressure bottle was cooled using a liquid nitrogen/ethanol solution to approximately -30 to -50 °C and gaseous chloroethane (EtCl) was condensed into the bottle. The mole ratio of n-MeIm to EtCl was varied between 1:2 and 1:5 with 1:3 being the preferred. The bottle was sealed under nitrogen using a chemically inert teflon screw cap. The reaction flask was heated in a hood using both a water or oil bath between 25 and 60 °C with 40-50 °C being the preferred temperature range. Depending on the temperature, the reaction was stirred for 24 hours or up to 10 days. The reaction progress was monitored by observing the amount of the immiscible EMImCl layer formed at the bottom of the flask. The reaction flask was removed from the heat and cooled to 0 °C. Depending on the purity of the EMImCl, it would crystallize upon cooling. Once cooled, the reaction flask was opened under nitrogen in a dry bag. If the bottom of EMImCl layer had solidified, the top reactant layer was decanted into a new bottle. If it did not crystallized the reactant layer would be removed in \( \text{vacuo} \). In this case, the EMImCl was dissolved in a small amount of dry acetonitrile. The EMImCl was repercipated from this solution by adding diethyl either. Upon cooling, the EMImCl would crystallize in from of large white crystals. The crystals were dried in \( \text{vacuo} \) filtered by a Shlenk Filter. Under dry \( \text{N}_2 \) EMImCl was transfer to a glove box where it was stored until use.
Preparation of 1-Ethyl-3-Metylimidazolium Tetrafluoroborate in Acetone

1-Ethyl-3-Metylimidazolium Tetrafluoroborate (EMImBF$_4$) was prepared from 1-ethyl-3-methylimidiazolium chloride (EMImCl) by metathesis with the tetrafluoroborate anion. Several approaches are made to replace the chloride anion with the tetrafluoroborate anion, but NaBF$_4$ gave a pure product of EMImBF$_4$. 1-Ethyl-3-Metylimidazolium Chloride, EMImCl (95.55 g) and NaBF$_4$ (71.54 g) was dissolved in 100 ml of acetone and stirred for 24 hours. The precipitate, NaCl was filtered off using a porosity E 2 glass filtering funnel, and the acetone was removed by rotary evaporation. The ionic liquid was then place on high vacuum (10$^{-5}$ mmHg) to remove any excess of water. The excess of Cl$^-$ impurity in ionic liquids was removed by potentiometrie titration with AgBF$_4$ solutions. An aqueous solution of ionic liquid (1:1) was titrated with AgBF$_4$ solution until the equivalence point potential was obtained. The potential was measured by using an Ag electrode as an indicator electrode and as a Hg | Hg$_2$SO$_4$, K$_2$SO$_4$ reference electrode. The equivalence potential was separately obtained from a titration curve (E ml AgBF4) as shown in Figure 7. AgCl precipitate was filtered using an E porosity filter funnel. After, evaporation of water ionic liquid without Cl$^-$ impurity was obtained.
III. Results and Discussion

In this work we have investigated the electrochemical properties of EtOH in EMImBF$_4$ ionic liquid and compared it to the properties of EtOH in HClO$_4$ solution. We have also examined the influence of temperature on the rate of oxidation of EtOH. The possible use of ethanol in fuel cells containing EMIBF$_4$ ionic liquid was investigated. As shown previously when studying the electrochemical properties of EtOH in aqueous solution Pt working electrode very readily gets “poisoned” by formation of PtO films.

The first step in this process involves the oxidation of Pt and the formation of Pt(OEt).

\[
\text{Pt} + \text{EtOH} \rightarrow \text{Pt(OEt)} + \text{H}_2 + e^-
\]

In the presence of H$_2$O the Pt(OEt) can be further oxidized to Pt(O).

\[
\text{H}_2\text{O} + \text{Pt(OEt)} \rightarrow \text{Pt(O)} + \text{CH}_3\text{CH}_2\text{OH} + e^- + \text{H}^+
\]

As a consequence the Pt electrode is coated with Pt(O) film and the electrode becomes electrochemically inactive. For that reason the electrode has to be regenerate by dissolving Pt(O) films.
We have found that the best reactivation of Pt electrode could be achieved by heating the poisoned electrode in concentrated H₂SO₄ overnight then by washing it in H₂O. The regenerated electrode is stored in H₂O until use.

Cyclic voltammogram of EtOH in 0.1 M HClO₄ using a poisoned Pt electrode before cleaning and after cleaning are shown in the figure 10 and 11.

**Figure 10.** Cyclic Voltammogram EtOH in 0.1 M HClO₄ using poisoned electrode 2
Figure 11. Cyclic Voltammogram 0.1 M EtOH in 0.1 M HClO$_4$ using Pt electrode 2

It is clearly visible that after cleaning the oxidation peaks characteristic for oxidation of EtOH become well pronounced. Several different Pt electrodes were cleaned and their CV of oxidation of 0.1 M ethanol in 0.1 M HClO$_4$ is shown the figures 12-17.
Figure 12. Cyclic voltammogram of 0.1 M EtOH in 0.1 M HClO$_4$ using large Pt electrode (1cm$^2$) after cleaning
Figure 13. CV of 0.1M EtOH in 0.1M HClO₄ using large (1cm²) Pt electrode (#2) after being cleaned
Figure 14. CV of 0.1M EtOH in 0.1M HClO₄ using small Pt disc electrode (1mm²) after cleaning (electrode 1)
Figure 15. CV of 0.1M EtOH in 0.1M HClO$_4$ using a small PT disc electrode (1mm$^2$) after being cleaned (electrode 2)
Figure 16. CV of 0.1M EtOH in 0.1M HClO₄ using a small Pt disc electrode (1mm²) after being cleaned (electrode 3)
Figure 17. CV of 0.1M EtOH in 0.1M HClO₄ using a small Pt disc electrode (1mm²) after being cleaned (electrode 4)
The cyclic voltammogram’s shown in figure’s 11-17 displays two oxidation peaks on the positive scan. On the reverse scan a new oxidation peak at 0.45 V was obtained. However the sharpness and relative height of peaks was slightly different for each Pt electrode.

Influence of the temperature on CV of EtOH in HCLO₄

The magnitude of oxidation peaks at E = 1.1 V of .1M EtOH in .1M HClO₄ is significantly dependent upon temperature. From Figure 17, it is closely visible that as the temperature increase from 24.6 °C to 61 °C the oxidation peaks became stronger and better defined. The similar behavior is observed for the Pt electrode #2. The overlay of the CV’s obtained at different temperature for electrode #3 and #5 are shown in figure 12. The CV’s shown in Figure 13 was obtained after temperature was increase to 61 °C and then cooled back down the room temperature. By obtaining CV at higher temperature with different electrode clearly shows that high temperatures make the oxidation peak more pronounced.
At room temperature the oxidation peaks are not well defined. The first oxidation peak at 0.2V is hardly visible. As the temperature is increased from 25 to~25°C, the first oxidation peak becomes more defined. Thus indicating that the oxidation reaction of EtOH is faster at elevated temperatures and no poisoning of the Pt electrode occurs.
Electrochemistry of EtOH in EMIMBF4 Ionic Liquid

Electrochemical properties of EtOH in EMImBF$_4$ ionic liquid were investigated and compared to the electrochemical properties obtained in 0.1 M HClO$_4$/H$_2$O using a Pt electrode. A special precaution was taken that ionic liquid EMImBF$_4$ did not contain water impurities. The cyclic voltammogram of EMImBF$_4$ ionic liquid using a Pt electrode is shown in Figure 30. The voltammogram displays a wide potential window of 4.2 V. No impurities due to Cl$^-$ or H$_2$O were observed. A cyclic voltammogram of 0.1M EtOH in EMImBF$_4$ is shown in Figure 31. The scan was initiated at 0 V and ran first in the negative direction.

Figure 19. Cyclic Voltammogram of EMImBF$_4$ using a Pt electrode
The scan was initiated at 0.0V and scan first in the positive direction. After reversing the scan at -0.8V it was continued into positive direction. At about 1.2V anodic current increased giving a peak at -1.9V. Upon reversing the scan at -2.1 V no corresponding reduction peak was observed indicating that the oxidation process is irreversible, continuing scanning in the negative direction a new cathodic peak at -0.3V, which correspond to the reduction of electro generated acet aldehyde, at peak -0.7V

\[
\begin{align*}
\text{C}_2\text{H}_5\text{OH} + \text{Pt} - e^- &\rightarrow \text{C}_2\text{H}_5\text{O}-\text{Pt} + \text{H}^+ \\
\text{C}_2\text{H}_5\text{O}-\text{Pt} - e^- &\rightarrow \text{Pt} + \text{CH}_3\text{COH} + \text{H}^+
\end{align*}
\]

**Figure 20.** Cyclic Voltammogram of 0.1M EtOH in EMImBF$_4$ Ionic liquid

While in 0.1M HClO$_4$/H$_2$O solution increased concentration of EtOH from 0.1M to
1M causing poisoning of the electrode (Figure 31 and 32), increased concentration of EtOH in ionic liquid does not cause poisoning of the electrode. Cyclic voltammogram of oxidation of EtOH in EMImBF$_4$ ionic liquid are shown in Figure 33. As the concentration of EtOH increases from 1M to 5M the oxidation peak of EtOH linearly increased. This clearly shows that no poisoning of Pt electrode occurs due to formation of Pt(O) solution.

**Figure 21.** Cyclic voltammogram of EtOH in EMImBF$_4$ ionic liquid a) 1M EtOH, b) 2M EtOH, c) 5M EtOH,
Possible use of EtOH as a fuel cell using EMImBF4 electrolyte fuel cell was investigated. For that perposed a PAFC, phosphoric acid fuel cell was used. The electrode was a Pt and the membrane was a nafion membrane. Schamatic diagram of fuel cell is shown in figure 22.

**Figure 22.** PAF cell
EMImBF$_4$ was used on both sites. In the cathodic compartment, $O_2$ was introduced under perm on the anodic side EtOH dissolved in EMImBF$_4$ was introduced. An open cell voltage of 0.24V was obtained. A polarization current is shown in figure 24.

**Figure 23.** PAF cell with EMImBF$_4$ as an electrolyte
Figure 24. Polarization curve for 2M EtOH in EMImBF$_4$ electrolyte contained in a commercial PAFC.

As the current drawn from the cell increased from 0.0025 A/cm$^2$ the voltage decreased to 0.07V. Lowering the load on the cell face to 0 the voltage increased to 0.24 V.

A commercial phosphoric acid fuel cell (electrochemical model FC 25-02PA) was used, using EMImBF$_4$ ionic liquid as an electrolyte solution instead of the phosphoric acid. When EtOH was used as a fuel, an open cell voltage of 0.25V was observed at 30 °C. The fuel cell experiment were done at AFRL Wright Patterson AFB, Dayton OH.
For comparison the source commercial phosphoric acid fuel cell was tested using hydrogen fuel and EMImBF$_4$ ionic liquid as an electrolyte instead of phosphoric acid. An open cell voltage 0.8 V was obtained at 50 °C. The open cell voltage varied between 0.55 and 0.8 depending on the cell temperature. For comparison the source cell when 85% H$_3$PO$_4$ was used an open cell voltage of 0.92 V at 100 % was obtained. The polarization curves for H$_2$ cell with EMImBF$_4$ are shown in figure 25.

![Polarization curve](image)

**Figure 25.** Polarization curve for phosphoric acid fuel cell using H$_2$ as a fuel and EMImBF$_4$ as an Electrolyte (IL3-50 = EMImBF$_4$ at 50 °C, IL3-20 = EMImBF$_4$ at 20 °C)
IV. Conclusion

In this study EMImBF$_4$ was synthesized and investigated. Cyclic voltammogram of ethanol in percholric acid was first studied. It was studied with increasing temperatures. The CV show the oxidation peaks increase in magnitude as the temperature increases. Increasing concentration on ethanol in percholric acid was also investigated. And with increasing concentrations of ethanol where was more PtO being produce which eventually caused poisoning of the Pt electrode. So it was found that you can only use up to 2M ethanol anymore would poison the electrode.

We have found that the best procedure for removal of PtO from the Pt electrode is heating the electrode in concentrated H$_2$SO$_4$. Cyclic voltammograms obtained after cleaning several Pt electrodes conforms that this treatment gives clean Pt electrodes without any PtO. Electrochemical oxidation of EtOH in EMImBF4 ionic liquid show that is poisoning of Pt electrode by formation of PtO occurs even at high EtOH concentration (1mA).

After that we investigated different concentrations of ethanol in ionic liquid. I ran CV of increasing concentration of ethanol in IL and no poisoning occurred. These results are good because EMImBF$_4$ would be a good electrolyte because it can be ran out room temperature and it more excusable.
V. References


