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Comparison of the Electrochemical Properties of Ethanol in Perchloric Acid and Ionic Liquids

Sandra Felix-Balderrama
Wright State University

COMPARISON OF THE ELECTROCHEMICAL PROPERTIES OF ETHANOL IN
PERCHLORIC ACID AND IONIC LIQUIDS

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

By

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2009
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SCHOOL OF GRADUATE STUDIES

November 2, 2009

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY
SUPERVISION BY <u>Sandra Felix-Balderrama</u> ENTITLED <u>Comparison of the
Electrochemical Properties of Ethanol in Perchloric Acid and Ionic Liquids</u> BE
ACCEPTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE
DEGREE OF <u>Master of Science.</u>

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ABSTRACT

Felix-Balderrama, Sandra. M.S., Department of Chemistry, Wright State University, 2009. Comparison of the Electrochemical Properties of Ethanol in Perchloric Acid and Ionic Liquids.

1-Ethyl-3-Methylimidazolium Tetrafluroborate (EMImBF$_4$) and 1-Ethyl-3-Methylimidazlium Bis(trifluoromethanesulfonyl)imide (EMImTFSI) ionic liquids were synthesized and characterized in order to study the electrochemical oxidation of ethanol in these ionic liquids on a platinum surface electrode.

It was found that pure EMImBF$_4$ exhibits an electrochemical window of 4.4 V, while EMImTFSI exhibits an electrochemical window of 5.0 V.

Electrochemical study of ethanol in perchloric acid showed that the oxidation of ethanol strongly depends on the concentration of ethanol and on the temperature of the solution. The poisoning of the platinum electrode only depends on the concentration of ethanol. At a low concentration of ethanol (0.1 M), electro-oxidation of ethanol on a platinum electrode showed one oxidation peak (peak 2) at a temperature of 22.6 °C and two oxidation peaks (peak 2 and 3) at 70.1 °C. It was found that, with increasing temperature from 22.6 to 70.1 °C, the cyclic voltammograms showed an increase in oxidation. Electrochemical studies of ethanol at higher concentration of ethanol (> 0.2 M), showed three oxidation peaks. The poisoning of the electrode occurred at 1 M ethanol solution via formation of PtO.

The electrochemical studies of ethanol in EMImTFSI and EMImBF$_4$ ionic liquids showed that poisoning of the electrode does not occur even at higher concentration of ethanol. It was proved that oxidation of ethanol in ionic liquids produces acetaldehyde and acetic acid.

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ACKNOWLEDGEMENT

I would like to thank Dr. Katovic for his guidance, kindness and support during my time working with him. "Thank you Dr. Katovic, your support has been very important to the completion this work".

I would like to thank my husband who has supported me and helped me a lot. Also I would like to thank my little baby. I am sorry "pequeñito" for leaving you so many hours. I just want you to be proud of me.

Finally, I would like to thank Dr. Lunsford and Dr. Grossie for helping me successfully defend this thesis.

I.   INTRODUCTION

In recent years, development of renewable and clean energy technology has been of great interest due to environmental concerns and to the depletion of fossil fuels around the world.[1]

Among the technology to produce clean and renewable energy, electrochemical power sources such as super capacitors, batteries (both electrochemical energy storage devices), and fuel cells (electrochemical energy conversion devices) have become extremely attractive in the technological community in the last decade. [1, 2, 3]

Among these electrochemical power sources, development and improvement of fuel cells has grown tremendously, not only because they are considered as the most efficient and clean alternative energy technology, but because of their wide range of applications which include stationary power generation (MW), portable power generation (KW), and electric vehicles (KW).[4]

Though fuel cells represent a novel alternative as a clean and efficient energy technology, challenges such as cost reduction, and improving durability have to be overcome to guarantee their commercialization.[5]

Fuel Cells

A fuel cell is an electrochemical device that converts chemical energy directly to electrical energy. A fuel cell consists of an electrolyte, an ion containing solution, liquid or solid in contact with two electrodes (an anode where the oxidation of the fuel takes place and a cathode where the reduction of oxygen occurs). In the production of electricity in fuel cells, the only byproducts are: some heat, carbon dioxide and water, thus fuels cells can be considered to be an environmentally clean energy production device.[4]

Classification of Fuel Cells

Usually, fuel cells are classified by the kind of electrolyte they use. The electrolyte determines the kind of chemical reactions that takes place in the fuel cell, the operating temperature rate, and other factors that affect the applications, for which the fuel cell is most suitable, as well as its advantages and limitations.[2]

A basic, but most commonly nomenclature used to describe fuel cells based on the electrolyte they use, is the following:

1. Proton Exchange Membrane (polymer electrolyte) Fuel Cells (PEFC)
2. Alkaline Fuel Cells (AFC)
3. Phosphoric Acids Fuel Cells (PAFC)
4. Molten Carbonate Fuel Cells (MCFC)
5. Solid Oxide Fuel Cells (SOFC)

Additional sub-classification of fuel cells can be made, based on parameters such as nature and type of fuel used, whether the fuel is processed outside, external reforming, or inside, internal reforming, (e.g. hydrogen PEFC or direct ethanol DEFC), and the temperature range of operation.[4, 6]

In Table 1, operating temperatures, electrolyte material, and possible applications for the most common type of fuel cells are given. Each fuel cell has its own advantages, and can be used for certain applications. Low-temperature fuel cells include proton exchange membrane (PEFCs) and alkaline fuel cells (AFCs). The primary advantages of operating these fuel cells at low temperatures are high efficiency and quick start-up. However, because of the low temperatures at which they work, expensive catalysts (e.g., platinum) are required and much larger heat exchangers to eliminate waste. High-temperature fuel cells (e.g., SOFC, MCFC) have an advantage in raw material (catalysts) cost and easy rejection of waste heat. Medium-temperature fuel cells (e.g., PAFC) have some of the advantages of both high- and low-temperatures fuel cells.[6]

Table 1. Characteristics and other Features of Different Types of Fuel Cells.[2, 4, 6]

Fuel cell Type	PEFC	AFC	PAFC	MCFC	SOFC
Electrolyte Material	Flexible solid per-fluorosulfonic acid polymer	Solution of potassium hydroxide in water	Solution of phosphoric acid in porous silicon carbide matrix	Molten alkali metal (Li/K or Li/Na) carbonates in porous matrix	Yttria (Y_2O_2) stabilized zirconia (ZrO_2)
Operating Temperature	30 - 100°C	60 - 100°C	150 - 220°C	600 - 800°C	600 - 1000°C
Electrodes	Pt	Ni/Ag metal oxides, noble metals	Pt	Ni anode, NiO cathode	Co-ZrO_2, Ni-ZrO_2 anode, Sr-$LaMnO_3$ cathode, Y_2O_3-stabilized ZrO_2 electrolyte
Major Poison	CO, Sulfur, metal ions, peroxide	CO_2	Sulfur, high levels of CO	Sulfur	Sulfur
Charge Carrier	H^+	OH^-	H^+	CO_3^{2-}	O^{2-}
Cell Reactions	$H_2 \rightarrow$ $2H^+ + 2e^-\,(a)$ $\frac{1}{2}O_2 + 2e^- +$ $2H^+ \rightarrow H_2O(c)$	$H_2 + 2OH \rightarrow$ $2H_2O + 2e^-\,(a)$ $\frac{1}{2}O_2 + H_2O +$ $2e^- \rightarrow H_2O(c)$	$H_2 \rightarrow$ $2H^+ + 2e^-\,(a)$ $\frac{1}{2}O_2 + 2e^- +$ $2H^+ \rightarrow H_2O(c)$	$H_2 + CO_3^{2-} \rightarrow$ $H_2O +$ $CO_2 + 2e^-\,(a)$ $\frac{1}{2}O_2 + CO_2 +$ $2e^+ \rightarrow CO_3(c)$	$H_2 + O^{2-} \rightarrow$ $H_2O + 2e^-\,(a)$ $\frac{1}{2}O_2 + 2e^- \rightarrow$ $O^{2-}(c)$

4

Fuel cell Type	PEFC	AFC	PAFC	MCFC	SOFC
System output	<1kW–250kW	10kW–100kW	50kW–1MW (250kW module typical)	<1kW–1MW (250kW module typical)	5kW–3MW
Electrical Efficiency	53–58% (transportation) 25–35% (stationary)	60%	32–38%	45–47%	35–43%
Water management	Evaporate		Evaporate	Gaseous products	Gaseous products
Applications	Electrical utility, portable power, transportation	Military and space, residential plants	Electric utility and transportation	Electric utility	Electric utility
Advantages	Low temperature, rapid start, solid electrolyte reduces corrosion and electrolyte management problems	High performance, the cathode reaction is faster in alkaline electrolyte, simple design	High efficiency, can tolerate impure hydrogen fuel, demonstrated durability	High efficiency, flexibility of fuel cell types, can use a variety of catalysts	High efficiency, low temperature, flexible of fuel, solid electrolyte reduces corrosion and management problems, possible internal reforming
Disadvantages	Sensitive to fuel impurities, expensive catalyst, water management	Expensive removal of CO_2 from fuel and air supplies	Low power density, expensive, platinum catalyst used, slow start up	Electrolyte dissolves cathode catalyst, extremely long start-up time	High temperatures enhances corrosion and breakdown of cell components

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Basic Design of Fuel Cells and their Mode of Operation

A design of a hydrogen-oxygen (or air) proton exchange membrane fuel cell is shown in Figure 1. A single cell consists of a solid polymer electrolyte ion exchange membrane, and two electrodes – a negative anode and a positive cathode – sandwiched around the electrolyte.[2]

In simple terms, the mode they operate is by feeding hydrogen on one side of the cell which flows through channels to the electrically negative electrode, or anode. The anode which is porous so that the hydrogen can pass through it, is composed of platinum (catalyst) uniformly supported on carbon particles and surrounded by a thin layer of proton-conducting ionomer. Hydrogen fuel on the anode side moves through the electrode and encounter the platinum catalyst, here an oxidation reaction takes place and the hydrogen molecules separate into protons and electrons. While the protons are conducted through the ionomer and the ion exchange membrane to the other side of the cell, the stream of the negatively-charged electrons follows an external circuit to the cathode. This flow of electrons through the external circuit is electricity that can be use to do work.

On the other side of the cell, oxygen gas, typically from the air, flows to the electrically positive electrode, or cathode. Like the anode, the cathode is made of platinum particles uniformly supported on porous carbon particles so that oxygen can move through it. Reduction reactions, involving the gaining of electrons take place at the cathode. When the electrons (which have traveled through the external circuit) return

from doing work, they react with oxygen and the hydrogen protons (which have moved through the ion exchange membrane) at the cathode to form water. Most of the water is collected and reused within the system, but a small amount is released in the exhaust as water vapor. Heat is generated from this reaction and from the frictional resistance of ion transfer through the membrane. This thermal energy can be used outside the fuel cell.[2]
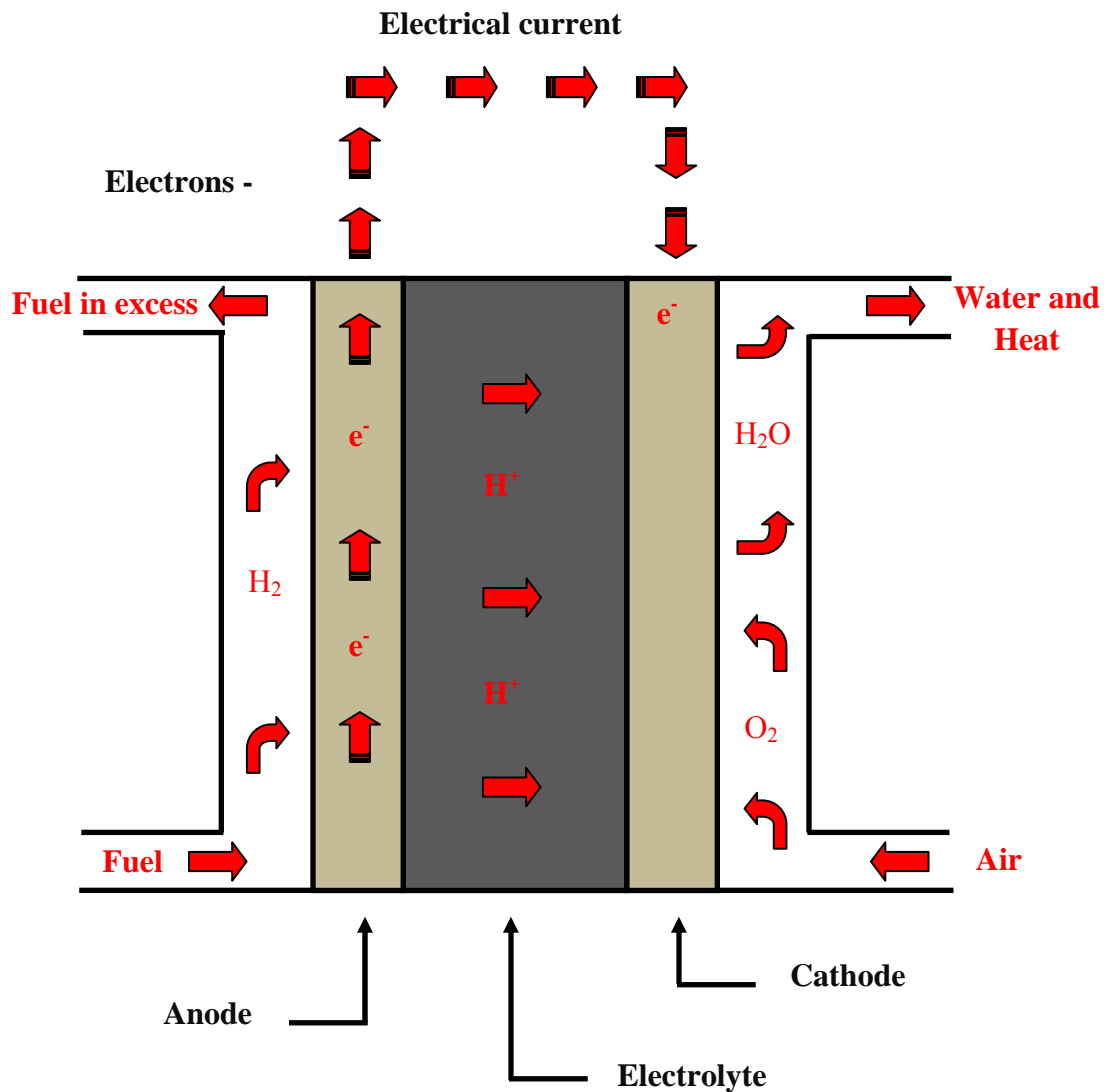
Figure 1: Basic Design of a Proton Exchange Membrane Fuel Cell.[2]

Direct Alcohol-Based Fuel Cells

Although proton exchange membrane (polymer electrolyte) fuel cells(PEFC), technology regarded as the most promising fuel cells among the various types, are suitable both mobile and stationary applications, and show high performances when fed with hydrogen, hydrogen as a fuel represents a key limitation due to its relatively low volumetric density energy (0.53 kWh/l, H_2 gas at 20MPa), and to its permeability into material which make transportation, storage and delivery to be big challenges.[7, 8, 9]

An alternative to overcome these challenges is the use of direct alcohol-base fuel cells (DAFCs). Compared to hydrogen, alcohols have higher theoretical energy densities/specific energy, and they are more ease to store, transport, and refuel.[10] In Table 2, specific energies as well as other thermodynamic features at 25°C and 1 atm are given for some DAFCs.

Table 2: Thermodynamic Features of DAFCs at 25°C and 1 atm.[8] (M_w: fuel molecular weight; n: number of electrons involved; $E°$: cell voltage; E_{sp}: theoretical specific energy; C: current capacity of the pure compound; η: theoretical energy conversion efficiency)

DAFC	Alcohol	Fuel/Oxidant	M_w (g mol^{-1})	n	n/M_w (e$^-$/g mol^{-1})	$E°$ (v)	E_{sp} (Wh kg^{-1})	C (Ah kg^{-1})	η (%)
DEFC	Ethanol	C_2H_5OH/O_2	46.07	12	0.260	1.15	8028	6981	97
DMFC	Methanol	CH_3OH/O_2	32.04	6	0.187	1.21	6073	5019	97
DMPFC	1-Methoxy-2-Propanol	$CH_3OCH(OH)CH_3/O_2$	76.10	16	0.210	α	α.5635	5635	-
DP1FC	1-Propanol	$CH_3CH_2CH_2OH/O_2$	60.10	18	0.300	1.13	9070	8027	97
DP2FC	2-Propanol	$CH_3CH(OH)CH_3/O_2$	60.10	18	0.300	1.12	8990	8027	97

In general, a DAFC is a PEFC in which the alcohol is directly fed into the anode without the requirement of a fuel reformer. The simplicity of DAFCs has been shown with methanol and ethanol as well with other small alcohols. Although DAFCs offer great advantages, they also show several drawbacks. Several limitations of these fuel cells are the slow dynamics of alcohols oxidation, the alcohol crossover across the membrane and the stability and poisoning of the anode.

The most common type of alcohol used for DAFCs is methanol (Direct Methanol Fuel Cells DMFCs). Methanol as a fuel offers a relatively high electrochemical activity compared to other liquid fuels. However, methanol is toxic, and is neither a primary not a renewable fuel.[10] Hence ethanol has been recently gaining considerable attention as a substitute of methanol due to ethanol is a facile and abundant renewable fuel which can be easily produced from agricultural products and through the fermentation of biomass.[10, 11]

Direct Ethanol Fuel Cells (DEFCs)

As stated before, ethanol has been recently gaining considerable attention as a fuel, not only because it is a renewable fuel which can be easily produced from agricultural products and through fermentation of biomass, but because ethanol possesses distinct characteristics if compared to other alcohols specially with methanol such as lower toxicity, low permeability across proton exchange membranes, and higher energy density (8.01 kWh/kg for ethanol versus 6.09kWh/kg for methanol). [11]

Direct ethanol fuel cells (DEFCs) is based in the oxidation of ethanol, involving

12 electrons ($E° = 1.15$ V). The complete ethanol anodic oxidation, oxygen cathodic

reduction, and overall reaction of DEFC could be described as follows:[12]

Anode $\qquad$ $CH_3CH_2OH + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12e^-$ $\qquad$ (Equation 1)

Cathode $\qquad$ $3O_2 + 12H^+ + 12e^- \rightarrow 3H_2O$ $\qquad$ (Equation 2)

Overall $\qquad$ $CH_3CH_2OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$ $\qquad$ (Equation 3)
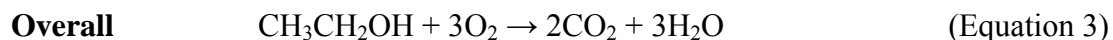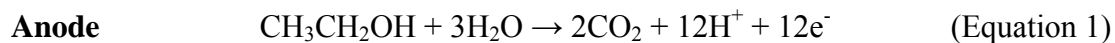
Electro-oxidation of ethanol involves a complex mechanism not only because the

reaction involves a greater number of electrons exchange, but because the cleavage of the

C-C bond   at the anode for a total oxidation to CO_2 is required to eliminate the partial

oxidation products such as acetaldehyde (CH_3CHO) and acetic acid (CH_3COOH). It is

believed that cleavage of the C-C bond has a determining effect on the fuel cell efficiency

and the electrical energy yield.[13]

Because the electro-oxidation of ethanol is extremely complicated, a significant

objective in the development of DEFCs is the creation of enhanced catalytic materials for

the anodic reaction.[14]

Platinum based catalysts are by far the most studied catalytic surfaces for ethanol

anodic oxidation. Moreover platinum alloys have proven to be the best catalysts for the

anodic reaction. However, because of the high cost of Pt, and because poisoning of the

electrode occurs due to adsorbed intermediate oxidation products like, e.g. CO,

investigations are centered on the development of a second or third additive material that

will reduce the amount of Pt-loading needed, and will maintain high electro-catalytic efficiency.[12, 15, 16]

Anode Catalysts

The most common catalytic materials for the anodic reaction in DEFCs are Pt-Ru and Pt-Sn catalysts, as well as the correlated ternary Pt-Ru-based and Pt-Sn-based catalysts.[13]

According to several studies made on this materials, the superior performance of these binary and ternary electro-catalysts for the ethanol oxidation with respect to Pt alone is attributed to the bifunctional effect (promoted mechanism), and to the electronic interaction between Pt and alloyed metals (intrinsic mechanism). According to the promoted mechanisms, the oxidation of the strongly adsorbed oxygen-containing species is facilitated in the presence of Ru(Sn) oxides by supplying oxygen atoms to adjacent site at a lower potential than the accomplished by pure Pt. The intrinsic mechanism postulates that the presence of Ru(Sn) modifies the electronic structure of Pt, and, as a consequence, the adsorption of oxygen containing species.

Binary Catalysts

Pt-Ru/C

Regarding the oxidation mechanism of ethanol using Pt-Ru/C catalyst researchers have made different observations. Schmidt et al. observed that the formation of chemisorbed species coming from dissolved ethanol is partially inhibited by the presence of Ru.[13, 17] Similarly; Camara et al. found that dissociation of adsorbed ethanol seems to

be inhibited by Ru. Probably this effect is due to the diminution of neighboring Pt sites, which are necessary for the cleavage of the C-C bond.[13, 18] In the other hand, according to Fujiwara et al. the promoter action of Ru seems to enhance the oxidation of strongly-bound adsorbed intermediates to give a higher relatively yield of CO_2 than on pure Pt.[13, 19] Lee et al. investigated the effect of the temperature on the electro-oxidation of ethanol by cyclic voltammetry (CV); their results showed that with increasing temperature from 25 to 80°C, Pt-Ru/C catalyst increased currents by a factor of 8 times compared to that of Pt/C based catalyst. According to the authors, the ruthenium addition remarkably enhanced ethanol oxidation performance probably due to the strong adsorption of OH.[13, 20] According to several authors, the amount of Ruthenium in a Pt-Ru catalyst is also an important parameter in the oxidation of ethanol. According to Lamy et al. a catalyst with an atomic ratio of 4:1 (Pt:Ru) shows a poor activity at room temperature for the oxidation of ethanol.[13, 21] According to Camara et al., there is a relatively narrow range of Pt-Ru composition having a high rate of ethanol oxidation: for a Ru content lower than 20 wt.%, there are not enough Ru sites to effectively assist the oxidation of adsorbed residues and the oxidation current remains almost at the same levels obtained for pure Pt. Based on Camara's founds, the low Ru content could explain the poor activity of the Pt-Ru (4:1) catalyst observed by Lamy et al.[13,18] Spinace et al. studied the activity of a Pt-Ru/C catalyst (range investigated Pt:Ru 1:3) by cyclic voltammetry measurements. He also found that the activity of Pt-Ru for the oxidation of ethanol increases with the increase of the content of ruthenium in the catalyst.[13, 22] Finally, Olivera Neto et al. investigated the activity of Pt-Ru/C catalyst (range investigated Pt:Ru 3:2) for the

oxidation of ethanol. He found that the activity of Pt-Ru increases with the content of the second metal.[13, 23]

Pt-Sn/C

According to different group of researches, the electro-oxidation of ethanol in Pt-Sn/C based catalyst performance depends on its preparation procedure. Lamy et al. prepared and studied Pt-Sn/C electrocatalysts with Pt:Sn atomic ratios varying from 90:10 to 50:50 using different methods. Based on these studies, this group of researchers found that an optimum composition for this type of catalyst was in the range of 10-20 wt%.[13,21] Conversely, Zhou et al. found that Pt-Sn/C electrocatalysts with Pt:Sn molar ratios of 66:33, 60:40, and 50:50 are more active than electrocatalysts with 75:25 and 80:20 molar ratios, with an optimum composition in the range 33-40 wt.% depending on the direct ethanol fuel cell (DEFC) temperature.[13, 24] Spinace et al. studied the activity for the electro-oxidation of ethanol in Pt-Sn/C electrocatalyst with different Sn content using cyclic voltammetry. The results of CV measurements show that electro-oxidation of ethanol starts at low potentials (~0.25V) for Pt-Sn/C electrocatalysts with Pt:Sn molar ratio of 50:50 and 25:75, showing similar current values in the range of 0.25-0.40.[13,22]

Other binary Pt-M catalysts (M=W, Pd, Rh, Re, Mo, Ti, Ce) different than Pt-Ru and Pt-Sn have been also investigated for the ethanol oxidation reaction. In general, these catalysts showed an ethanol oxidation reaction activity higher than that of Pt alone but lower than that of Pt-Ru and Pt-Sn.[13]

Ternary Catalysts

Even though investigations show that binary catalysts exhibit higher electro-catalytic activity for ethanol oxidation than Pt alone, oxidation products are species containing C-C bond, which have a negative effect on the fuel cell performance. For this reason, it was proposed the addition of a third element to modify the Pt-Sn/C and Pt-Ru/C catalysts to present higher specific activity of dehydrogenation, C-O and C-C bond cleavage during the ethanol oxidation.

Pt-Ru Based Catalysts

Investigations on Pt-Ru-based catalysts include the addition of different materials to this catalyst (e.g., W, Mo, Sn, Au, Ni, and Pb). It has been found that performance of direct ethanol fuel cells with Pt-Ru-W, Pt-Ru-Mo and Pt-Ru-Sn catalysts is higher than that with Pt-Ru but inferior to that employing Pt-Zn. Conversely to the last results; it has been found that the performance of Pt-Ru-W electro-catalysts deposited onto a Au substrate is higher compared to that of binary alloys such as Pt-W, Pt-Sn, and Pt-Ru. Studies made on Pt-Ru-Ni based catalyst have been found that Pt-Ru-Ni catalyst presents a higher catalytic activity compared to that of Pt-Ru alloys. For this particular catalyst, electro-oxidation of ethanol is particularly significant at low potentials. Finally, studies made on Pt-Ru-Pb based catalyst have showed that the addition of Pb to Pt and Pt-Ru increases the ethanol oxidation reaction, especially at high potentials.[13]

Pt-Sn Based Catalysts

Electro-oxidation of ethanol on Pt-Sn based catalysts includes the addition of Ni, Rh, and Ru as the third element to modify the performance of this catalyst. Regarding Pt-Sn-Ni based catalyst, it has been found that the substitution of a small amount of tin by nickel increases the current values in comparison to those obtained on Pt-Sn electrocatalyst. Studies made on Pt-Sn-Ru catalyst have showed that the addition of Ru to Pt-Sn greatly enhanced the electrical performance of the direct ethanol fuel cell, e.g. the activity of the catalyst but did not modify the product distribution. Finally, studies made on Pt-Sn-Rh catalyst by linear sweep voltammetry indicated that for potentials higher than 0.45 V versus RHE, the ternary alloy catalyst posses the highest activity for ethanol electro-oxidation, while for potential lower than 0.45 V versus RHE the electrochemical activity of the ternary catalyst was lower than that of the binary Pt-Sn catalyst.[13]

Besides investigators working in the creation of an enhanced catalytic material that can be used in DEFC's for the anodic reaction, several studies have been made on the ethanol oxidation in ionic liquids due to ionic liquids have unique chemical and physical properties[30].

Ionic Liquids

Room temperature ionic liquids (RTILs) can be defined as salts with a melting temperature below the boiling point of water. Most salts identified in the literature as ionic liquids are liquid at room temperature, and often to substantially lower temperatures. A general feature of ionic liquids is that most consist of organic cations such as 1-alkyl-3-methylimidazolium, 1-alkylpyridinium, N-methyl-N-

alkylpyrrolidinium and ammonium ions, and inorganic anions such as simple halides, which generally inflect high melting points, to inorganic anions such as tetrafluoroborate and hexafluorophosphate and to large organic anions like bistriflimide, triflate or tosylate.[25, 26]
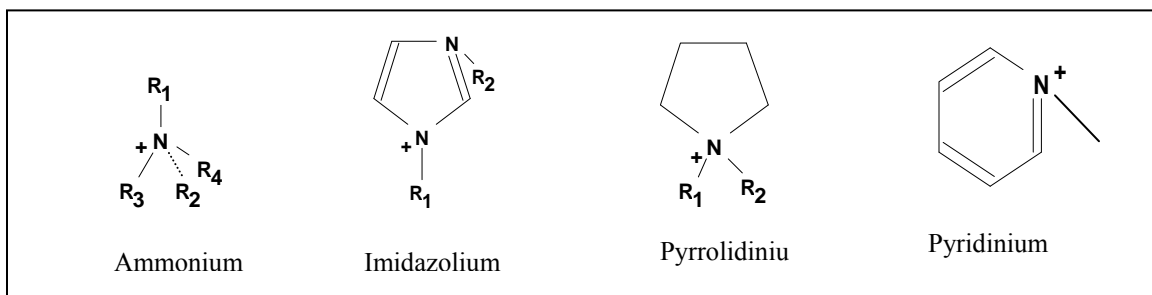
Figure 2: Commonly Used Cations for Ionic Liquids
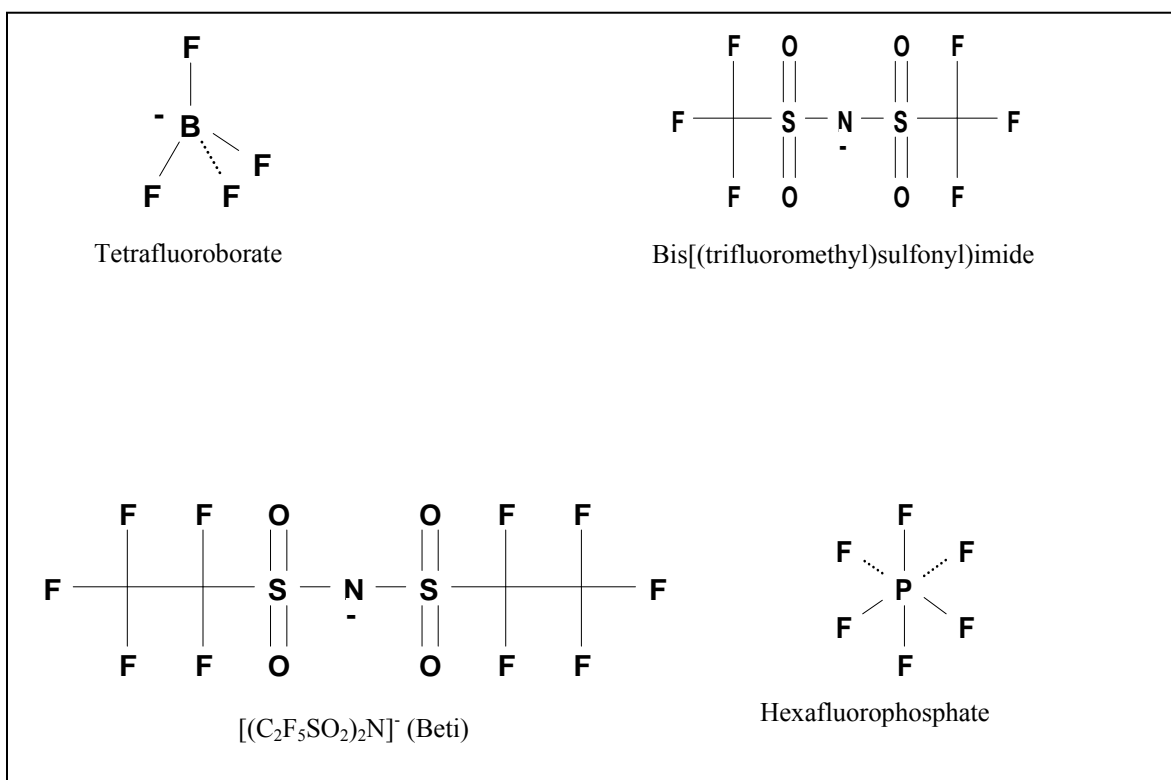
Figure 3: Commonly Used Anions for Ionic Liquids

Physical and Chemical Properties of Ionic Liquids

The physical and chemical properties of RTILs depend on the nature and size of both the cation and the anion constituents. Knowledge of the physical properties of RTILs and the phase behavior with gases, liquids and solids (including inorganic salts) is important for evaluating and selecting RTILs for each application as well as process design.

RTILs have become very popular as potential solvents for industrial applications in many different disciplines of science and environment due to their unique properties such as a negligible vapor pressure, good thermal stability, tunable viscosity and miscibility with water, inorganic and organic substances, a wide electrochemical window, high conductivity, high heat capacity and solvents available to control reactions. Despite their wide range of polarity and hydrogen-bonding ability, these new solvents are liquid form 180 K (glass transition) to 600 K.

Densities and Viscosities

RTILs tend to be denser than water with values ranging from 1 g cm^{-3} for a typical RTIL to 2.3 g cm^{-3} for fluorinated RTILs. For example, the densities of the following two salts are: [C$_8$C$_1$Im][BF$_4$] 1.08 g cm^{-3} or [C$_{10}$C$_1$Im][BF$_4$] 1.04 g cm^{-3} at T = 298.15 K. Density depends strongly on the size of the ring in the cation, on the length of the alkyl chain in the cation, on the symmetry of the ions and on the interaction forces between the cation and the anion. RTILs with aromatic head ring, in general, present greater densities then pyridinium head ring RTILs and than do imidazolium ring RTILs. Density increases with increasing symmetry of their cations. The increases of an alkyl

chain diminish the densities in a systematic manner (sometimes only slightly, as was shown above). RTILs with functional groups reveal higher densities than those of alkyl chains. The densities of RTILs based on 1,3-dialkylimidazolium cations (the most popular RTIL in experimental laboratory work worldwide) increase for typical anions in the following order: $[BF_4]^- < [C_2SO_4]^- < [PF_6]^- < [TF_2N]^-$.

Viscosity of RTILs, typically at the level of 10-500 cP (centipoise) at room temperature, is much higher than that characteristic of water ($\eta(H_2O) = 0.89$ cP at 298.15 K) and aqueous solutions. Such as high dynamic viscosity (viscosity coefficient) of RTILs causes difficulties in practice since it affects the diffusion of solutes due to problems such as stirring and pumping. The viscosity of RTILs is determined by van der Waals forces and hydrogen-bonded structures. Electrostatic forces as well as the shift of charge at the anion may also play an important role.

Melting Point, Glass Transition, and Thermal Stability

Melting points of RTILs depend both on the cation and on the anion. Usually, the increase in anion size and its asymmetric substitution as well as the increase in cation size and its symmetry leads to a decrease in the melting point. Another important factor affecting melting points of RTILs is the flexibility of the cation and the anion. An increase of alkyl chain length enhances the molar volume and chain flexibility of the cation. For example, increasing the alkyl chain length from 0 to 8 the melting point temperature decreases whereas increasing from 8 to 20 it causes a monotonous increasing of the melting point.

The glass transition temperatures for the most popular RTILs are between 213 and 783K. In general, changes of glass transition temperatures with changing length of the alkyl chain are much smaller than the melting temperatures.

Common RTILs are thermally stable up to 700 °C. Thermal stability is limited by the same factors that contribute to the melting temperature.[27]

Electrochemical Properties

The early history of RTILs research was dominated by their applications as electrochemical solvents. One of the first recognized uses of ionic liquids was as a solvent system for the room-temperature electrodeposition of aluminum. In addition, much of the initial development of RTILs was focused on their use as electrolytes for battery and capacitor applications. Until recently, electrochemical studies in the room temperature ionic liquids were primary done in haloaluminate-based systems and this work has been extensively reviewed. Development of non-haloaluminate ionic liquids over the past fifteen years, however, has led to an explosion of research on these systems. Much of the initial interest in these new room temperature ionic liquids has been in areas other than electrochemistry. However, this initial slight has been largely corrected, as evidenced by the dramatic growth over the past five years in electrochemically related publications involving non-haloaluminate room temperature ionic liquids and the appearance of several good reviews on the subject.

Room temperature ionic liquids possess a variety of properties that make them desirable as solvents for investigating electrochemical processes. They often have wide

electrochemical potential windows; they have reasonably good electrical conductivity and solvent transport properties as mention before.

Electrochemical Potential Window

A key criterion for the selection of a solvent for electrochemical studies is the electrochemical stability of the solvent. This is most clearly manifested by the range of potential over which the solvent is electrochemically inert. This useful electrochemical potential "window" depends on the oxidative and the reductive stability of the solvent. In the case of RTILs, the potential window depends primarily on the resistance of the cation to reduction and the resistance of the anion to oxidation. In addition, the presence of impurities can play an important role in limiting the potential window of RTILs.

The most common method used to determine the potential window of RTILs is cyclic voltammetry. In a three-electrode system, the potential of an inert working electrode is scanned out to successively greater positive (anodic) and negative (cathodic) potentials until background currents rise dramatically due to oxidation and reduction of the room temperature ionic liquid, respectively. The electrochemical potential window is the difference between these anodic and cathodic potential limits.

It must be noted that impurities in the ionic liquids can have a profound impact on the potential limits and the corresponding electrochemical window. During the synthesis of many non-haloaluminate RTILs residual halides and water may remain in the final product. Halide ions (Cl^-, Br^-, I^-) are more easily oxidized than the fluorine-containing anions used in most non-haloaluminate RTILs. Consequently, the observed anodic

potential limit could be appreciably reduced if significant concentrations of halide ions are present.

During the initial development of the non-haloaluminate air and water stable room temperature ionic liquids, researches often ignored potential contamination by water and the corresponding effects on the physical and chemical properties of the ionic liquid. However, as work on these new room temperature ionic liquids has progressed it has become apparent that water is an important contaminate to control. Water can be reduced and oxidized within the electrochemical potential window of many ionic liquids. Consequently, contamination of an ionic liquid with significant amounts of water can decrease the overall effective electrochemical window.

Glassy carbon (GC), platinum (Pt), and tungsten (W) are the most common working electrodes used to evaluate electrochemical windows in room temperature ionic liquids. The choice of the working electrode has some impact on the overall electrochemical window measured. This is due to the effect of the electrode material on the irreversible electrode reactions that take place at the oxidative and reductive limits.

Ionic Conductivity

The ionic conductivity of a solvent is of critical importance in its selection for an electrochemical application. There are a variety of DC and AC methods available for the measurement of ionic conductivity. However, in the case or room temperature ionic liquids the vast majority of data in the literature has been collected using one of two AC techniques, the impedance bridge method or the complex impedance method. Both of

these methods employ simple two electrodes cells to measure the impedance of the ionic liquid (Z).

The conductivity of an electrolyte is a measure of the available charge carriers and their mobility. On the surface one would expect room temperature ionic liquids to possess a very high conductivity because they are composed entirely of ions. Unfortunately, this is not the case. As a class, ionic liquids possess reasonably good ionic conductivities, comparable to the best non-aqueous solvent/electrolyte systems. However, they are, in general, significantly less conductive than concentrated aqueous electrolytes. The smaller than expected conductivity of ionic liquids can be attributed to the reduction of available charge carriers due to ion pairing and /or ion aggregation, and to the reduced ion mobility resulting from the large ion size found in many ionic liquids.

Transport Properties

The behavior of ionic liquids as electrolytes is strongly influenced by the transport properties of their ionic constituents. These transport properties relate to the rate of ion movement, and to the manner in which the ions move (as individual ions, ion-pairs, or ion aggregates). The two quantities often used to evaluate the transport properties of electrolytes are ion diffusion coefficients and ion transport numbers. The diffusion coefficient is a measure of the rate of movement of an ion in a solution, and the transport number is a measure of the fraction of charge carried by that ion in the presence of an electric field.

Applications of Ionic Liquids

Until now RTILs have received most attention for electrochemical and chemical research. However, it is important to mention that there are some applications of the ionic liquids outside the classic chemical use as solvents or process chemicals. In these cases ionic liquids are used as performance chemicals and engineering fluids.

Applications of Ionic Liquids in Chemical Processes

Acid Scavenging: The BASIL™ Process

The so-called BASIL™ process (BASIL = Biphasic Acid Scavenging utilizing Ionic Liquids) is used for the synthesis of alkoxyphenylphosphines, which are important raw materials in the productions of BASF's Lucirines substances that are used as photo-initiators to cure coating and printing inks by exposure to UV light. In this process, the ionic liquid acts as an auxiliary   and the benefits of using the ionic liquid are: non handling of solids, better heat transfer, higher chemical yield, lower investment cost, and higher sustainability of the process.

Extractive Distillation

In many cases, the formation of azeotropes does not allow the separation of two or more compounds by simply distillation. Very well known azeotropes with and industrial relevance are, for example, water/ethanol. Sometimes the azeotrope can be broken by the addition of another compound. These compounds are called entrainers. It was found that ionic liquids work as entrainers for a whole range of azeotropic systems. Very high separation factors can be achieved, especially if water is part of the azeotropic

mixture. Some benefits of using ionic liquids as extrainers are: breaking of azeotropes, less energy consumption, less equipment (distillation columns), and lower investment.

Chlorination with "Nucleophilic HCl"

Industrial chlorinating agents for alcohols are CCl_2O, $SOCl_2$, PCl_3, and PCl_5. Phosgene is a cheap raw material and usually gives excellent yield. However, the handling of phosgene requires enormous safety efforts. In principle, the chlorination of alcohols can also be achieved by reaction with HCl gas. Unfortunately, in the case of diols, conversion is usually less than 100% and the reaction stops after formation of cyclic or open-chain ethers.

Surprisingly the reactivity profile completely changes when the reaction is performed in ionic liquid. Obviously either the nucleophilicity of HCl or nucleofugicity of the leaving group (water) is drastically increased. Apparently, the either side products are cleaved, allowing further reaction to the desired bischlorinated product. In this process, the ionic liquid acts as a solvent, and the benefits of using ionic liquids as a solvent are: HCl substitutes for phosgene and high selectivity at high conversion.

Cleavage of Ethers

Eli Lilly (pharmaceutical company) has published de-methylation of an aromatic methoxy group in ionic liquids. Usually the cleavage of aromatic methoxy ethers requires very harsh conditions and inconvenient reagents, such BBr_3 or HBr in boiling acetic acid. It has been found by Eli Lilly that de-methylation of an aromatic methoxy (4-Hydroxyphenylbutyric acid) can be made using the ionic liquid pyridinium hydrochloride

([PyH]Cl). In this process, the ionic liquid acts as a catalyst/reagent and the specific benefits offer by the ionic liquid are: HCl can be used as a cheap cleaving agent of aromatic methoxy groups and lower cost.

Dimerization of Olefins

The Institut Francaise du Petrol (IFP) was the first to develop an ionic liquid based process to a pilot scale (DIFASOL Technology) for the dimerization of olefins. In dimerization of olefins, the ionic liquid acts as a solvent, and the benefits of the ionic liquid are: higher catalyst activity, higher catalyst stability, and higher selectivity.

Oligomerization of Olefins

Chevron Phillips has invented a process utilizing acidic ionic liquid for olefin oligomerization. The process produces synthetic lubricant base oil which is used in a variety of lubricants including gear oils, greases and automotive engine lubricants. Synthetic lubricants are of considerable interest due to tightening lubricant specifications. In oligomerization of olefins the ionic liquid acts as a catalyst, and the benefits of the ionic liquid are: provides product with a unique viscosity profile useful for application as a lubricant.

Hydrosilylation

The hydrosilylation reaction is a widely used method for the synthesis of organo-modified silanes and siloxanes. The addition of Si-H to C-C double bonds is usually catalyzed by homogenous or colloidal Pt catalysts. The major drawback of this reaction is that the catalyst cannot easily be removed from the product after completion of the

reaction. To lower losses of precious metal catalysts, the amount of catalyst is usually decreased, but this decreases reaction speed. Degussa has managed to develop an elegant biphasic approach to run the hydrosilylation reaction.

The catalyst is now dispersed in the ionic liquid phase, from which the pure product separates as a new liquid phase that can be easily decanted after the reaction. The ionic liquid catalyst phase is still active and can be reused. Degussa has been running this process on a pilot scale achieving conversions of >99%. In this process, the ionic liquid acts as a catalyst, and the benefits of the ionic liquid are: recovery and reusability of the catalyst phase, shorter reaction times due to higher catalyst loadings, and improvement in product quality.

Fluorination

Fluorinated hydrocarbons are used as refrigerants in the air-conditioning and refrigeration industry. Chlorofluorocarbons are being phased out according to the Montreal protocol due to their ozone depletion potential. This is mainly attributed to the chlorine content. Hence chlorofluorocarbons will be replaced by chlorine free hydrofluorocarbons (HFCs). HFCs can be manufactured from chlorinated hydrocarbons by reacting them with HF in order to achieve a chlorine/fluorine substitution. The state-of-the-art catalyst for this reaction is $SbCl_5$. However, this catalyst suffers from a reductive deactivation with the formation of Sb(III) species. To overcome the loss of catalyst, chlorine is co-fed for re-oxidation of Sb(III) to Sb(V). This is technically feasible, but consumes chlorine as a raw material and leads to back-chlorination of the fluorinated products, and hence to significantly lower yields. Arkema has demonstrated at

a pilot scale that imidazolium-based ionic liquids with a $[SbF_6]^-$ ion can eliminate the deactivation problem. In this process, the ionic liquid acts a catalyst, and the benefits offer by the ionic liquid are: higher catalyst activity, higher stability of the catalyst to reductive deactivation, avoidance of chlorine co-feed, and a higher selectivities towards perfluorinated products.

Applications of Ionic Liquids in Electrochemistry

Electroplating of Chromium

The deposition and dissolution of metals is a multi-million industry that is almost totally based on aqueous acids and alkalis. The use of water limits the metals that can be deposited and produces large volumes of aqueous waste. The processes are often hindered by low current efficiencies.

One of the largest sectors of electroplating market is that of chromium deposition. The major disadvantage of the current process of chromium plating is that it requires the use of chromic acid-based electrolytes comprising hexavalent chromium. The toxicity and the carcinogenicity associated with Cr(VI) have resulted in wide-ranging environmental legislation in the USA and Europe to reduce its use. Other disadvantages of the existing technology are economic, such as the low current efficiency for the reduction of Cr(VI) in acid media. Furthermore, the difference in overpotential between chromium and hydrogen reduction results in the evolution of hydrogen gas, which can lead to embrittlement in the substrate, thus reducing quality and yield.

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Scionix, a joint venture company between the University of Leicester and Whyte Chemicals Ltd, has developed ionic liquid containing Cr (III) salts, which are significantly less toxic than the carcinogenic Cr(VI) species. The process also operates with >90% current efficiency, resulting in significantly reduced power consumption and making the ionic liquid technology a more environmentally benign form of plating. Moreover, since these are not aqueous solutions, there is negligible hydrogen evolution. In this process, the ionic liquid act as an electrolyte, and the specific benefits offer by the ionic liquid are: usage of less toxic Cr(III) salts rather than highly toxic Cr(VI) as raw material for chromium plating, and reduced power consumption.

Electropolishing

Electropolishing of stainless steel is an effective way of increasing corrosion resistance and decreasing wear, in addition to the obvious esthetic benefits. Current electropolishing technology primarily uses sulfuric and phosphoric acids mixtures. These are naturally corrosive, harmful to work with and must be neutralized before disposal. Acid-based electropolishing is an inherently inefficient process: only 10-20% of the energy supplied is utilized for metal dissolution. The scale of this activity worldwide represents a significant environmental concern.

Scionix has developed an alternative concept to forming eutectic-based ionic liquids which is to complex the chloride anion with a hydrogen-bonding compound rather than a metal halide. The ionic liquid allow electropolishing with high current efficiency (>80%), improved surface finish and improved corrosion resistance.

Scionix is currently developing a commercially viable medium-to-large-scale electropolishing plant using these novel electrolytes in collaboration with UK-based Anopol Ltd. The new process significantly reduces the total volume of effluent and its toxicity. In this process, the ionic liquid acts as an electrolyte, and the specific benefits of the ionic liquid are: high current efficiency, improved surface finish, and improved corrosion resistance.

Applications of Ionic Liquids as Performance Chemicals and Engineering Fluids

Ionic Liquids as Antistatic Additives for Cleaning Fluids

The cleaning of high value surfaces, e.g. in the automotive, furniture or electronic industry, is a challenging problem, in particular if small charged particles have to be removed. Wandres Micro-Cleaning GmbH has developed a cleaning system that uses moistened instead of dry filaments.

The liquid film (water) is brought onto the filament with the help of very small, micrometer-sized water droplets. The droplets are generated in a Venturi nozzle. To avoid electrostatic charging of the surface, a supporting salt is usually added that facilitates electrical conductivity. If sodium chloride is used as a supporting salt; a solid is precipitated in the nozzle leading to encrusting and blocking of the system.

Ionic liquids can offer a unique solution to this problem, since as liquid salts they can provide electrical conductivity without precipitation of a solid, hence without formation of deposits. The ionic liquid solution to this problem was developed and established by Iolitec in cooperation with Wandres Micro-Cleaning GmbH. In this

process, the ionic liquid acts as cleaning agent, and antistatic, and the benefits of the ionic liquid are: enables electric conductivity without formation of solid residues.

Ionic Liquids as Compatibilizers for Pigment Pastes

Up to now only a very little attention has been paid to ionic liquids as performance chemicals. Degussa has managed to develop an application of ionic liquids as so-called compatibilizers for pigment pastes.

Paints and coatings can be tinted by adding a small amount of a color concentrate –the pigments paste- to a white based paint. The advantage is clear. One can derive more or less any color from the same base paint formulation, just by adding the right mix of pigments. To achieve a homogenous and stable coloring, the paste needs some additives which for example, prevent the pigments from sedimentation or flocculation. For environmental reasons, it is preferable to use water-based pigment pastes. However, the water-based system cannot be used universally for both water and solvent-based paints. This problem has been solved by addition of ionic liquids to the pigment paste. Now the pigments are stable in both water-based paints and in solvent-based ones. In this process, the ionic liquid acts as a compatibilizers, and the benefits of using the ionic liquid are: stabilize pigments in pigment pastes, provide truly universal water-based pigment pastes suitable for water- and solvent-based paints and coatings.

Use of Ionic liquids for Storage of Gases

The semiconductor manufacturing industry uses a number of hazardous specialty gases as phosphine (PH_3), arsine (AsH_3) and boron trifluoride (BF_3) for doping, etching, and thin-film deposition. These gases are highly toxic and pyrophoric. Therefore storage and handling is challenging and requires enormous safety efforts. For example, storage of toxic gases under high pressure in metal cylinders is often unacceptable due to the possibility of leakage or rupture of the cylinder. To overcome the risks of high-pressure storage, these gases are often stored under low pressure by adsorption o solid support such as zeolites.

Disadvantage of this technology include: low capacities, delivery limitation and lo thermal conductivity. Air Products has developed an entirely new technology to solve this problem. Ionic liquids are used as a liquid support for the storage of gases. To increase the affinity of the gas to the ionic liquid a Lewis acid-Lewis base interaction is utilized. This allows high gas storage capacities without the need for high pressure. In this process the ionic liquid acts as a liquid support, and the benefits of the ionic liquid are: storage of hazardous gases possible without pressure, and higher safety.[28]

Review of Electrochemical Techniques

Cyclic Voltammetry

Among all electrochemical methods, cyclic voltammetry (CV) is the most widely used method to obtain information related to analyte concentration, electrode reaction kinetics, diffusional distributions, redox properties of compounds and mechanisms of

redox reactions. In a typical cyclic voltammetry experiment, an analyte is electrolyzed

(oxidized or reduced) by placing the solution in contact with an electrode surface, and

then making the surface sufficiently positive or negative in voltage to force electron

transfer. In simple cases, the potential of a working electrode is started at a particular

voltage with respect to a reference electrode such as calomel or Ag/AgCl. Then the

electrode voltage is changed to more positive or negative voltage at a linear rate, and

finally, the voltage is changed back to the original value at the same linear rate. When the

electrode becomes sufficiently negative or positive, a solution species may gain electrons

from the electrode or transfer electrons to the electrode. This results in a measurable

current in the electrode circuitry. However, if the solution is not mixed, the concentration

of electro-active species nears the surface of the electrode decreases, and the electrolysis

current then decreases. When the voltage cycle is reversed, it is often the case that

electron transfer between electrode and chemical species will also be reversed, leading to

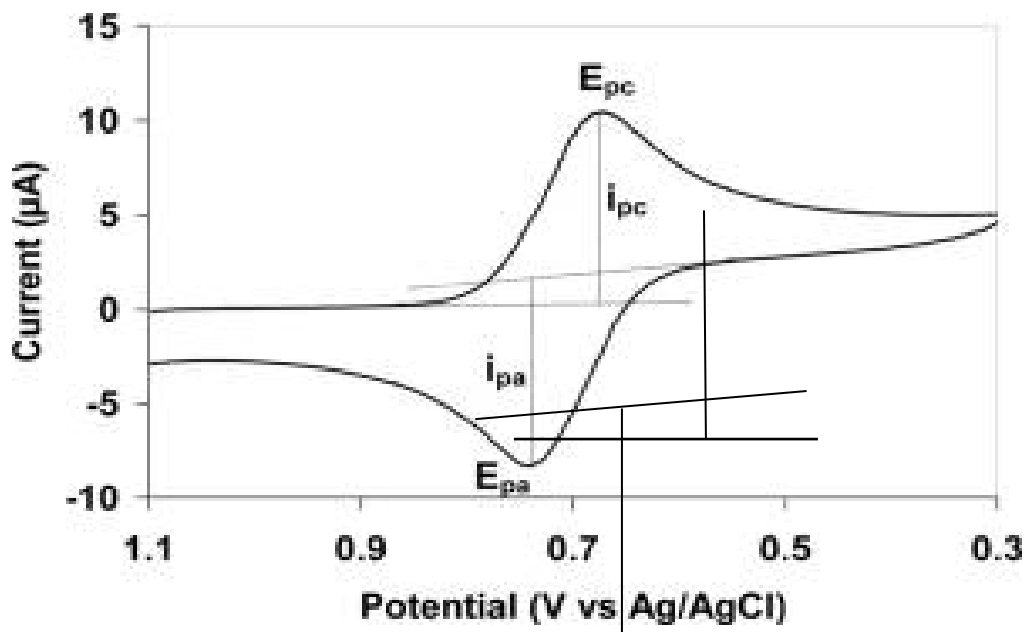an "inverse" current peak. These features are illustrated in Figure 2.

Figure 4: Typical Cyclic Voltammogram for an Electro-Active Species

A typical cyclic voltammogram for an electro-active species is defined by four parameters: cathodic peak current, I_{pc}, anodic peak current, I_{ac}, cathodic peak potential, E_{pc}, and the anodic peak potential, E_{ac}. Other parameters as the formal reduction potential, $E°$, the number of electrons involved in the redox process, n, and the half-cell potential, $E_{1/2}$, can be calculated from the four measurable quantities, I_{pc}, I_{ac}, E_{pc}, and E_{ac}.

In a cyclic voltammogram the signal of primary interest is the height of the reduction/ oxidation peak. In this method, the peak height (I_p) is described by Randles-Sevcik equation, and is directly proportional to the analyte concentration as follows:

$$I_p = \left(2.687\,X10^5\right) n^{3/2}\ v^{1/2}\ D^{1/2}\ A\ C \qquad \text{(Equation 4)}$$

where n is the number of electrons involved in the process, A is the area of the working electrode (cm^2), D is the diffusion coefficient ($cm^2 s^{-1}$), C is the bulk concentration of the analyte ($mol\ cm^{-3}$), and v is the rate at which the potential is sweep ($V\ s^{-1}$). The formal reduction potential, E°, for an electrochemically reversible couple can be calculated knowing E_{pc} and E_{pa} by:

$$E° = \frac{E_{pa} + E_{pc}}{2} \qquad \text{(Equation 5)}$$

For a reversible redox couple, the number of electrons transferred in the electrode reaction can be determined by the separation between the peak potentials, ΔE_p:

$$\Delta E_p = E_{pa} - E_{pc} = \frac{0.0592}{2} \qquad \text{(Equation 6)}$$

where a reversible one-electron process has an expected potential peak separation of 0.0592 V at 25°C.

Finally the half-cell potential, $E_{1/2}$ is calculated by the following equation:

$$E_{1/2} = E_{pc} + 1.11\frac{RT}{nF} \qquad \text{(Equation 7)}$$

where R is the gas constant, T is the temperature of the system (K), F is Faraday's constant and n is the number of electrons involved in the reaction.

Electrochemically reversible systems are characterized by a rapid electron transfer and a peak current ration, I_{pc}/I_{pa} equal to one, which is independent of the scan rate. Deviation of the ratio I_{pa}/I_{pc} from unity is indicative of homogeneous kinetic or other complication in the electrode process.[29, 30, 31]

II.   EXPERIMENTAL

Materials

1-Methylimidazole (99+%) was purchased from Aldrich Chemical Company,
Inc., and redistilled prior to use at a temperature of 90 to 100 °C under vacuum (15 mm
Hg). 1-Chloroethane gas (99.7+%) was obtained from Aldrich Chemical Company, Inc.,
and used as received. Sodium Tetrafluoroborate (95+%) and Silver Tetrafluoroborate
were obtained from Alfa Aesar Co., and used as received. Lithium-bis-
(trifluoromethanesulfonyl)imide (HQ-115) was obtained from 3M Corporation and used
as received. Acetonitrile with a gradient grade of +99.9% was purchased from Sigma-
Aldrich and used as received. Diethyl Ether was obtained from Fisher Co. and used as
received. Perchloric acid, 70%, 99.9985% (metal basis) was purchased from Alfa Aesar
Co., and used as received. Ethyl alcohol was purchased from AAPER Alcohol and
Chemical Co., and used as received. Sulfuric Acid was purchased from Pharmaco-
AAPER Alcohol and Chemical Co.

Instrumentation

Determination of Water in Ionic Liquids

The water concentration in ionic liquids was determined using a Denver
Instruments Coulometric Karl Fisher Titrator – Model 260. The size of each sample used
was 50.00 µL. All samples were injected into the tritator using a glass syringe with a

stainless steel needle. Prior to use, the syringe was washed with acetonitrile and dried in an oven at a temperature of 60–80 °C.

Electrochemical Measurements

The electrochemical measurements were performed in two types of electrochemical cells; one for small volumes of the sample, and the other for large volumes of the sample using a conventional three-electrode assembly. The working electrodes in the small cell were 1mm Pt in glass or 1.5 mm Pt in plastic obtained from Cypress Systems Inc. The working electrode in the large cell was a 1 cm Pt disk in plastic obtained from Pine Industries Co. The counter (auxiliary) electrode was a Pt wire, and the reference electrode a Ag wire.
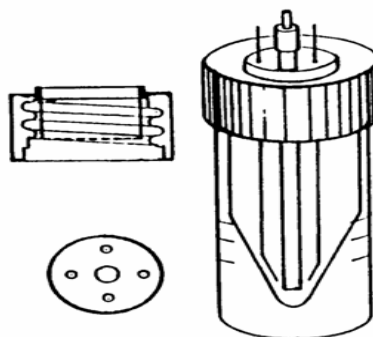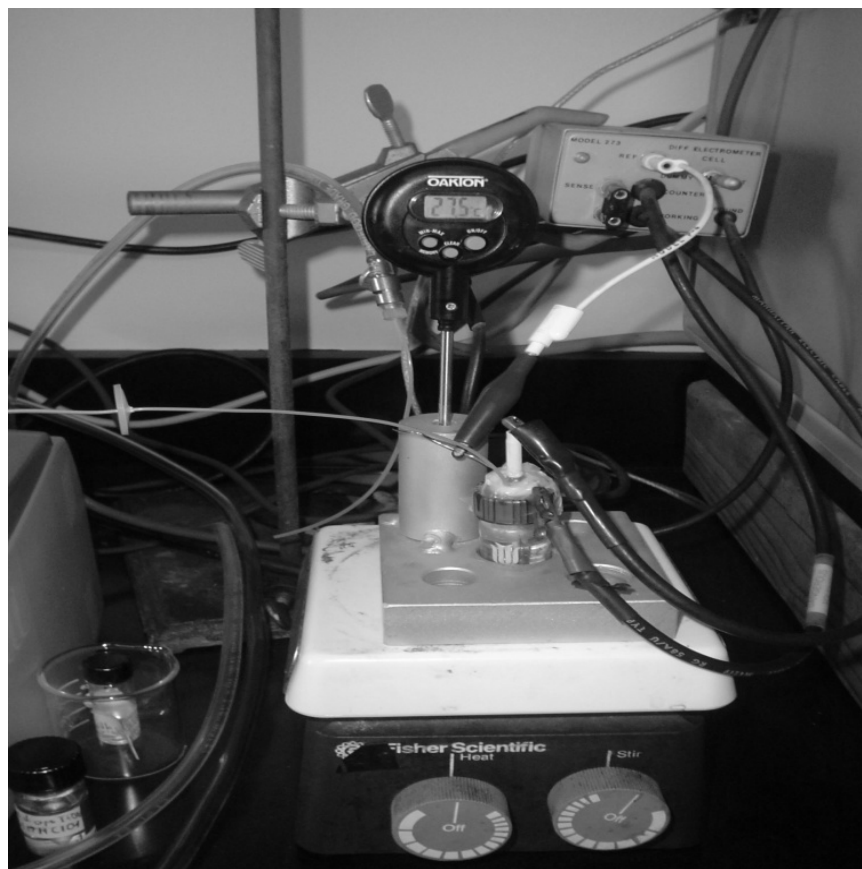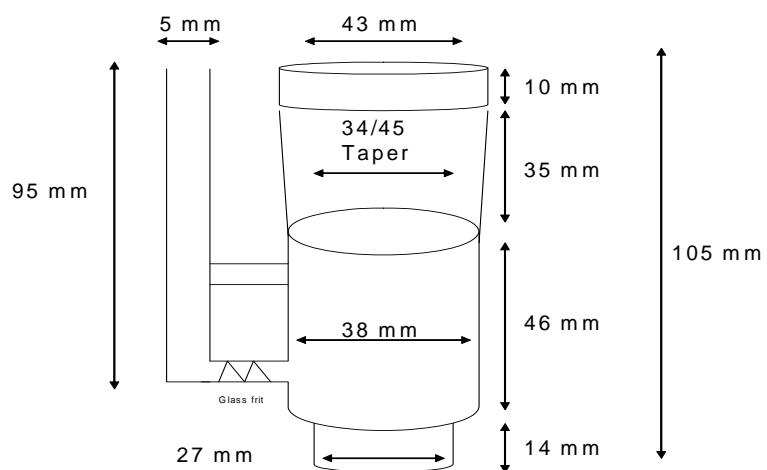
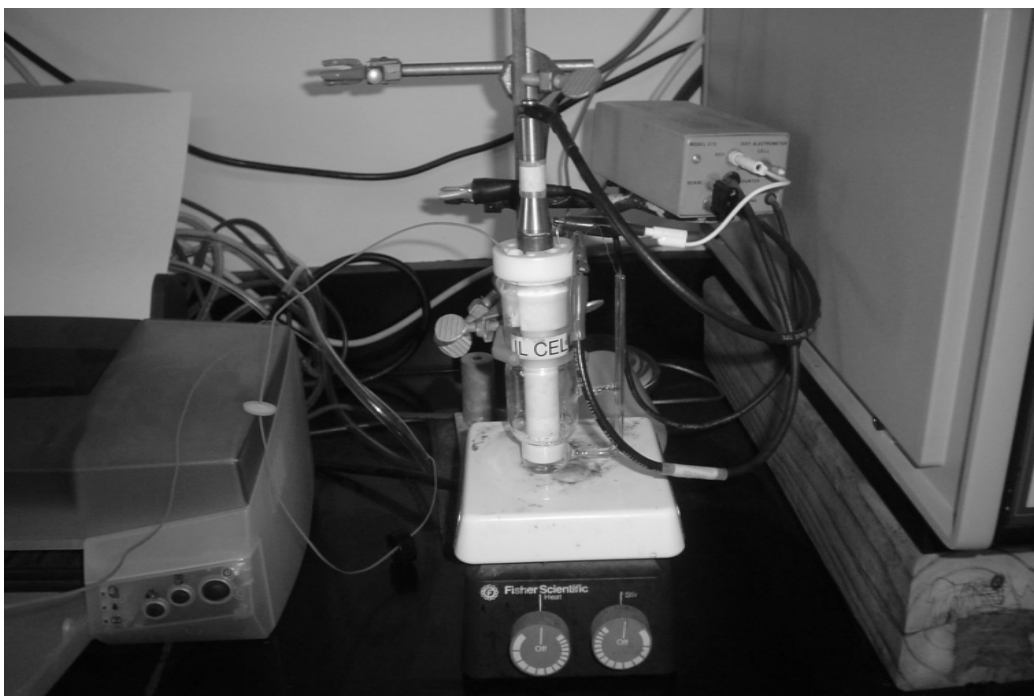**Figure 5: Small Volume Electrochemical Cell**

Figure 6: Large Volume Electrochemical Cell

Electrochemical measurements were made using a computer-aided

Potentiostat/Galvanostat (EG&G Princenton Applied Research model 273) interface with

e-corder model 201.

Method Used for Cleaning Platinum Electrode

Poisoned platinum electrode was cleaned by soaking the electrode in concentrated

sulfuric acid (H_2SO_4) overnight to dissolve PtO or $Pt(OH)_2$ deposited on the electrode.

After soaking in sulfuric acid, the electrode was soaked in distilled water and placed in a

sonicator for a few hours to remove any debris. After a few hours, the electrode was

removed from the water, and was polished on a clean piece of paper. After polishing the

electrode, it was rinsed off several times with several small portions of distilled water,

and stored in distilled water until use. The electrode was reactivated by running several

cyclic voltammograms at potentials corresponding to the oxidation and reduction limits

of the platinum surface electrode in the solution at which the electrochemical

measurements would be made.

Synthesis of 1-Ethyl-3-Methylimidazolium Chloride

1-Methylimidazole with a purity grade of 99% was distilled at a

temperature of 90-100°C under vacuum (15 mm Hg). In an I^2R glove bag filled with

nitrogen gas, an equimolar amount (44 g) of gaseous Chloroethane was condensed into an

ACE glassware reinforced pressure bottle, using a bath of liquid nitrogen/ethanol solution

at a temperature of -30 to -50°C. 1-Methylimidazole was added into the bottle, and then

the bottle was sealed using a chemically inert Teflon screw cap, and removed from the

glove bag. The reaction flask was heated on a hot plate using an oil bath at a temperature

of 55°C. The solution was left to react for four days. After the reaction was completed, the reaction flask was removed from the heat and cooled down to room temperature, and then, it was refrigerated for around 12 hrs to crystallize white crystals of 1-Ethyl-3-Methylimidazole Chloride. Once the crystals were formed, excess liquid was decanted and the crystals of EMImCl were dissolved in acetonitrile, recrystallized with diethyl ether and refrigerated until recrystallization was completed. The crystals were filtered under N_2 using a Schlenk filtration flask and the crystals of 1-Ethyl-3-Methylimidazole Chloride were dried under vacuum for two days. The dry 1-Ethyl-3-Methylimidazolium Chloride was stored under dry nitrogen until use.

1-Methylimidazole   Chloroethane   1-Ethyl-3-Methylimidazolium Chloride
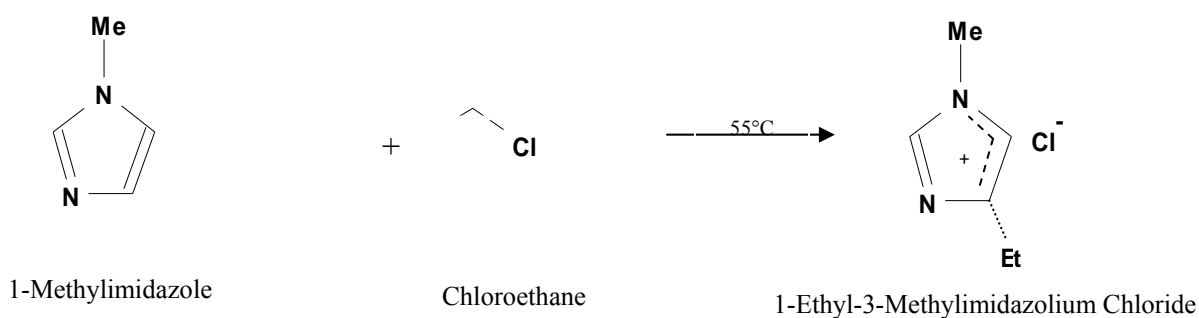
Synthesis of 1-Ethyl-3-Methylimidazolium Tetrafluoroborate

1-Ethyl-3-Methylimidazolium Tetrafluoroborate was prepared by an ion exchange reaction between 1-Ethyl-3Methylimidazolium Chloride and Sodium Tetrafluoroborate in water. 0.605 Moles (88.66 g) of 1-Ethyl-3-Methylimidazolium Chloride were dissolved in 300 ml of distilled water, then an equimolar amount of Sodium Tetrafluoroborate (67 g) dissolved in 300 ml of distilled water was added. The reaction flask was stirred on a stirring plate, and the solution was left to react for 24 hrs. After the reaction was completed, water was removed from the solution by rotatory evaporation under vacuum at a temperature of 80 °C. After water was removed, a solution of 1-Ethyl-3-

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Methylimidazolium Tetrafluoroborate was filtered to remove NaCl using a fine porosity

(4-8 μ) sintered-glass funnel. Any excess of chloride in the solution was removed by

dissolving 1-Ethyl-3-Methylimidazolium Tetrafluoroborate in distilled water and

potentiometrically titrating the excess of Cl^- with $AgBF_{4(aq)}$ until an equivalence point of

297 mV on Ag│AgCl electrode was reached. An Ag|AgCl, HgSO₄|Hg reference

electrode was used to measure the equivalent point potential. Again, water removal was

performed by rotatory evaporation at 80 °C under vacuum. 1-Ethyl-3-Methylimidazolium

Tetrafluoroborate was filtered to remove any precipitated AgCl. After the solution was

filtered, 500 ml of acetonitrile was added, and the solution was evaporated under vacuum.

1-Ethyl-3-Methylimidazolium Tetrafluoroborate was tested with $AgNO_3$ to confirm the

absences of chloride ions. 1-Ethyl-3-Methylimidazolium Tetrafluoroborate was dried on

the high vacuum (5 x 10^{-4} mm Hg) to remove any excess of water present.

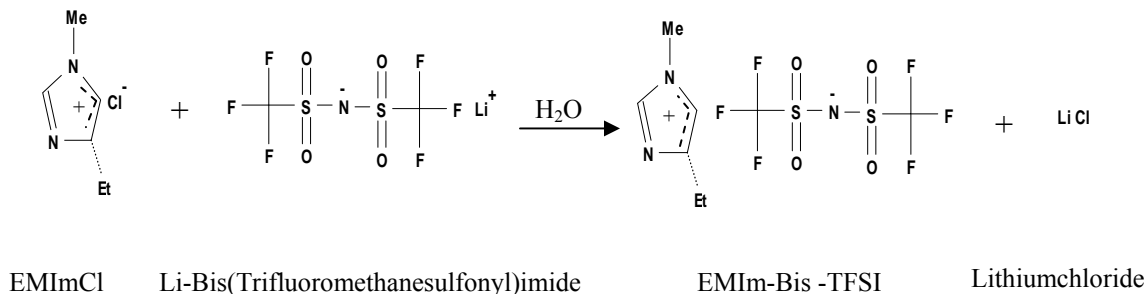EMImCl   Sodium Tetrafluoroborate   EMImBF₄   Sodium Chloride
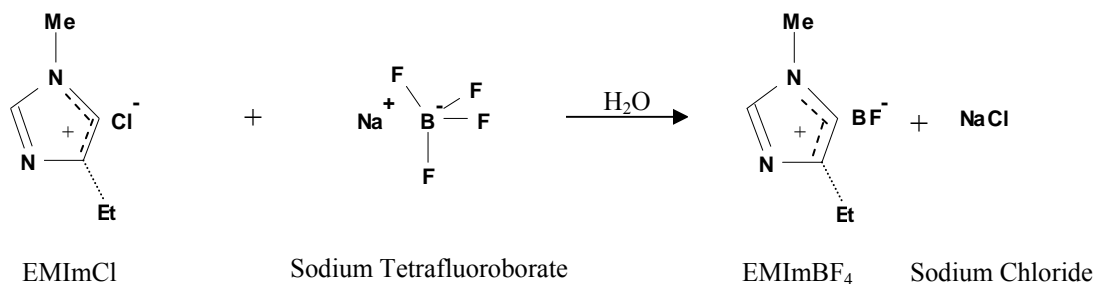
Synthesis of 1-Ethyl-3-MethylimidazliumBis(trifluoromethanesulfonyl)imide

1-Ethyl-3-Methylimidazolum Bis(trifluoromethanesulfonyl)imide

(EMImTFSI) was prepared by an ion exchange reaction, from 1-Ethyl-3-

Methylimidazolim Chloride and Lithium-bis-(trifluoromethanesulfonyl)imide.

EMImCl   Li-Bis(Trifluoromethanesulfonyl)imide   EMIm-Bis -TFSI   Lithiumchloride

1-Ethyl-3-Methylimidazolium Chloride (65 g) was dissolved in 300 ml of

distilled water. Then an equimolar amount of Lithium-bis(trifluoromethanesulfonyl)imide

(129 g) was dissolved in 300 ml of distilled water was added. The reaction flask was

stirred for 24 hrs. After the reaction was completed, 1-Ethyl-3-Methylimidazolium

Bis(trifluoromethanesulfonyl)imide layer was separated, and washed with several

portions (7 small portions) of distilled water using a separatory funnel to remove any

excess of chloride. The presence of chloride was tested with $AgNO_3$.

III.   RESULTS AND DICUSSION

The objective of this work was to synthesize and characterized the room temperature ionic liquids 1-ethyl-3-methylimidazolium tetrafluoroborate (EMImBF$_4$) and 1-ethyl-3-methylimidazolium Bis(trifluoromethanesulfonyl)imide (EMImTFSI), and to study the electrochemical behavior of ethanol, and propanol in these ionic liquids on a platinum electrode. In accordance with previous literature data, the chemical oxidation of ethanol on platinum electrode in acid media involves several reaction pathways. One predominant pathway involves oxidation of ethanol to acetaldehyde which can be further oxidized to acetic acid. However, at higher ethanol concentration (> 1 M) the poisoning of the Pt electrode occurs. Poisoning of the electrode is due to the formation of PtO and Pt(OH)$_2$. For that reason it is necessary to reactivate poisoned Pt electrode.

It is expected that use of the room temperature ionic liquids, EMImBF$_4$ and EMImTFSI, as electrolytes in the electrochemical oxidation ethanol, and propanol should have some advantages in comparison to aqueous HClO$_4$, such as eliminating the poisoning of the Pt electrode and favoring one of these pathways and possible oxidize ethanol to CO$_2$.

Synthesis and Characterization of Ionic Liquids

   1-Ethyl-3-Methylimidazolium Tetrafluoroborate

As mention before, a key criterion for the selection of a solvent for electrochemical study is the electrochemical stability of the solvent. This is most clearly manifested by the range of potential over which the solvent is electrochemically inert. This useful electrochemical potential window depends primarily on the resistance of the cation to reduction, the resistance of the anion to oxidation and the presence of impurities (e.g. halide ions, water). [28]

It is known from previous investigations that while 1-ethyl-3-methylimidazolium tetrafluoroborate (EMImBF$_4$) is commercially available, this is not electrochemically pure due to presence of impurities (Cl$^-$, H$_2$O) making it unsuitable for electrochemical studies.

In our case, EMImBF$_4$ was synthesized from 1-methylimidazole. The synthesis involved ethylation of 1-methylimidazole with ethyl chloride (CH$_3$CH$_2$Cl) and the formation of 1-ethyl-3-methylimidazolium chloride (EMImCl) at low temperature ($<$ 50 °C. The next step involved replacement of the Cl$^-$ ion with the BF$_4^-$ ion. This uses equivalent amounts of EMImCl with NaBF$_4$. Since EMImBF$_4$ is soluble in water, it was necessary to remove traces of Cl$^-$ with AgBF$_4$. In order to avoid addition of excess of Ag$^+$, the titration was carried up to the equivalence point which was determined using an Ag|AgCl, HgSO$_4$|Hg electrode.

As shown in Figure 7, EMImBF$_4$ prepared by the reaction of EMImCl with NaBF$_4$ does not contain Cl$^-$and exhibits an electrochemical window of 4.4 V at platinum working electrode which is very close to the potential window reported in previous
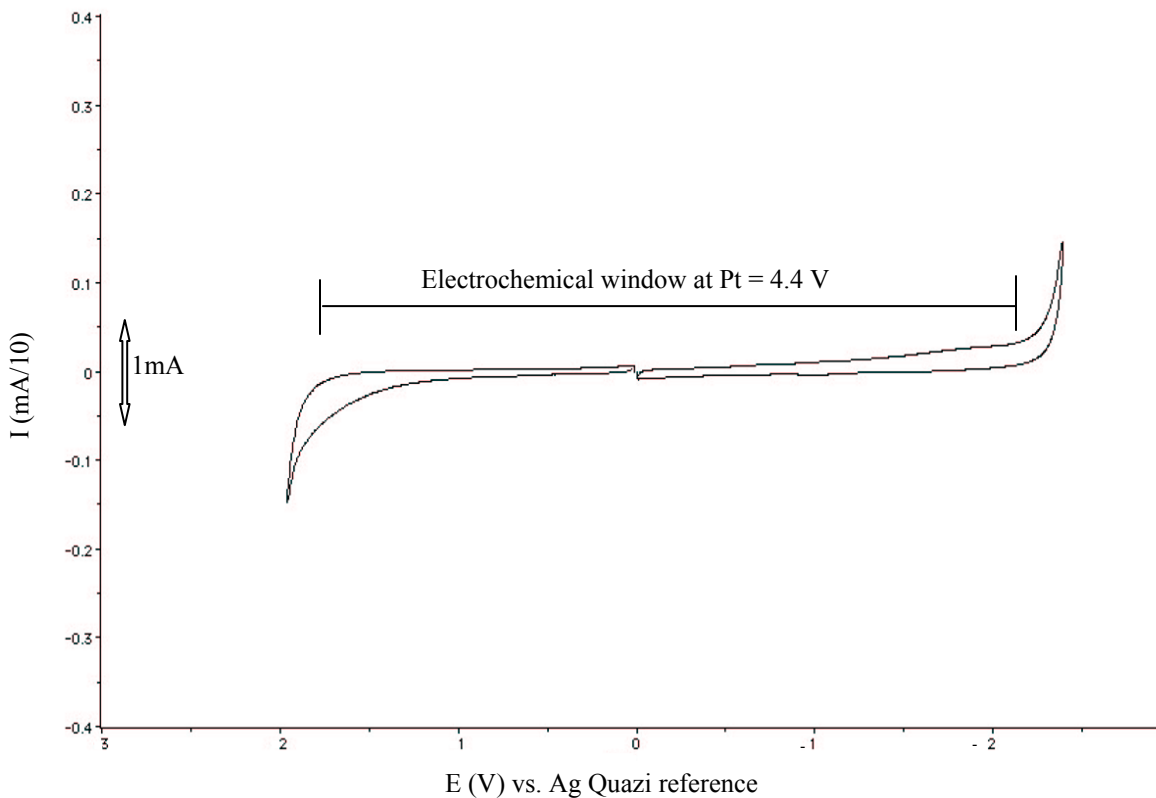
work[28].

Figure 7: Cyclic Voltammogram of EMImBF₄ at Platinum Working Electrode

1-Ethyl-3-Methylimidazlium Bis(trifluoromethanesulfonyl)imide

1-ethyl-3-ethylimidazolium Bis(trifluoromethanesulfonyl)imide (EMImTFSI) was made by an ion exchange reaction between 1-ethyl-3-methylimidazolim chloride with lithium-bis-(trifluoromethanesulfonyl)imide in water. Since EMImTFSI is not soluble in water, the excess of Cl⁻ was removed by washing the ionic liquid with H_2O.

As shown in Figure 8, EMImTFSI prepared by the ion exchange reaction of EMImCl with lithium-bis-(trifluoromethanesulfonyl)imide have an electrochemical

window of 5.0 V at platinum working electrode.
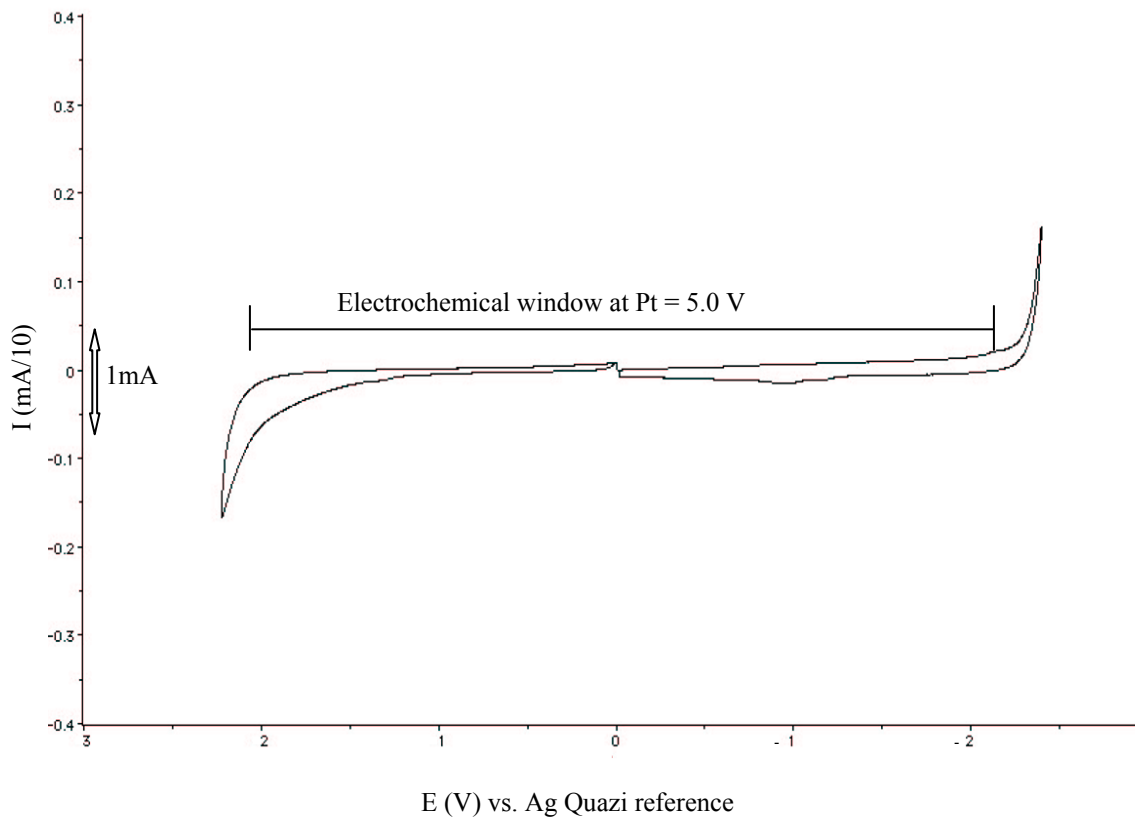
Figure 8: Cyclic Voltammogram of EMImTFSI at Platinum Working Electrode

Electrochemistry of Ethanol in HClO$_4$

In order to compare the electrochemical properties of ethanol in ionic liquids to the electrochemical properties in HClO$_4$/H$_2$O, the electrochemical properties in HClO$_4$ were studied. A cyclic voltammogram of HClO$_4$ without ethanol is shown in Figure 9. The voltammogram displays a strong reduction peak at E_{pc} = 500 mV at platinum working electrode which corresponds to reduction of H$^+$ to H$_2$, and a small oxidation peak at 0.85 V which is attributed to the oxidation of Pt to PtO.

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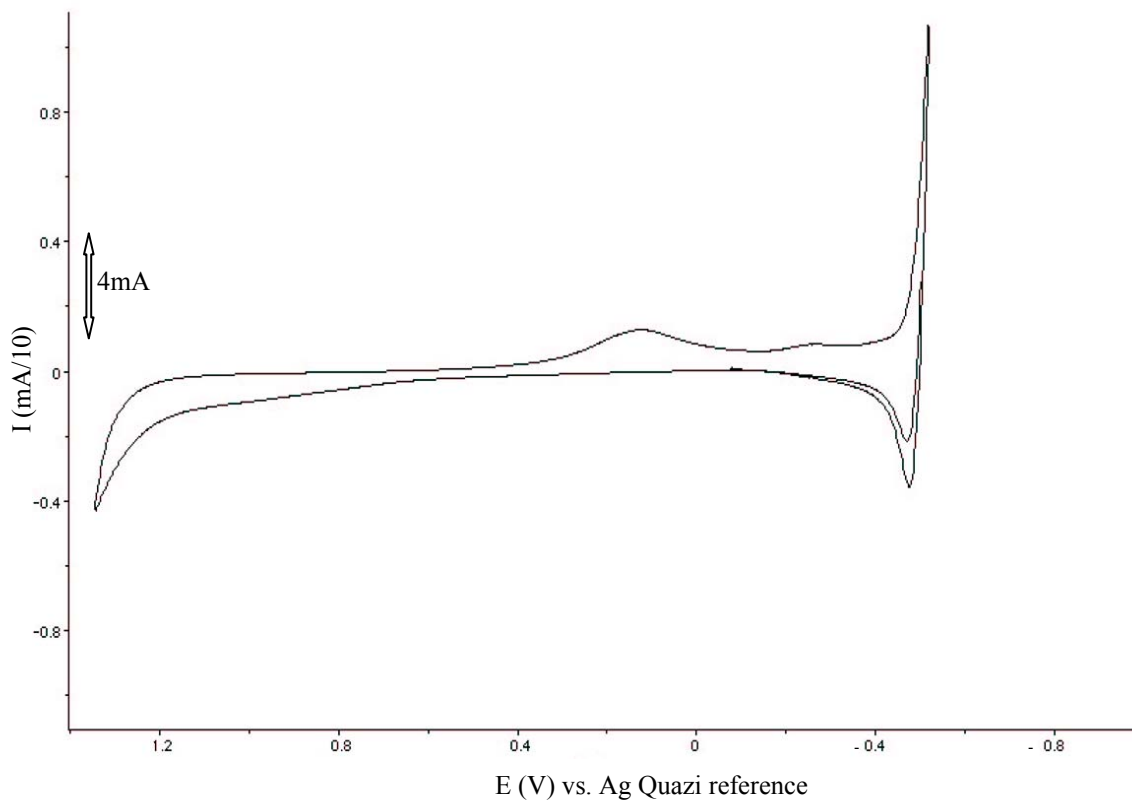
Figure 9: Cyclic Voltammogram of 0.1 M HClO$_4$ at Platinum Working Electrode

The electrochemical properties of ethanol on platinum working electrode in acidic medium were studied using different concentrations of ethanol (0.1, 0.2, 0.4, and 1 M) and different temperatures. In accordance with previous literature[30], three characteristic oxidation peaks were observed during the electrochemical oxidation of ethanol in HClO$_4$ depending of the conditions at which the experiment were made.
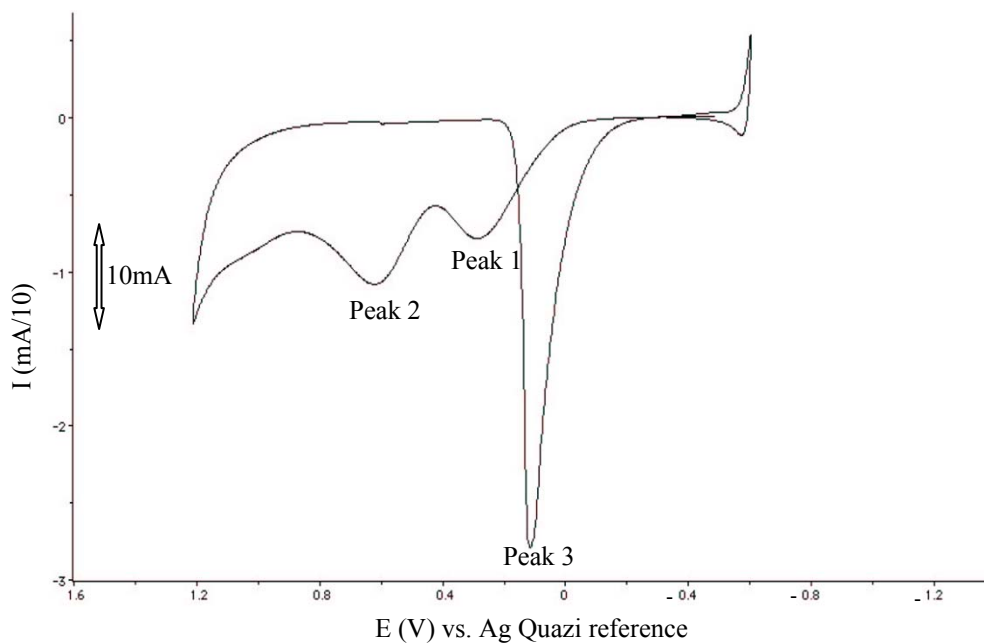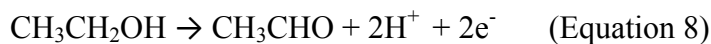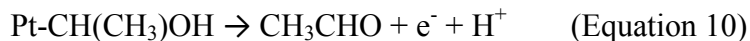
Figure 10: Cyclic Voltammogram of 1 M Ethanol in 0.1 M HClO₄ at Platinum Working Electrode at 70 °C

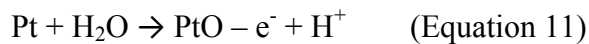These three peaks have been attributed to the following oxidation steps:

Peak 1 at $E_{pa} = 0.66$ V. This oxidation peak corresponds to a two electron oxidation of ethanol to acetaldehyde:

$$CH_3CH_2OH \rightarrow CH_3CHO + 2H^+ + 2e^- \qquad \text{(Equation 8)}$$

The overall process consists of two, one-electron steps. The first step involves chemisorptions of ethanol on Pt and fast one-electron oxidation, and then a slower one-electron oxidation of absorbed species to acetaldehyde:

$$Pt + CH_3CH_2OH \rightarrow Pt\text{-}CH(CH_3)OH + e^- + H^+ \qquad \text{(Equation 9)}$$

$$Pt\text{-}CH(CH_3)OH \rightarrow CH_3CHO + e^- + H^+ \qquad \text{(Equation 10)}$$
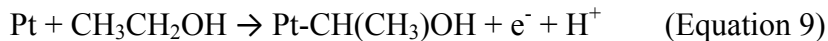
At the same potential, a surface oxidation of Pt to PtO occurs:

$$Pt + H_2O \rightarrow PtO - e^- + H^+ \qquad \text{(Equation 11)}$$
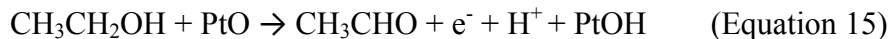
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Peak 2 at $E_{pa} = 1.1$ V. This oxidation peak involves a slow one-electron oxidation of Pt and the formation of Pt-OCH$_2$-CH$_3$. Followed the oxidation of Pt and the formation of Pt-OCH$_2$-CH$_3$, a one-electron oxidation of Pt-OCH$_2$CH$_3$ to PtO and the oxidation of Pt-OCH$_2$CH$_3$ to acetaldehyde takes place:

$$Pt + CH_3CH_2OH \rightarrow Pt\text{-}OCH_2CH_3 + e^- + H^+ \qquad \text{(Equation 12)}$$

$$Pt\text{-}OCH_2CH_3 + H_2O \rightarrow PtO + CH_3CH_2OH + e^- + H^+ \qquad \text{(Equation 13)}$$

$$Pt\text{-}OCH_2CH_3 \rightarrow Pt + CH_3CHO + e^- + H^+ \qquad \text{(Equation 14)}$$

It is believed, that at this potential, oxidation of acetaldehyde to acetic acid will also take place. It is important to notice that poisoning of the platinum electrode occurs by the formation of PtO. This will occur if reaction 13 is faster than reaction 14. If reaction 14 is faster than reaction 13, poisoning of the platinum electrode will not occur.

Peak 3 at $E_{pc} = 0.4$ V. Peak 3 is observed when the potential is reversed at +2V to the negative direction. According to the same literature data, this peak has been attributed to the reactivation of platinum surface by the reduction of PtO with CH$_3$CH$_2$OH to PtOH, and the re-oxidation of PtOH to PtO.

$$CH_3CH_2OH + PtO \rightarrow CH_3CHO + e^- + H^+ + PtOH \qquad \text{(Equation 15)}$$

$$PtOH \rightarrow PtO + e^- + H^+ \qquad \text{(Equation 16)}$$

Electrochemistry of 0.1 M Ethanol in 0.1 M HClO₄

Figures 11a - f show the cyclic voltammograms of 0.1 M ethanol in 0.1 M HClO₄ at different temperatures obtained on a platinum electrode. The potential is scanned from E_1 = -500 mV to E_2 = +2 V, and then reversed to negative direction from E_2 = +2 V to E_3 = -1V at scan rate of 50 mV/s.

Figure 11a shows a cyclic voltammogram of 0.1 M Ethanol in 0.1 M HClO₄ obtained at 22.6 °C. The voltammogram displays a small oxidation peak at 0.84 V (peak 2) due to oxidation of ethanol, which probably corresponds to the oxidation given in equation 12. However the CV does not displays the first oxidation peak at 0.66 V.
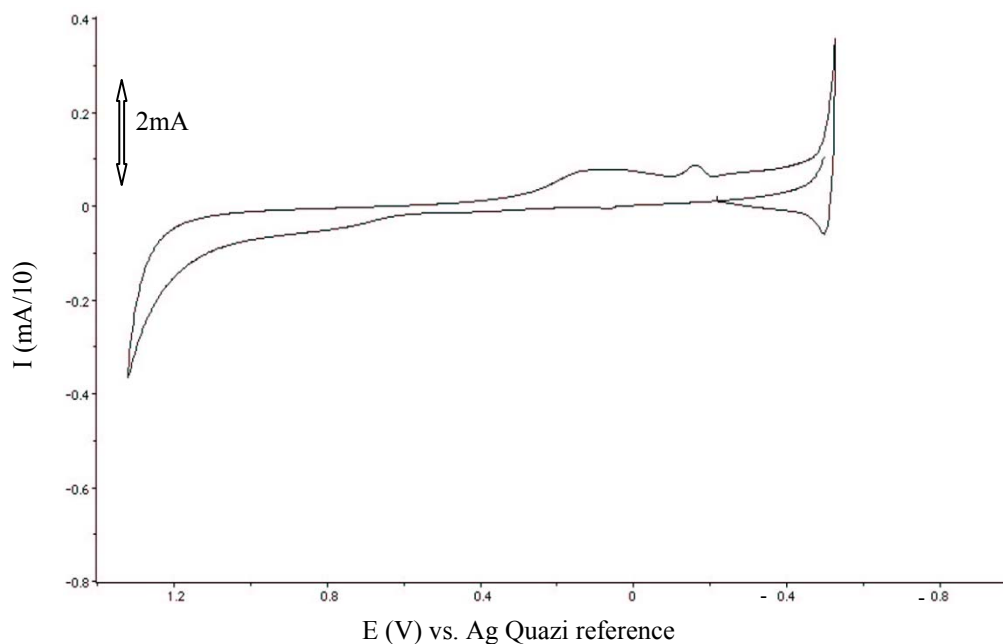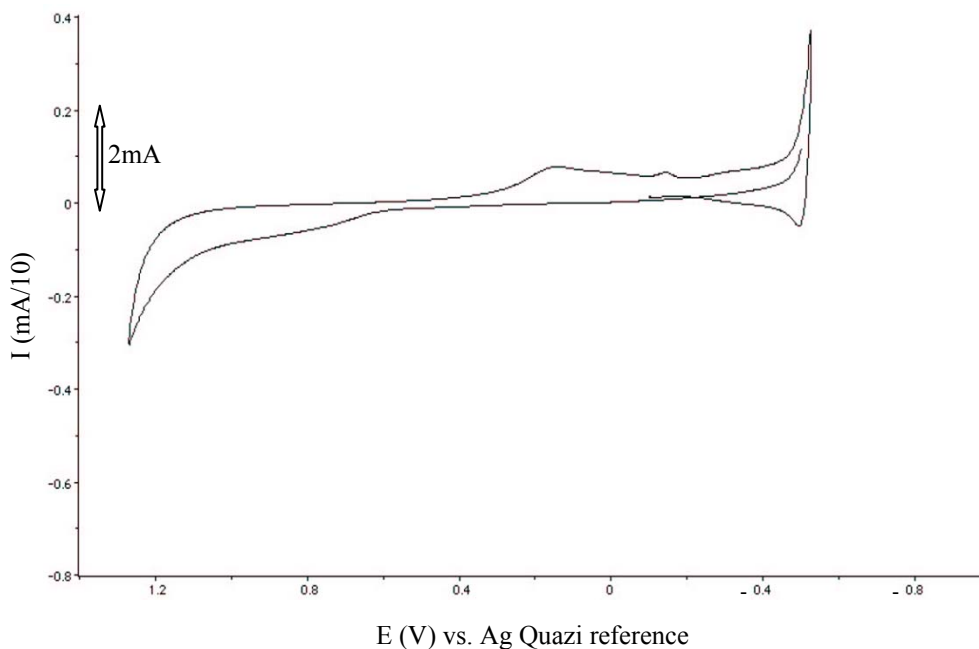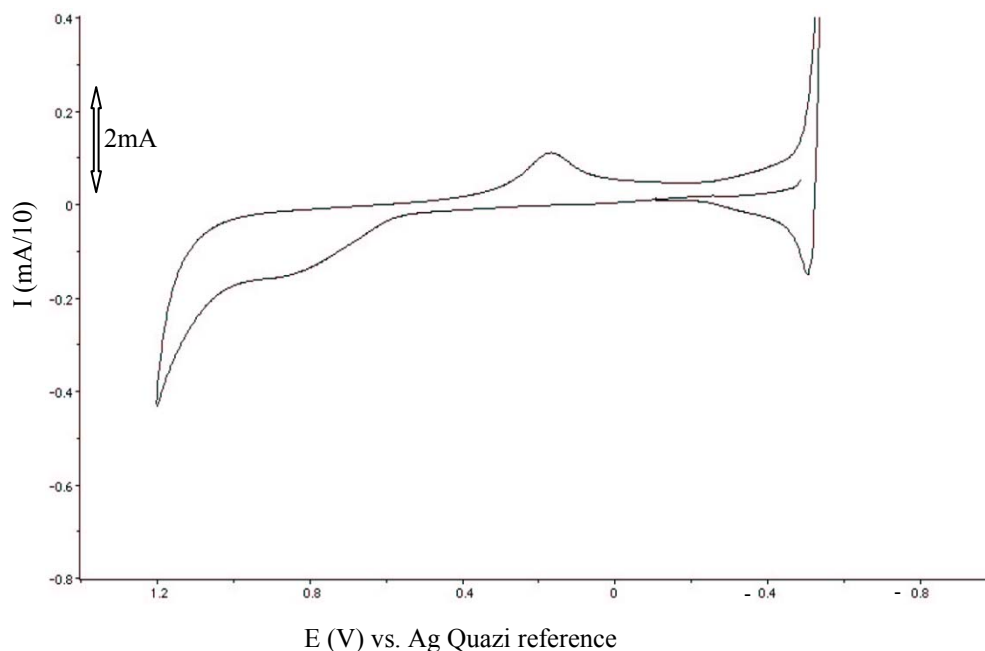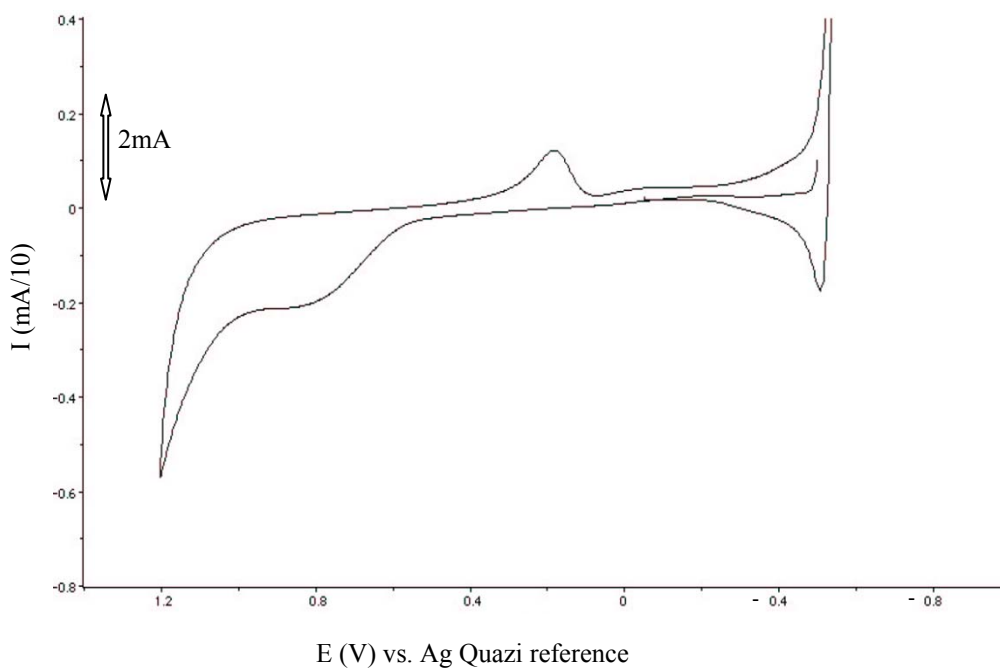

Figure 11a: Cyclic Voltammogram of 0.1 M Ethanol in 0.1 M HClO₄ at Platinum Working Electrode at 22.6 °C

Figures 11b – e show cyclic voltammograms of 0.1 M ethanol in 0.1 M HClO$_4$

obtained at 30.2, 40.6, 50.3 and 60.2 °C. At these temperatures, the cyclic

voltammograms also display an oxidation peak at 0.84 V (peak 2), but with increasing

temperature from 30.2 to 60.2 °C, CV's show that the oxidation peak becomes more

pronounced. The peak current increases from 0.5 mA to 2.5 mA.

Figure 11f shows a cyclic voltammogram of 0.1 M ethanol in 0.1 M HClO$_4$

obtained at 70.1 °C. At his temperature, the cyclic voltammogram displays in addition to

oxidation peak at 0.84 V (peak 2), a new oxidation peak at 0.13 V (peak 3) which

corresponds to the reduction of PtO with ethanol to PtOH (equation 16).

E (V) vs. Ag Quazi reference

Figure 11b: Cyclic Voltammogram of 0.1 M Ethanol in 0.1 M HClO$_4$ at Platinum Working Electrode at 30.2 °C

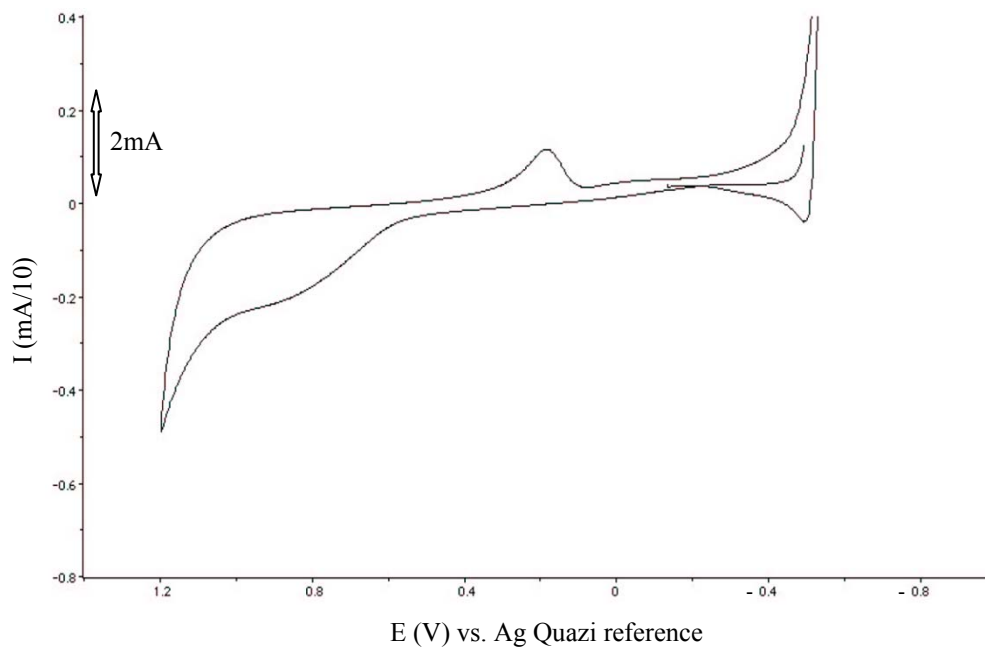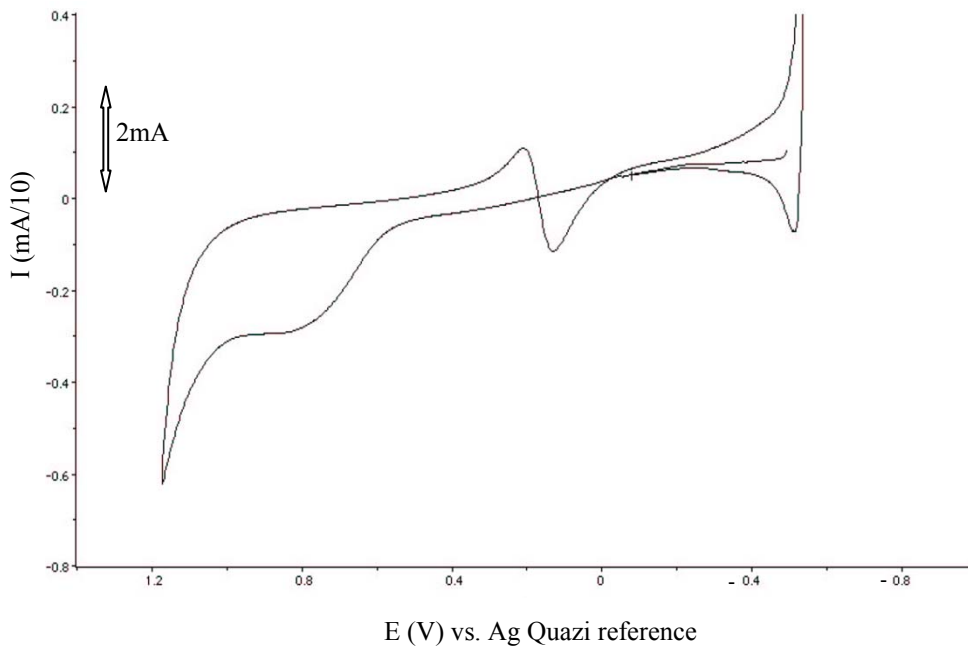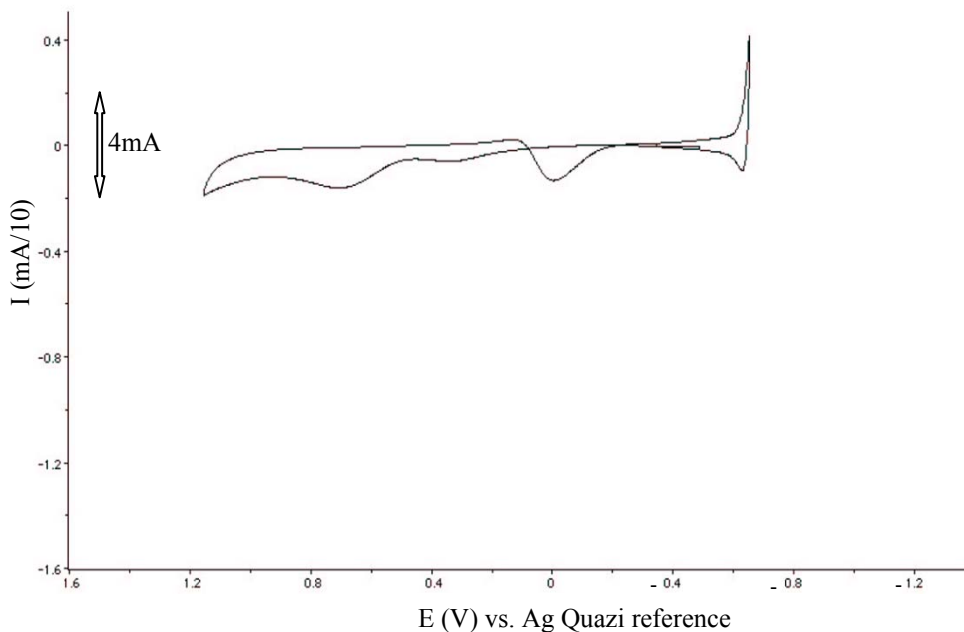**Figure 11c: Cyclic Voltammogram of 0.1 M Ethanol in 0.1 M HClO$_4$ at Platinum Working Electrode at 40.6 °C**

E (V) vs. Ag Quazi reference

Figure 11d: Cyclic Voltammogram of 0.1 M Ethanol in 0.1 M HClO$_4$ at Platinum Working Electrode at 50.3 °C

E (V) vs. Ag Quazi reference

Figure 11e: Cyclic Voltammogram of 0.1 M Ethanol in 0.1 M HClO$_4$ at Platinum Working Electrode at 60.2 °C

E (V) vs. Ag Quazi reference

Figure 11f: Cyclic Voltammogram of 0.1 M Ethanol in 0.1 M HClO$_4$ at Platinum Working Electrode at 70.1 °C

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Electrochemistry of 0.2 M Ethanol in 0.1 M HClO₄

Cyclic voltammograms of 0.2 M ethanol in 0.1 M HClO₄ on a platinum electrode at different temperatures, are shown in Figures 12a - f.

Figure 12a, shows the cyclic voltammogram of 0.2 M ethanol in 0.1 M HClO₄ at 23.0 °C. At this temperature, the voltammogram displays an oxidation peak at 0.84 V (peak 2), an oxidation peak at 0.13 V (peak 3) and a new oxidation peak at 0.30 V (peak 1). The cyclic voltammogram obtained at these conditions shows that peak 1, 2 and 3 give density currents of 0.6, 1.6 and 1.3 mA respectively. In comparison to the cyclic voltammograms obtained for 0.1 M ethanol (Figure 11e – f) these voltammograms show the oxidation peak at 0.30V. This peak corresponds to the oxidation of ethanol to CH_3CHO (equation 8).
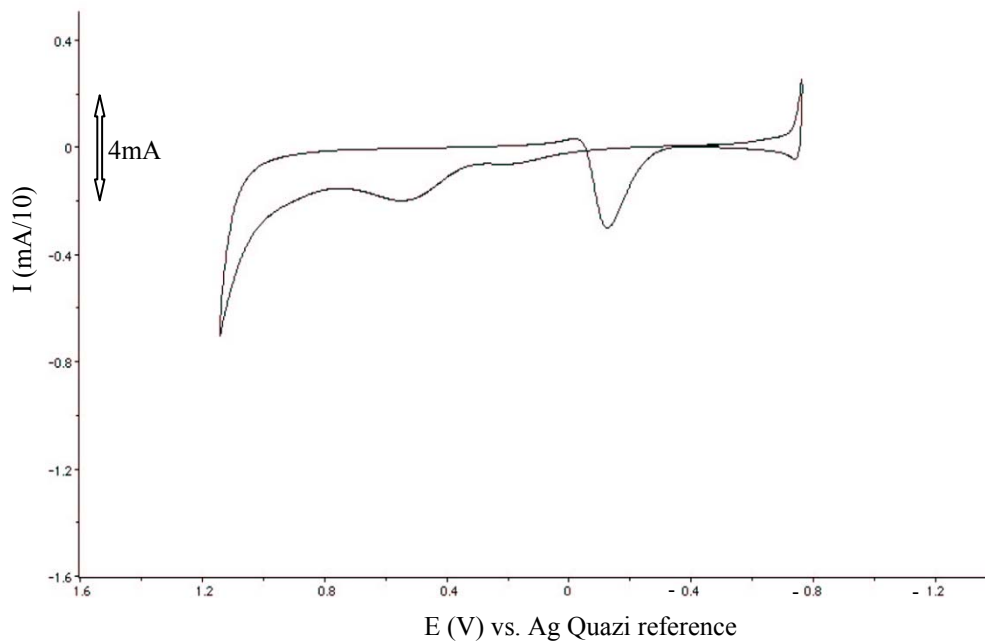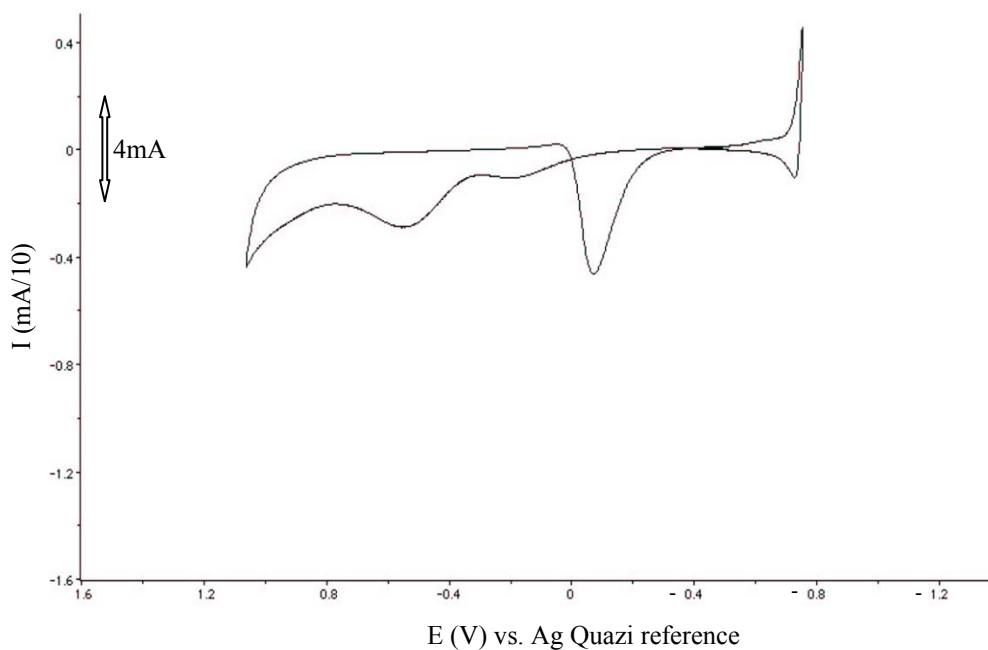

Figure 12a: Cyclic Voltammogram of 0.2 M Ethanol in 0.1 M HClO₄ at Platinum Working Electrode at 23.0 °C

Figures 12b – f show cyclic voltammograms of 0.2 M ethanol in 0.1 M HClO$_4$ obtained at 33.0, 43.0, 53.0, 63.0 and 73.0 °C. The cyclic voltammograms obtained at this concentration of ethanol and at these temperatures also display three oxidation peaks. However, as the temperature was increased from 23.0 to 73.0 °C, peak current increased (Table 3).

Table 3. Peak current obtained at 0.2 M ethanol in 0.1 M HClO$_4$.

T(°C)	Peak 1 (mA)	Peak 2 (mA)	Peak 3 (mA)
23.0	0.6	1.6	1.3
33.0	0.65	2	3
43.0	1	2.9	4.6
53.0	1.9	4	6.7
63.0	2.3	4.8	10.5
73.0	2.4	5	12.4

Figure 12b: Cyclic Voltammogram of 0.2 M Ethanol in 0.1 M HClO$_4$ at Platinum Working Electrode at 33.0 °C

Figure 12c: Cyclic Voltammogram of 0.2 M Ethanol in 0.1 M HClO$_4$ at Platinum Working Electrode at 43.0 °C
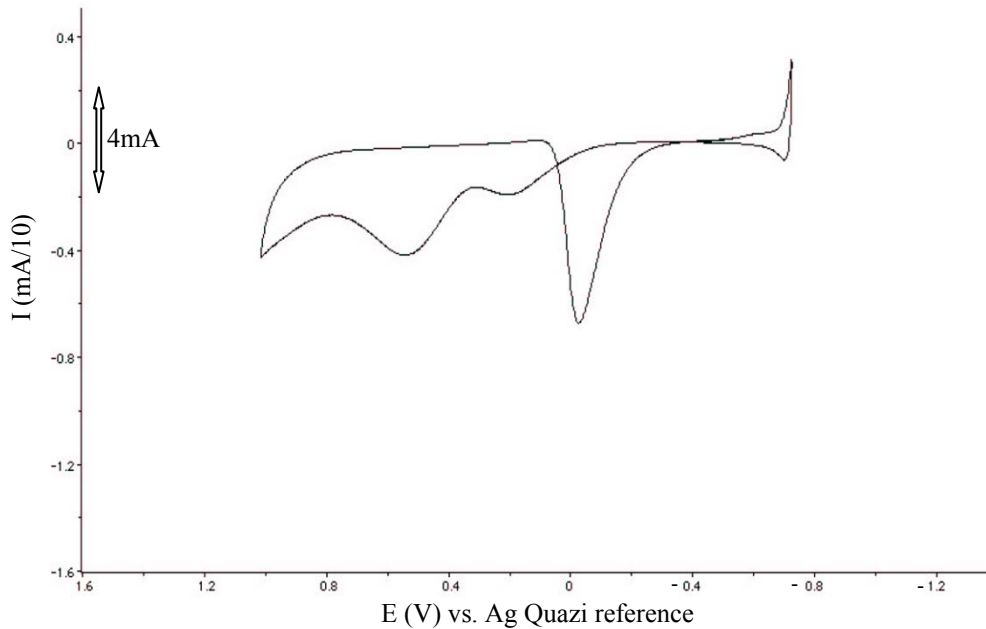
Figure 12d: Cyclic Voltammogram of 0.2 M Ethanol in 0.1 M HClO$_4$ at Platinum Working Electrode at 53.0 °C
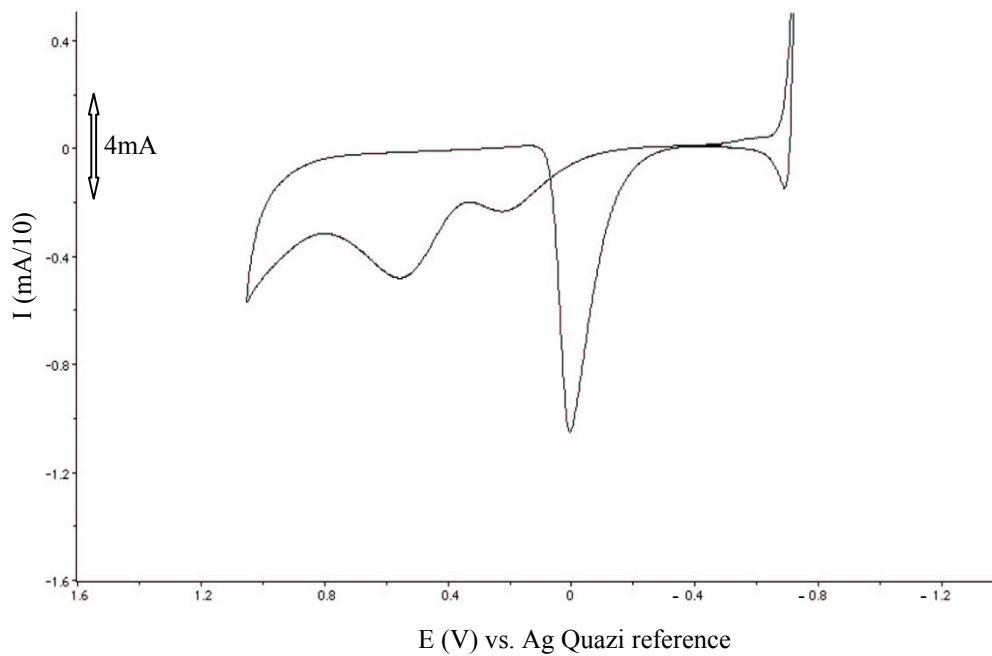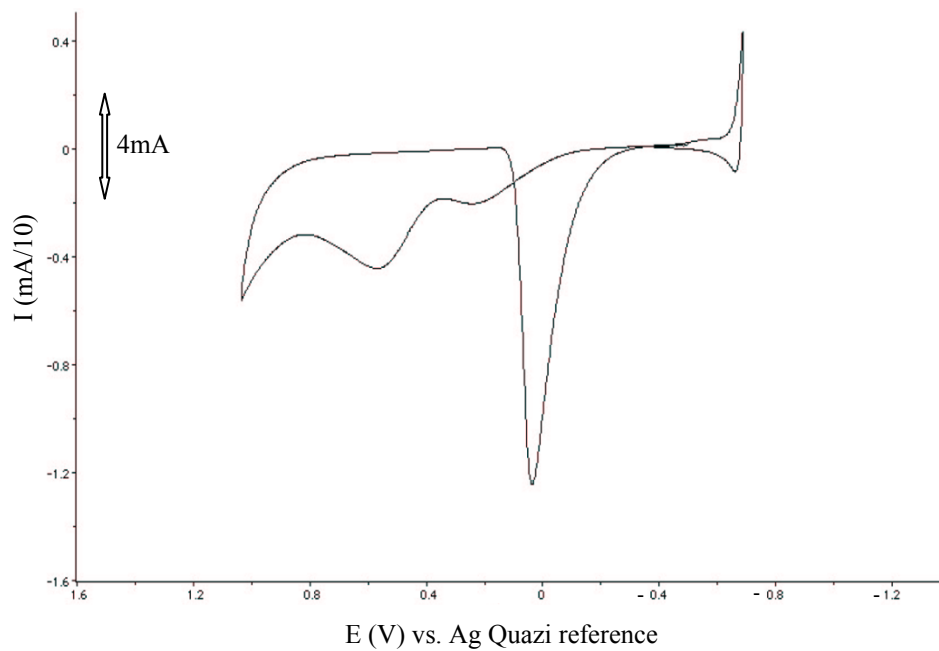

Figure 12e: Cyclic Voltammogram of 0.2 M Ethanol in 0.1 M HClO$_4$ at Platinum Working Electrode at 63.0 °C

Figure 12f: Cyclic Voltammogram of 0.2 M Ethanol in 0.1 M HClO₄ at Platinum Working Electrode at 73.0 °C

Electrochemistry of 0.4 and 1 M Ethanol in 0.1 HClO$_4$

Figure 13 shows the cyclic voltammograms of the oxidation of 0.4 M ethanol in HClO$_4$ obtained at 21.5, 32.8, 42.5, 51.5, 61.2, and 73.5 °C, and Figure 14 shows the cyclic voltammograms of ethanol obtained at 22.9, 32.0, 41.6, 50.1, 61.1, and 72.5 °C. The cyclic voltammograms obtained at these two concentrations of ethanol and at these temperatures also display three oxidation peaks, which increased with temperature. However, during the electro-oxidation of ethanol at a concentration of 1 M ethanol, it was found that poisoning of the electrode occurred. The poisoning is due to the formation of PtO and/or adsorption of some species. For that reason, reactivation of the Pt electrode was made after each scan according to the method described in section 2.
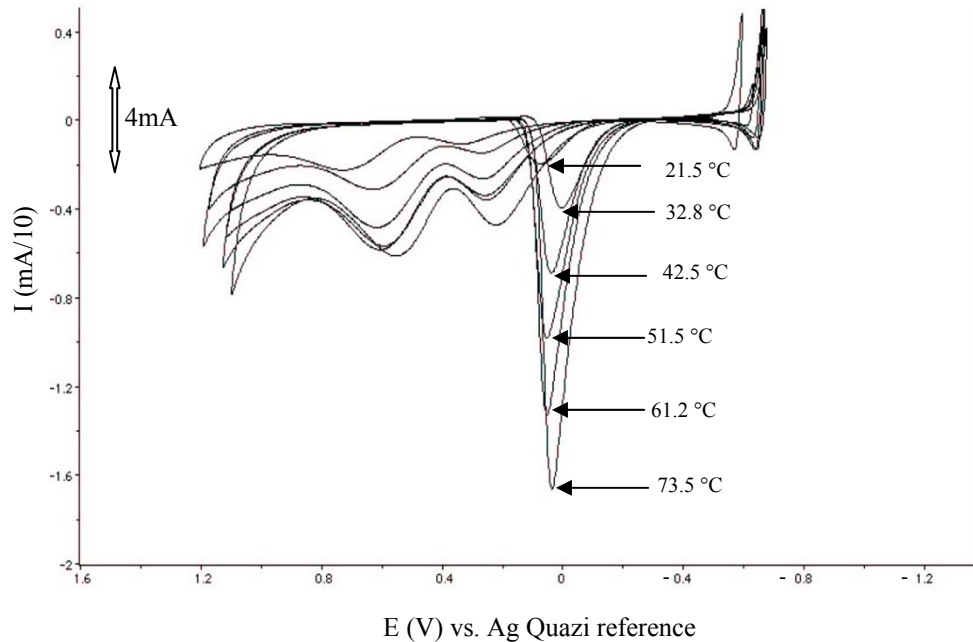
Figure 13: Cyclic Voltammogram of 0.4 M Ethanol in 0.1 M HClO$_4$ at Platinum Working Electrode at 21.5, 32.8, 42.5, 51.5, 61.2, and 73.5 °C
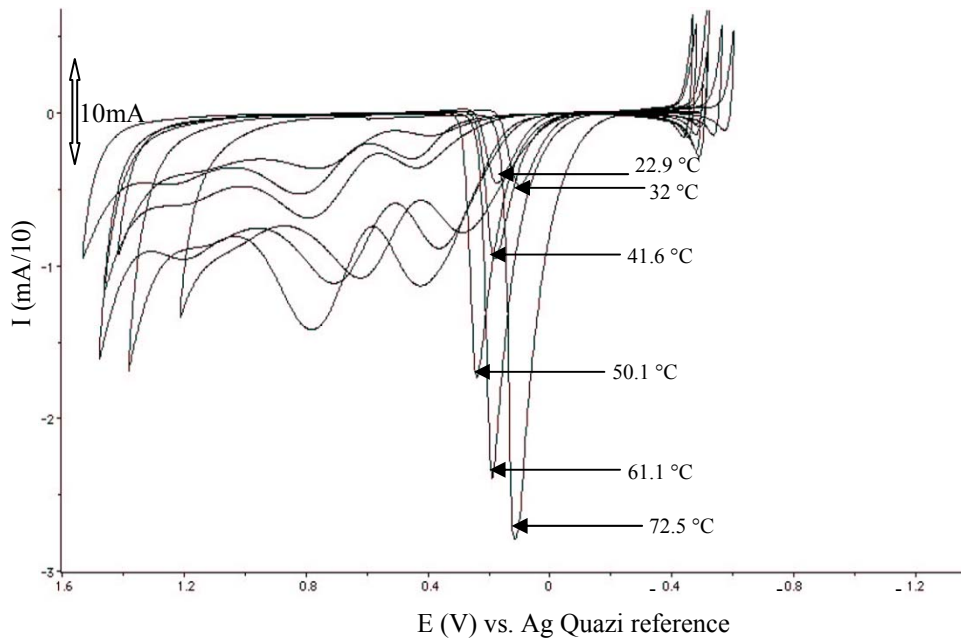

Figure 14: Cyclic Voltammogram of 1 M Ethanol in 0.1 M HClO$_4$ at Platinum Working Electrode at 22.9, 32.0, 41.6, 50.1, 61.1, and 72.5 °C

Electrochemistry of Ethanol in Ionic Liquids

The electrochemical study of ethanol in aqueous perchloric acid showed that the oxidation of ethanol strongly depends on the concentration of ethanol and on the temperature of the solution. Poisoning of the platinum working electrode occurred at higher concentration of ethanol. At a low concentration of ethanol (0.1 M), cyclic voltammograms showed one oxidation peak (peak 2) at a temperature of 22.6 °C and two oxidation peaks (peak 2 and peak 3) at a temperature of 70.1 °C. Oxidation peak current (peak 2) increased as the temperature increased. However, at higher concentration of ethanol (> 0.2 M), cyclic voltammograms showed three oxidation peaks, and at concentration of ethanol higher than 1 M poisoning of the electrode occurred due to the formation of PtO.

Previous work in this laboratory has shown that in ionic liquids the oxidation of ethanol, even at a very large ethanol concentration, does not show poisoning of the electrode by formation of PtO. In this study, the electrochemical properties of ethanol in 1-ethyl-3-methylimidazolium Bis(trifluoromethanesulfonyl)imide (EMImTFSI) and 1-ethyl-3-methylimidazolium tetrafluoroborate (EMImBF$_4$) was studied and compared to the electrochemical data obtained for ethanol in aqueous HClO$_4$. In addition, electrochemical properties of propanol in ionic liquids were also studied.

In the first set of experiments, an attempt to oxidize ethanol at low concentrations (0.1, 0.2, and 0.4 M) was made, but the cycle voltammograms did not show any activity on the platinum electrode. Therefore electrochemical studies of ethanol in ionic liquids were made at higher concentrations (1, 2, 5, 10, and 15 M).

Electrochemistry of Ethanol in EMImTFSI

Cyclic voltammograms of 1 M ethanol in EMImTFSI on platinum electrode at different temperatures are shown in Figures 15a – e.

Figure 15a displays the cyclic voltammograms of 1 M ethanol in EMImTFSI obtained at 25.4 °C. At these conditions, the cyclic voltammogram shows an irreversible oxidation peak (peak 1) at E_{pa} = 1.8 V. On reversed scan the voltammogram did not display cathodic current indicating the oxidized species undergo chemical changes (EC process). On the continuing negative scan a new cathodic peak was observed at Epc = 0.93 V (peak 2) and a new oxidation peak at E_{pa} = 0.05 V (peak 3). This indicates that the reduced species formed at peak 1 is stable and is reoxidized at 0.05 V. The peak potential separation ΔE_p ($E_{p2} - E_{p3}$) was rather large ΔE_p = 850 mV. This unusual large value of ΔEp is probably due to relatively high internal resistance of ionic liquid. It is probable, based on figure 16, that the whole process involves oxidation of ethanol to acetaldehyde or/and acetic acid (Peak 3) and peak 2 corresponds to the reduction of acetaldehyde or/and acetic acid $CH_3COOH + e^- \rightarrow CH_3COOH^-$.
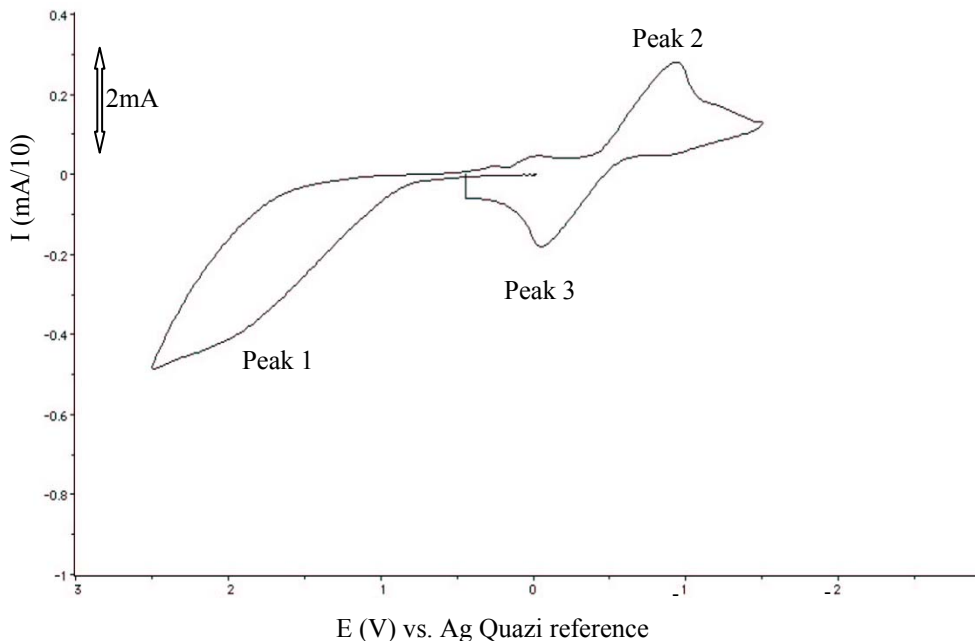
Figure 15a: Cyclic Voltammogram of 1 M Ethanol in EMImTFSI at Platinum Working Electrode at 25.4 °C

Figure 15b – e show the cyclic voltammograms of 1 M ethanol in EMImTFSI at 35.4, 42.3, 54.0, and 64.9 °C. At this concentration of ethanol, and at these temperatures, the cyclic voltammograms does not change their general appearance except that peak currents increased. However, at larger temperature, re-oxidation peak 3 becomes smaller indicating that the reduced species is not chemically stable and undergoes further chemical change.

Finally, the cycle voltammograms obtained at these conditions, display a new oxidation peak (peak 4) which becomes more pronounced as the temperature is increased.
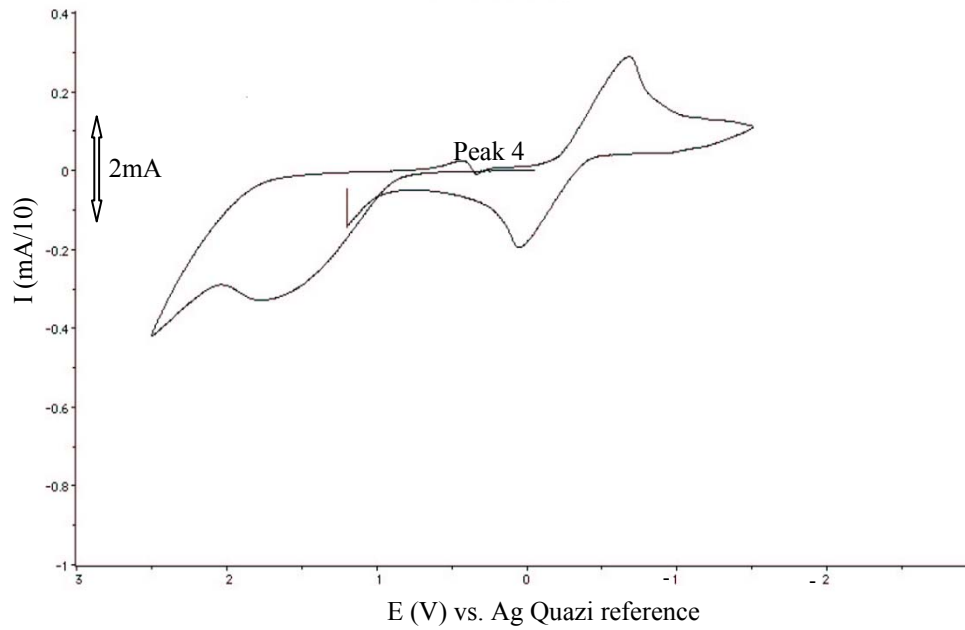
Figure 15b: Cyclic Voltammogram of 1 M Ethanol in EMImTFSI at Platinum Working Electrode at 35.4 °C
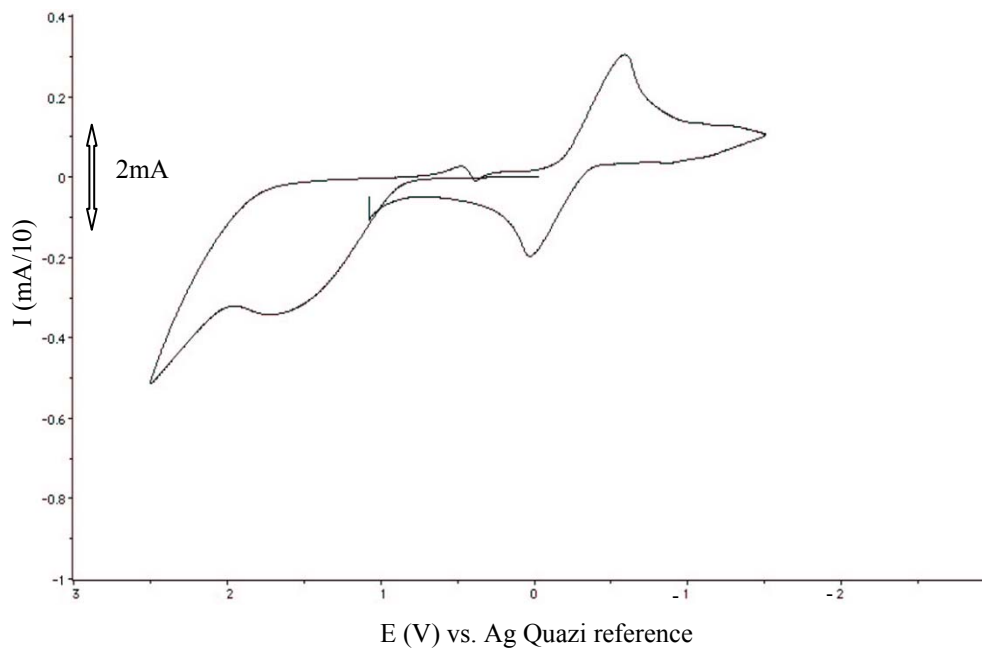

Figure 15c: Cyclic Voltammogram of 1 M Ethanol in EMImTFSI at Platinum Working Electrode at 42.3 °C
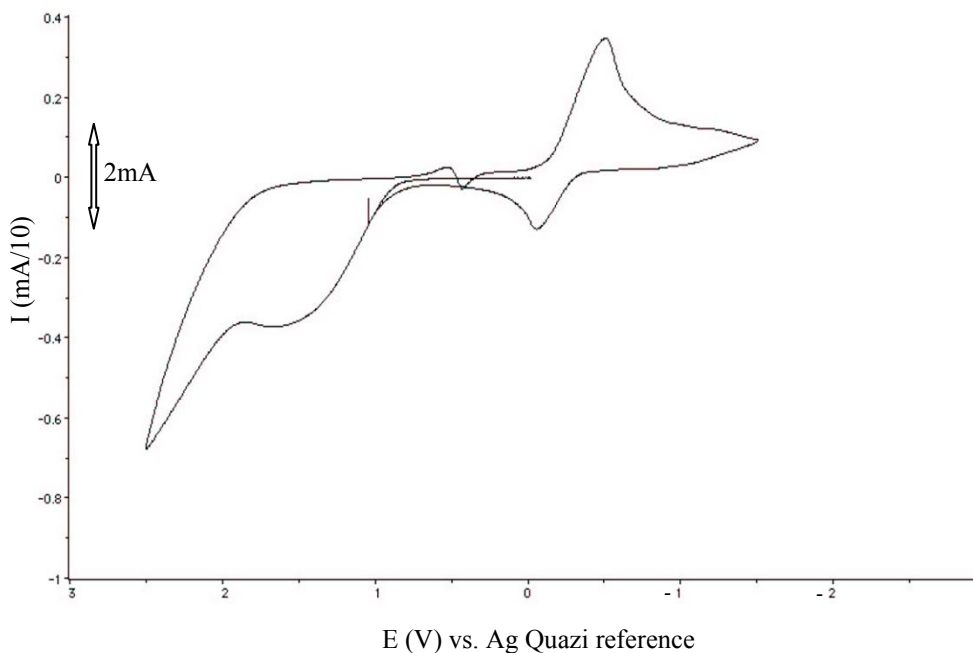
Figure 15d: Cyclic Voltammogram of 1 M Ethanol in EMImTFSI at Platinum Working Electrode at 54.0 °C
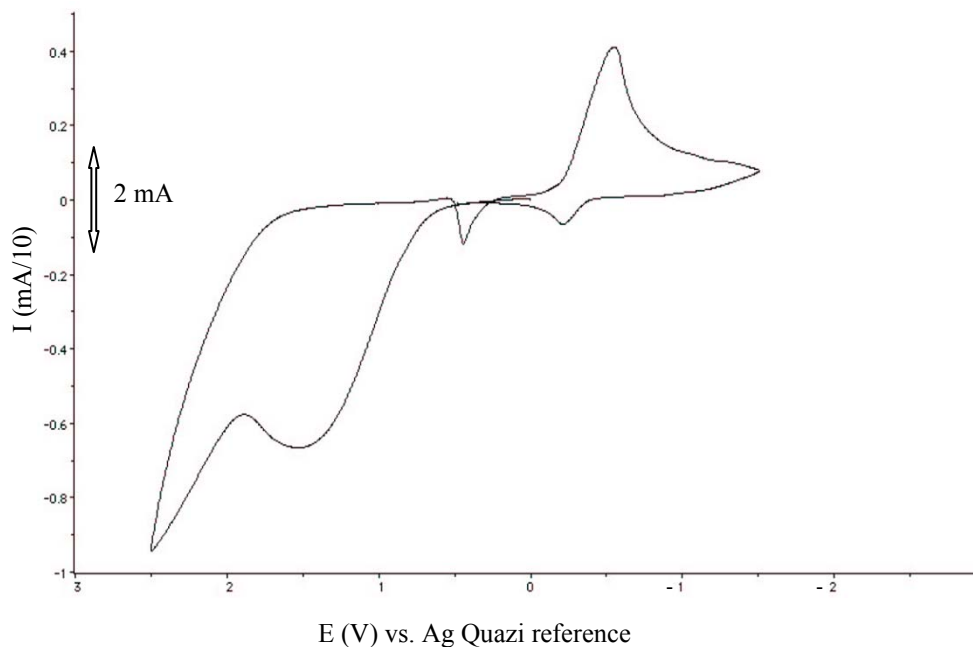

Figure 15e: Cyclic Voltammogram of 1 M Ethanol in EMImTFSI at Platinum Working Electrode at 64.9 °C
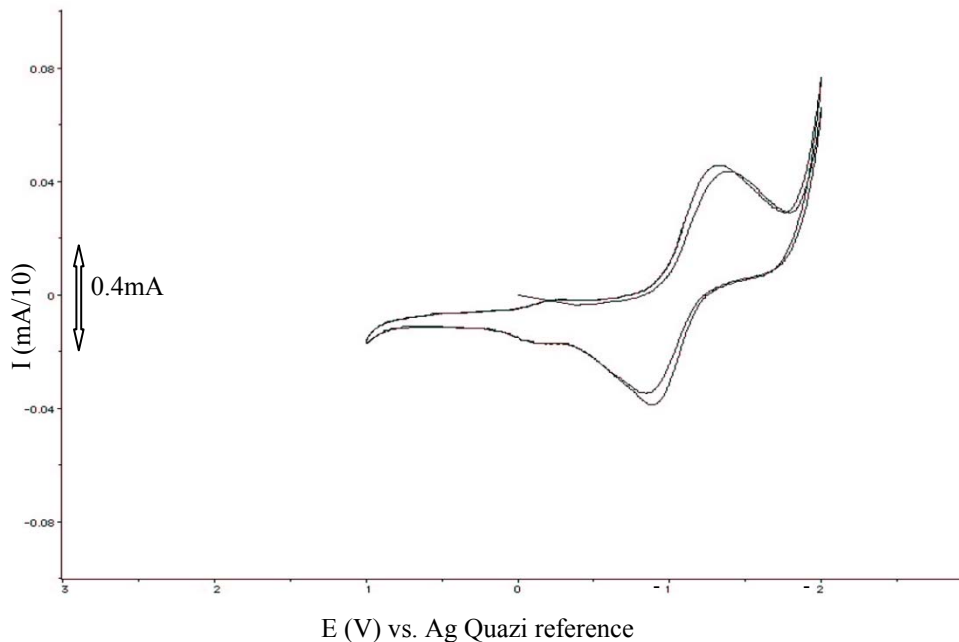
Figure 16: Cyclic Voltammogram of Acetaldehyde in EMImTFSI at Platinum Working Electrode.

Figures 17 – 20 show the cyclic voltammograms of 2, 5, 10, and

15 M ethanol in EMImTFSI obtained at different temperatures.

Cyclic voltammograms of ethanol obtained at these concentrations and at

these temperatures were similar to that of 1 M ethanol. However, with increasing

temperature and concentration, oxidation peaks 1 and 4 become more pronounced.

Through the study of the electrochemistry of ethanol in EMImTFSI, it

was found that the platinum working electrode showed high activity. When

concentrations of 1, 2, and 5 M of ethanol are used poisoning of the electrode does not

occur. At higher concentrations (10, and 15 M) poisoning of the electrode occurs.
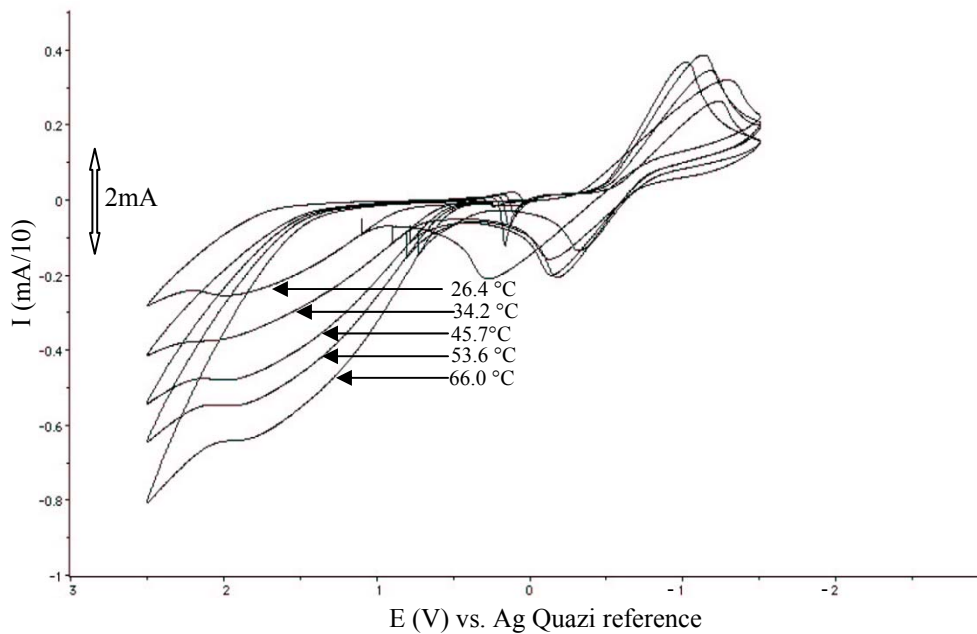
Figure 17: Cyclic Voltammogram of 2 M Ethanol in EMImTFSI at Platinum Working Electrode at 26.4, 34.2, 45.7, 53.6, and 66.0 °C
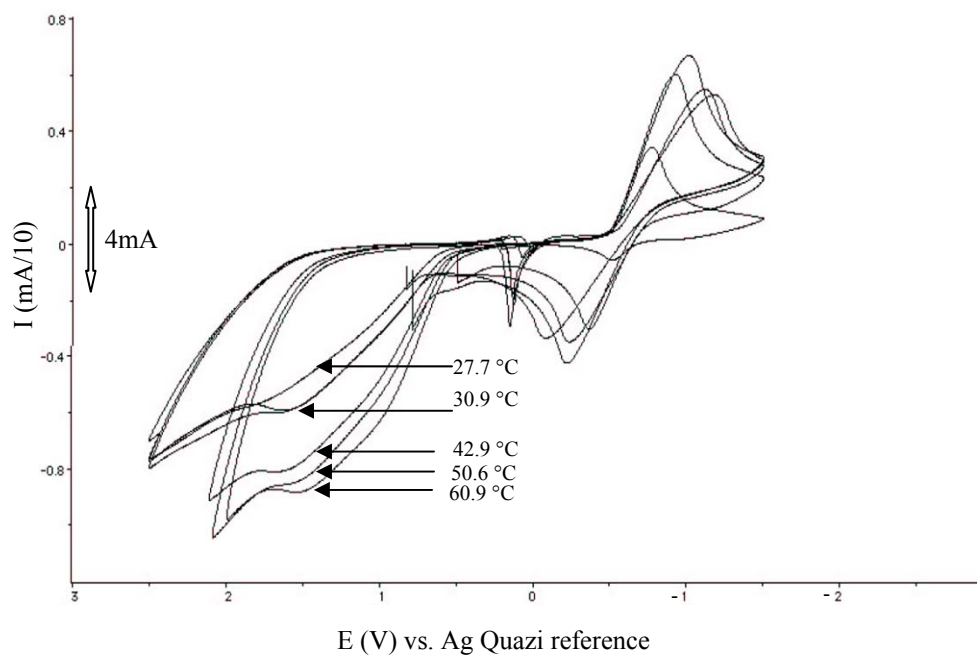

Figure 18: Cyclic Voltammogram of 5 M Ethanol in EMImTFSI at Platinum Working Electrode at 27.7, 30.9, 42.9, 50.6, and 60.9 °C
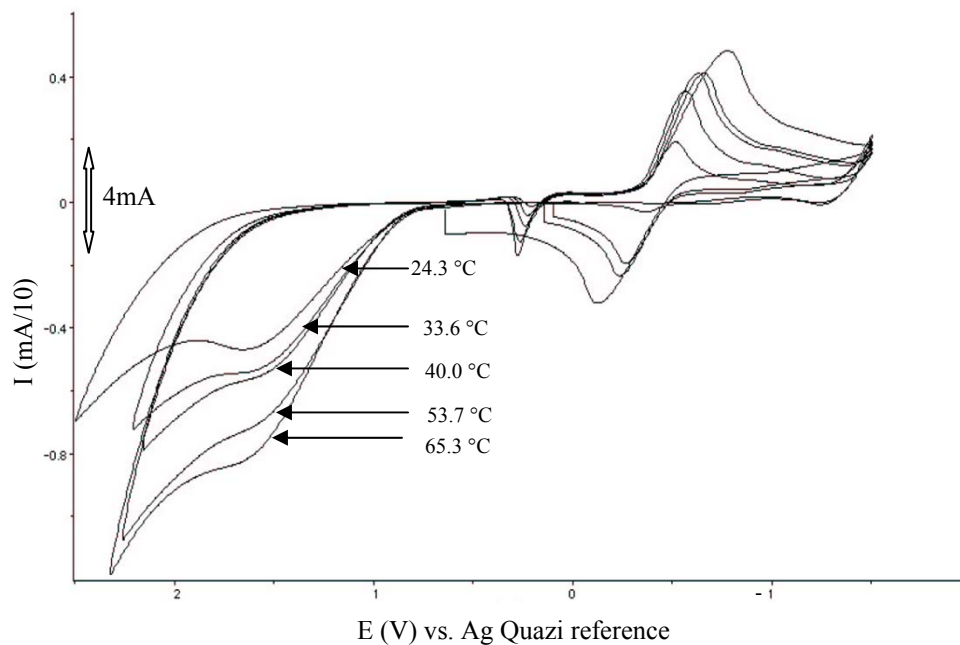
Figure 19: Cyclic Voltammogram of 10 M Ethanol in EMImTFSI at Platinum Working Electrode at 24.3, 33.6, 40.0, 53.7, and 65.3 °C
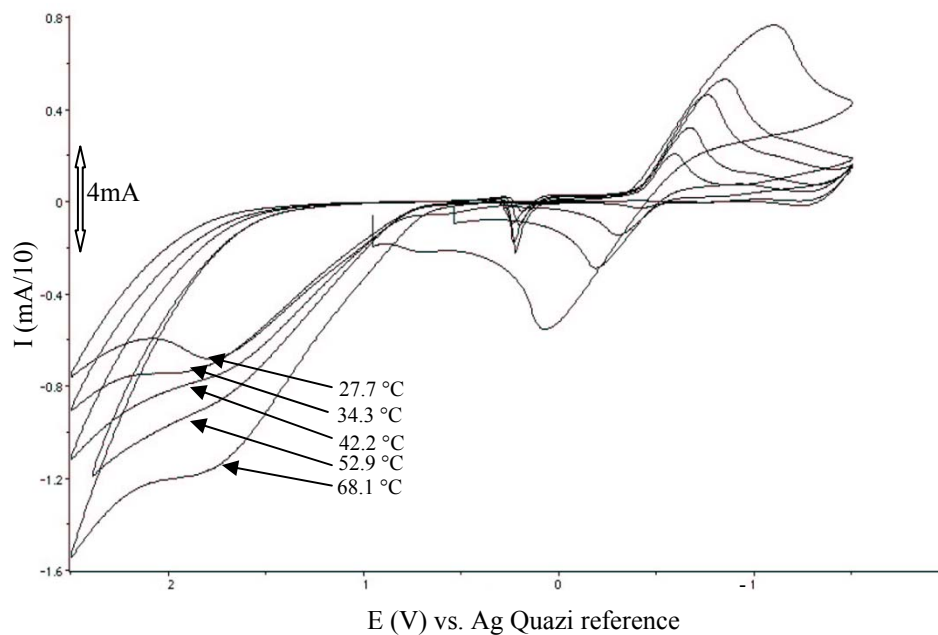

Figure 20: Cyclic Voltammogram of 15 M Ethanol in EMImTFSI at Platinum Working Electrode at 27.7, 34.3, 42.2, 52.9, and 68.1 °C

Electrochemistry of Ethanol in EMImBF$_4$

Cyclic voltammograms of 1, 2, 5, 10, and 15 M ethanol in EMImBF$_4$ are shown in Figures 21 – 25.

Figures 21 and 22 show the cyclic voltammograms of 1, and 2 M ethanol in EMImBF$_4$ obtained at different temperatures. At these conditions,   cyclic voltammograms show a large irreversible oxidation peak 1 at 1.6 V. On the reverse scan, two new reduction peaks (peak 2, and peak 5) are observed, indicating that two new oxidation products of ethanol were observed. Comparing these two new reductions peaks (peak 2 and 5) with the reduction of acetaldehyde and acetic acid (Figure 26), peak 2 could be assigned to the presence of acetaldehyde, and peak 5, to the presence of acetic acid.
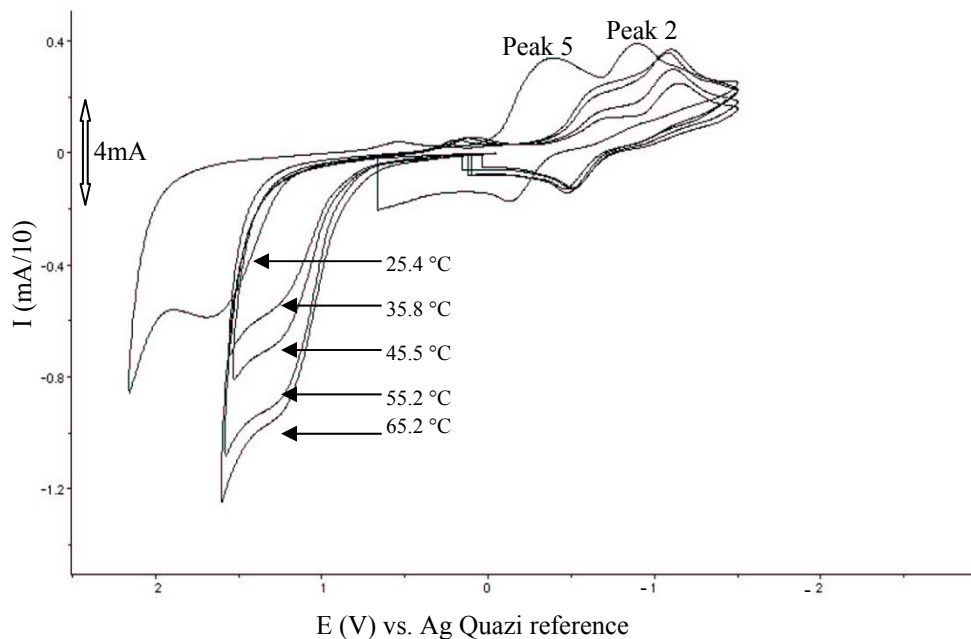

Figure 21: Cyclic Voltammogram of 1 M Ethanol in EMImBF$_4$ at Platinum Working Electrode at 25.4, 35.8, 45.5, 55.2, and 65.2 °C
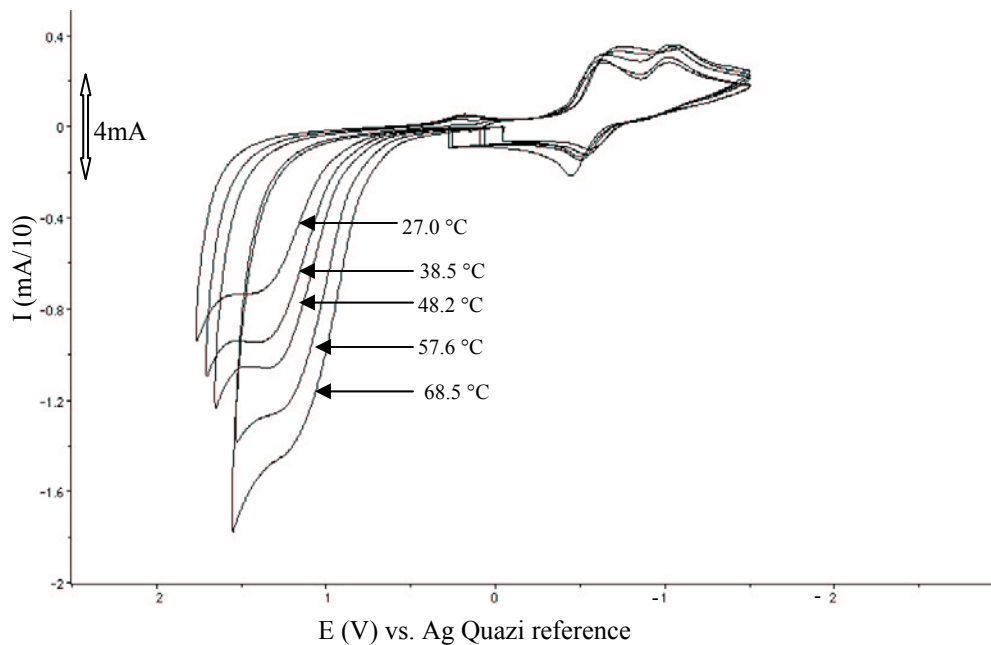
Figure 22: Cyclic Voltammogram of 2 M Ethanol in EMImBF₄ at Platinum Working Electrode at 27.0, 38.5, 48.2, 57.6, and 68.5 °C

Figure 23 – 25 show the cyclic voltammograms of 5, 10, and 15 M ethanol in EMImBF$_4$ recorded at different temperatures. Electrochemical properties of ethanol at higher concentrations are similar to that determined for 1 and 2 M ethanol.

In comparison to the CV of ethanol obtained in HClO$_4$, poisoning of the electrode occurs at much higher concentration of ethanol (> 10 M).

Similarly to the behavior in EMImTFSI, as the temperature and concentration of ethanol is increased, the oxidation current of peak 1 increased.
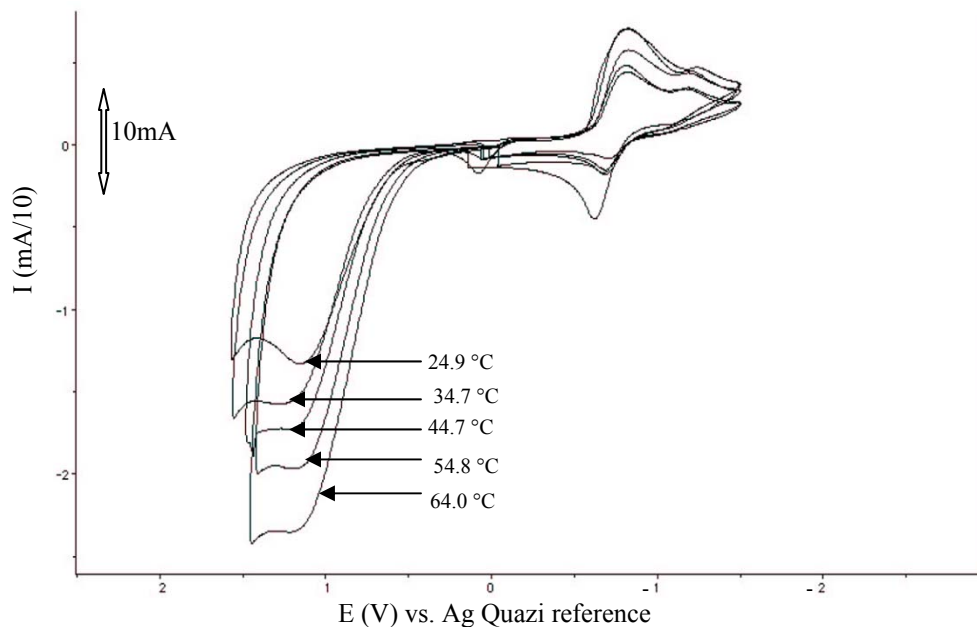
71

Figure 23: Cyclic Voltammogram of 5 M Ethanol in EMImBF$_4$ at Platinum Working Electrode at 24.9, 34.7, 44.7, 54.8, and 64.0 °C
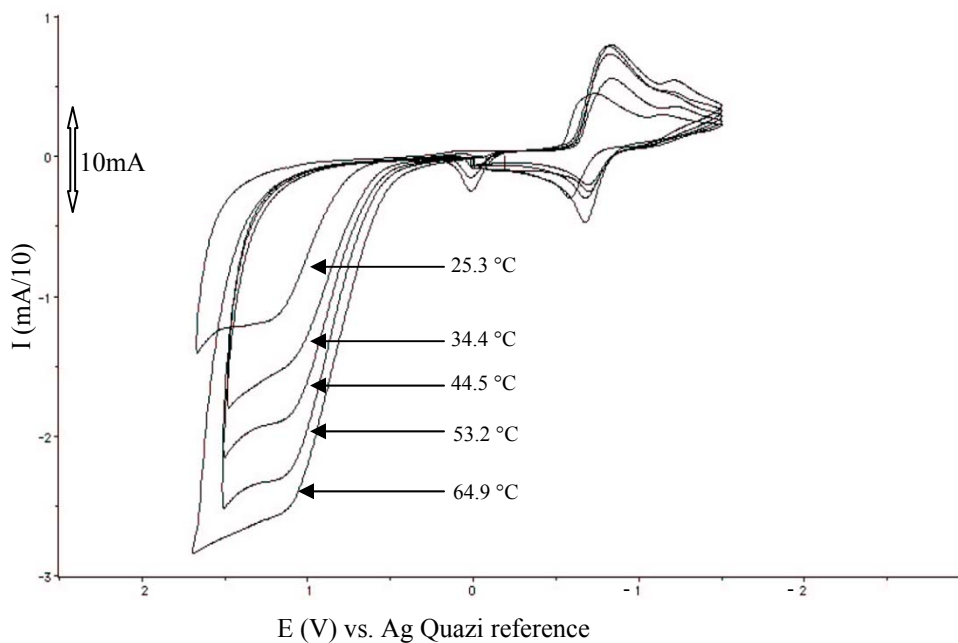

Figure 24: Cyclic Voltammogram of 10 M Ethanol in EMImBF$_4$ at Platinum Working Electrode at 25.3, 34.4, 44.5, 53.2, and 64.9 °C
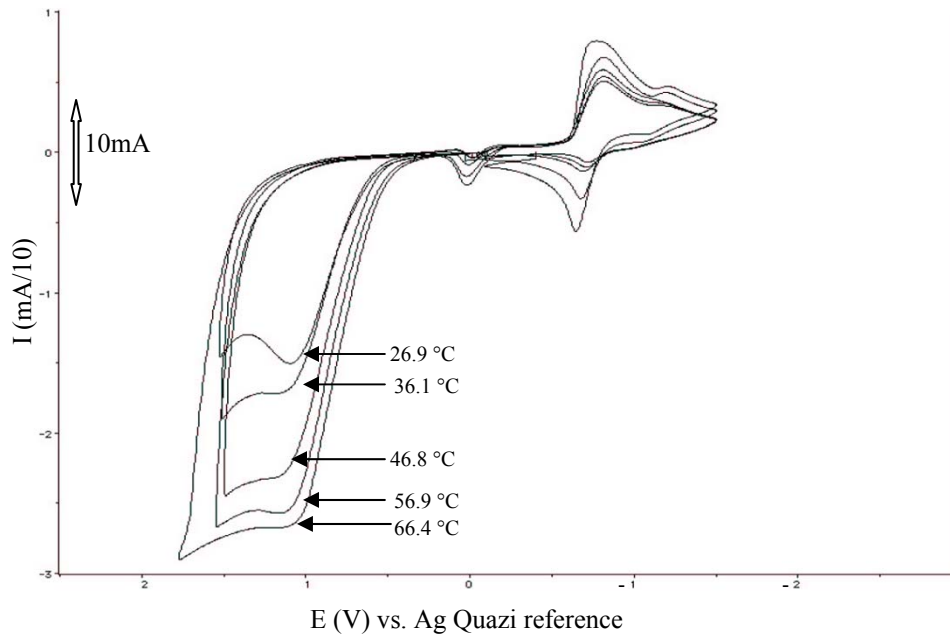
72

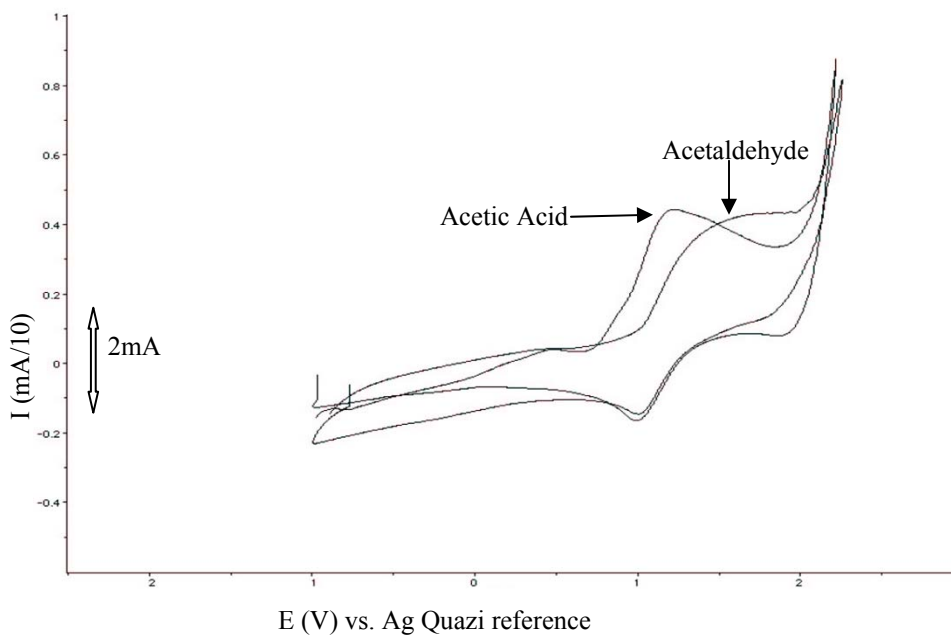**Figure 25: Cyclic Voltammogram of 15 M Ethanol in EMImBF$_4$ at Platinum Working Electrode at 26.9, 36.1, 46.8, 56.9, and 66.6 °C**

Figure 26: Cyclic Voltammogram of Acetic Acid and Acetaldehyde in EMIBF$_4$ at Platinum Working Electrode

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Electrochemistry of Propanol

Figure 27 shows the cyclic voltammograms obtained for the electro-
oxidation 1 M propanol in $HClO_4$ at 25.5, 35.9, 45.9, 58.0, 65.9, and 75.4°C on a
platinum electrode. At these conditions, oxidation of propanol in $HClO_4$ displays similar
voltammetric response to the oxidation of ethanol in acidic media. The cyclic
voltammogram obtained, shows two oxidation peaks at $E_{pa} = 0.90$ V, and peak 2 at $E_{pa} =$
1.41 V. Compared to oxidation of 1 M ethanol in $HClO_4$, oxidation of 1 M propanol in
acidic media shows much lower currents. However, current increases as the temperature
increases.

**Figure 27: Cyclic Voltammogram of 1 M Propanol in 0.1 M $HClO_4$ at Platinum
Working Electrode at 25.5, 35.9, 45.9, 58.0, 65.9, and 75.4 °C**

Figure 28 and 29 show the cyclic voltammograms of 1 M propanol in

EMImTFSI at 25.2, 35.9, 44.7, 54.5, 65.3, and 76.3°C and for the electro-oxidation of

propanol in EMImBF$_4$ at 29.1, 36.3, 49.3, 59.5, 67.3, and 77.2 °C on a platinum

electrode.

Compared to oxidation of 1 M ethanol in EMImTFSI, oxidation of

1 M propanol in this ionic liquid is very similar (Figure 28). The oxidation peak at E_{pa}=

1.5 V, probably corresponds to the oxidation of $CH_3CH_2CH_2OH$ to propionic acid

CH_3CH_2COOH, and the reduction peak at E_{pc} = -0.8 corresponds to the reduction of
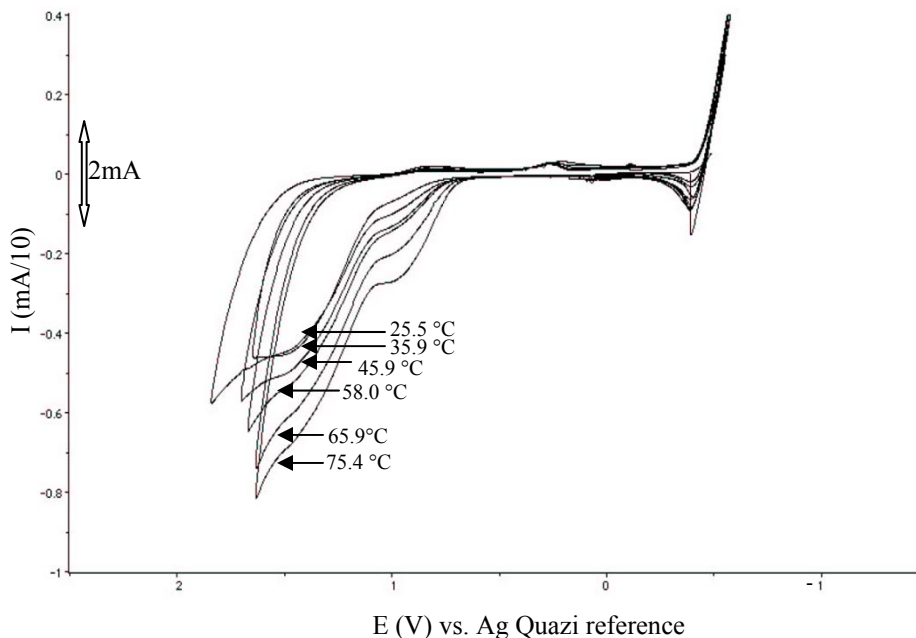
propionic acid.
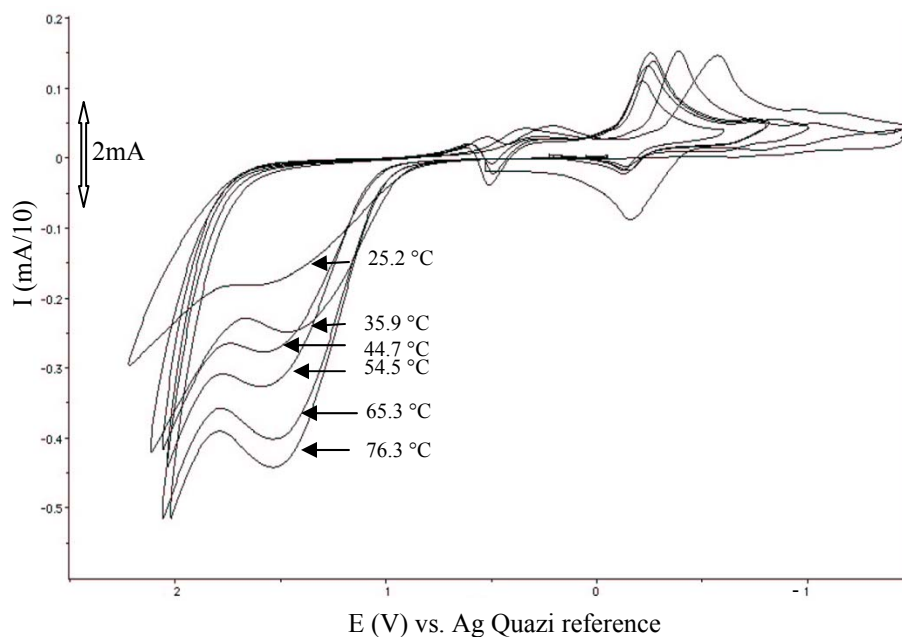
Figure 28: Cyclic Voltammogram of 1 M Propanol in EMImTFSI at Platinum Working Electrode at 25.2, 35.9, 44.7, 54.5, 65.3, and 76.3 °C

Figure 29 shows that, compared to the oxidation of 1 M ethanol in EMImBF$_4$, oxidation of 1 M propanol in this ionic liquid is also very similar. At these conditions a large oxidation peak (1) is observed. On the reverse scan, two new reduction peaks are obtained corresponding to the reduction of propionic acid and propionaldehyde.
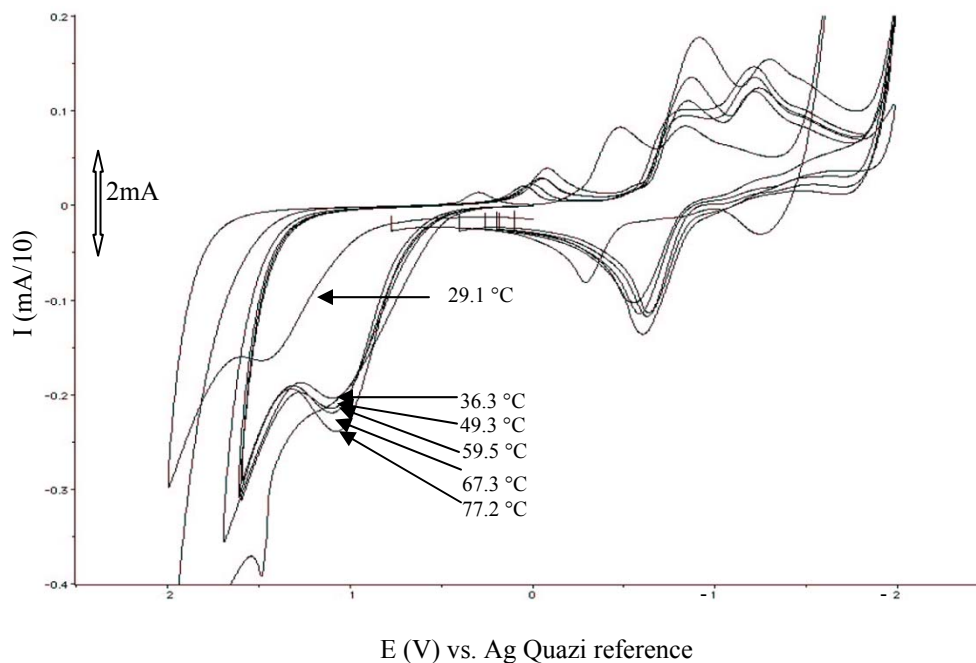

E (V) vs. Ag Quazi reference

Figure 29: Cyclic Voltammogram of 1 M Propanol in EMImBF$_4$ at Platinum Working Electrode at 29.1, 36.3, 49.3, 59.5, 67.3, and 77.2 °C

IV. CONCLUSION

In this study, 1-Ethyl-3-Methylimidazolium Tetrafluoroborate and 1-Ethyl-3-Methylimidazolium Bis(trifluromethanesulfonyl)imide ionic liquids were synthesized, and characterized.

Cyclic voltammograms indicated that 1-Ethyl-3-Methylimidazolium Tetrafluoroborate as well as 1-Ethyl-3-Methylimidazolium Bis(trifluromathanesulfonyl)imide exhibit a wide electrochemical window making them potential solvents for the electrochemical study of ethanol and other alcohols.

Cyclic voltammetry of ethanol in perchloric acid solution show that at a concentration of 0.1 M ethanol, voltammograms display an oxidation peak (peak2) at temperatures of 22.6, 30.2, 40.6, 50.3, and 60.2 °C, and two oxidation peaks (peaks 2 and 3)at a temperature of 70.1°C. It was also observed that, with an increase in temperature, an increase of current in peak 2 occurs.

Electrochemistry of 0.2, 0.4, and 1 M ethanol in $HClO_4$ at different temperatures was also studied. It was observed that oxidation of ethanol at these conditions show three oxidation peaks. Peak current density increases with temperature and concentration. Poisoning of the electrode occurs at higher concentration of ethanol (> 1 M).

Electrochemistry of ethanol in ionic liquids was similar. Cyclic voltammograms of ethanol in 1-Ethyl-3-Methylimidazolium Bis(trifluromathanesulfonyl)imide show three oxidation peaks (1, 3and 4), and reduction peak 2.

It is believed, based on Figure 16 (cyclic voltammogram of acetaldehyde in EMImTFSI), that peak 2 corresponds to one electron reduction of acetaldehyde, and peak 3 corresponds to the oxidation product of acetaldehyde. Through the study of the electrochemistry of ethanol in EMImTFSI, it was found that the platinum working electrode showed high activity hours when concentrations of 1, 2, and 5 M of ethanol are used (poisoning of the electrode does not occur), and when using concentrations of 10, and 15 M poisoning of the electrode occurs.

Cyclic voltammograms of ethanol in 1-Ethyl-3-Methylimidazolium Tetrafluoroborate shows oxidation peaks 1, 3 and 4, reduction peak 2, and a new reduction peak 5. It is believed; based on Figure 26, that reduction peak 2 is due the reduction of acetaldehyde, and peak 5, to the reduction of acetic acid.

Through the study of the electro-oxidation of ethanol in $EMImBF_4$, it was found that, the platinum working electrode showed high activity. When concentrations of 1, 2, and 5 M of ethanol are used, poisoning of the electrode does not occur, and when concentrations of 10, and 15 M are used, poisoning of the electrode occurs.

Electrochemistry of propanol in $HClO_4$, show that, compared to oxidation of 1 M ethanol, oxidation of 1 M propanol in acidic media shows similar behavior with somewhat lower currents. However, current increases as the temperature increases. Electro-oxidation of propanol in ionic liquids was similar to that of ethanol in this melts.

The study of the electro-oxidation of 1 M propanol in $HClO_4$, EMImTFSI and EMImBF4 showed that the platinum working electrode does not get poisoned.

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