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# SCHOLARLY RESEARCH PROGRAM

## Delivery Order 0007: Characterization of Ionic Liquids as Fuel Cell Electrolytes

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The object of this work was to synthesize the room temperature ionic liquids, $EMImBF_4$, $BMImBF_4$ and BMPBETI, and to study the electrochemical behavior of ethanol in these electrolytes on the Pt electrode. The electrochemical oxidation of EtOH on Pt electrodes in acidic medium involves several reaction pathways. The predominant pathway involves oxidation of bulk EtOH to $CH_3CHO$ which can be further partially oxidized to acetic acid. The secondary reaction involves oxidation of a strongly bound adsorbate, breaking the C-C bond and the formation of $CO_2$. The electrochemical behavior of EtOH in ionic liquid was investigated and compared to the one obtained in acid aqueous electrolyte. It is expected that the use of the room-temperature ionic liquids might prevent poisoning of Pt electrode, by formation of $PtO_2$ , and oxidize EtOH to $CH_3COOH$ or $CO_2$.

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## SUMMARY AND SCOPE

The object of this work was to synthesize the room temperature ionic liquids, $EMImBF_4$, $BMImBF_4$ and BMPBETI, and to study the electrochemical behavior of ethanol in these electrolytes on the Pt electrode. The electrochemical oxidation of EtOH on Pt electrodes in acidic medium involves several reaction pathways. The predominant pathway involves oxidation of bulk EtOH to $CH_3CHO$ which can be further partially oxidized to acetic acid. The secondary reaction involves oxidation of a strongly bound adsorbate, breaking the C-C bond and the formation of $CO_2$. The electrochemical behavior of EtOH in ionic liquid was investigated and compared to the one obtained in acid aqueous electrolyte. It is expected that the use of the room-temperature ionic liquids might prevent poisoning of Pt electrode, by formation of $PtO_2$ , and oxidize EtOH to $CH_3COOH$ or $CO_2$ .

## RESULTS

### A. Synthesis, Purification and Characterization of Ionic Liquids.-

*a. 1-Ethyl-3-Methylimidazolium Tetrafluoroborate*.-While 1-ethyl-3-methylimidaze tetrafluoroborate ($EMImBF_4$) is commercially available, it is not electrochemically pure, making it unsuitable for electrochemical studies. A cyclic voltammogram of a commercial sample of $EMImBF_4$ is shown in Figure 1. The strong anodic peak at $E_{p,a}$=1.5V shows the presence of a significant amount of $Cl^-$ in the sample, narrowing the potential window to less than 2.5 V.

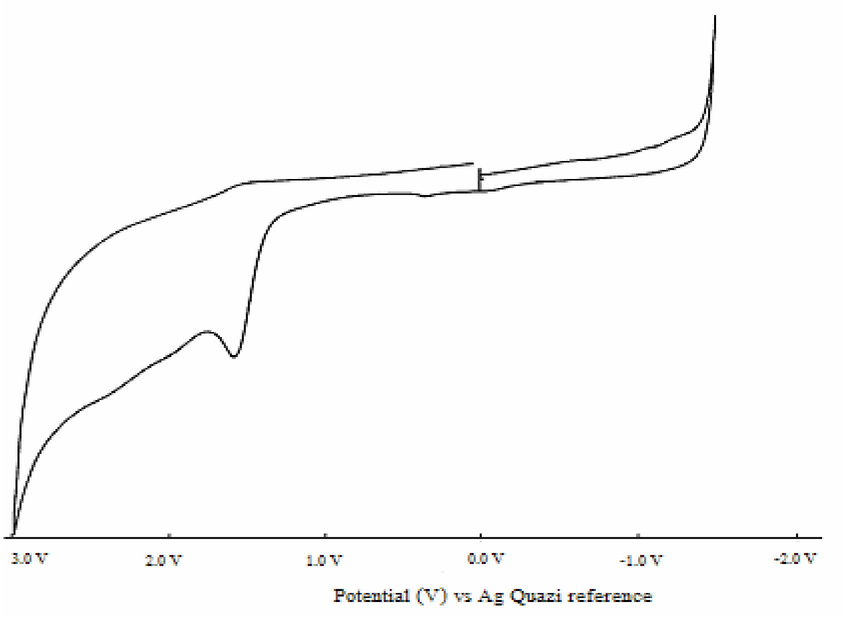
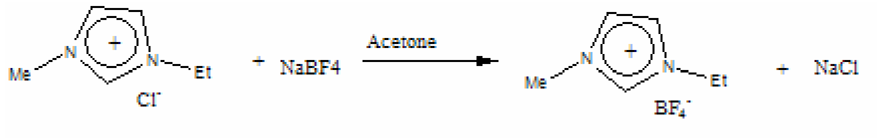


Figure 1 – Cyclic voltammogram of commercially available EMImBF4 containing $Cl^-$ Impurity (Ep=1.6V) (Glassy Carbon Electrode with a Scan Rate of 50 mV $s^{-1}$)

$EMImBF_4$ was synthesized from N-methylimidazolium. The synthesis involves ethylation of N-methylimidazole with ethyl chloride ($CH_3CH_2Cl$) and the formation of EMImCl. The next step involved replacement of the $Cl^-$ ion with the $BF_4^-$ ion. This was achieved by reaction of EMImCl with $NaBF_4$ and the extraction of $EMImBF_4$ in acetone and or water.



Our sample of $EMImBF_4$ prepared by metathesis reaction of EMImCl with $NaBF_4$ shows a wide electrochemical window of ~4.2V as shown in Figure 2.

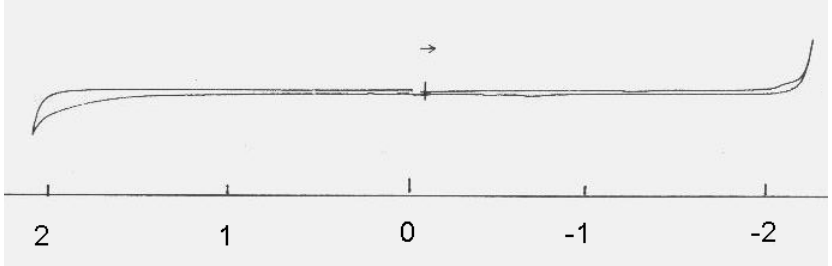
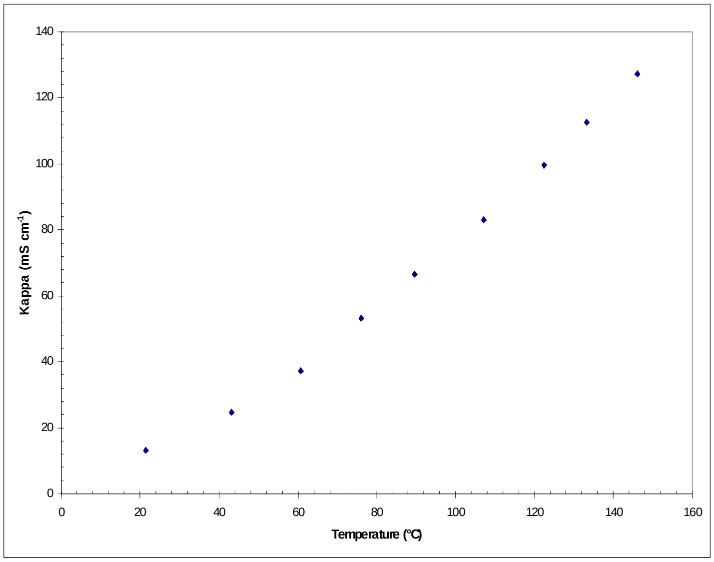


Figure 2 – Cyclic voltammogram of pure $EMImBF_4$ obtained from EMImCl by metathesis with $NaBF_4$ in Acetone (Glassy Carbon Electrode with a Scan Rate of 50 $mVs^{-1}$)

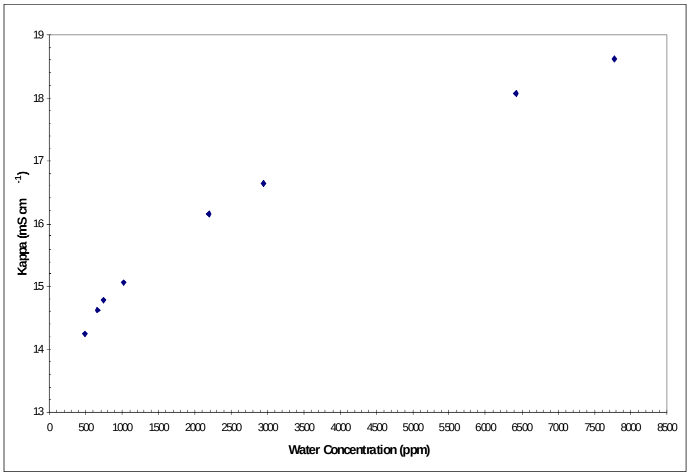
Our sample of $EMImBF_4$ was characterized by conductivity, IR spectroscopy, $^1$HNMR and cyclic voltammetry. A cyclic voltammogram of pure $EMImBF_4$, shown in Figure 2, exhibits a relatively large electrochemical window, in excess of 4.2 V. The pure $EMImBF_4$ sample, containing approximately 50 ppm of $H_2O$, has a specific conductance (kappa) of 13.4 mS $cm^{-1}$ at 21.5°C, which is in good agreement with the literature value of 12.2 mS $cm^{-1}$ at 20°C.[1] The temperature dependence of the conductivity of $EMImBF_4$ between 20°C and 150°C is shown in Figure 3. A special precaution was taken for the sample not to be exposed to the moist air, for the presence of $H_2O$ significantly alters the conductivity of the sample. The $EMImBF_4$ sample was placed in a dry cell in the dry box, and the previously calibrated dry electrode was fastened into place. The conductivity cell was placed in an oil bath, which was heated. Each measurement was taken after the cell was allowed to equilibrate to the desired temperature for ten minutes. All temperature measurements were made with a calibrated digital thermometer. The kappa value increases from 13.4 mS $cm^{-1}$ at 21.5°C to 127.4 mS $cm^{-1}$ at 146.1°C.



| Temperature (°C) | Specific Conductivity (mS/cm), K |
|---|---|
| 21.5 | 13.37 |
| 43.2 | 24.83 |
| 60.7 | 37.19 |
| 76.1 | 53.43 |
| 89.6 | 66.43 |
| 107.1 | 82.97 |
| 122.4 | 99.79 |
| 133.3 | 112.56 |
| 146.1 | 127.36 |

Figure 3 - Specific Conductance of Pure $EMImBF_4$ as a Function of Temperature

The conductivity of the $EMImBF_4$ is also strongly dependent on the amount of water present in the sample. $EMImBF_4$ is chemically inert toward water; however, it slowly absorbs water when exposed to air. The conductance of $EMImBF_4$ as a function of water concentration is shown in Figure 4. The electrochemical potential window of $EMImBF_4$ also depends upon the amount of water present in the sample as shown in Figure 5.[2] With a glassy carbon electrode, the electrochemical window does not change drastically, but with a platinum electrode, the electrochemical window decreases from an overall potential of 4.2 V to about 3.0 V.



| Temperature (°C) | $[H_2O]$ (ppm) | Specific Conductivity (mS/cm), K |
|---|---|---|
| 20 | 484.2 | 14.25 |
| 20 | 662.6 | 14.62 |
| 20 | 738.0 | 14.78 |
| 20 | 1019.0 | 15.06 |
| 20 | 2197.0 | 16.15 |
| 20 | 2944.0 | 16.64 |
| 20 | 6426.0 | 18.07 |
| 20 | 7775.0 | 18.63 |

Figure 4 - Specific Conductance at 20°C as a Function of Water Concentration for $EMImBF_4$

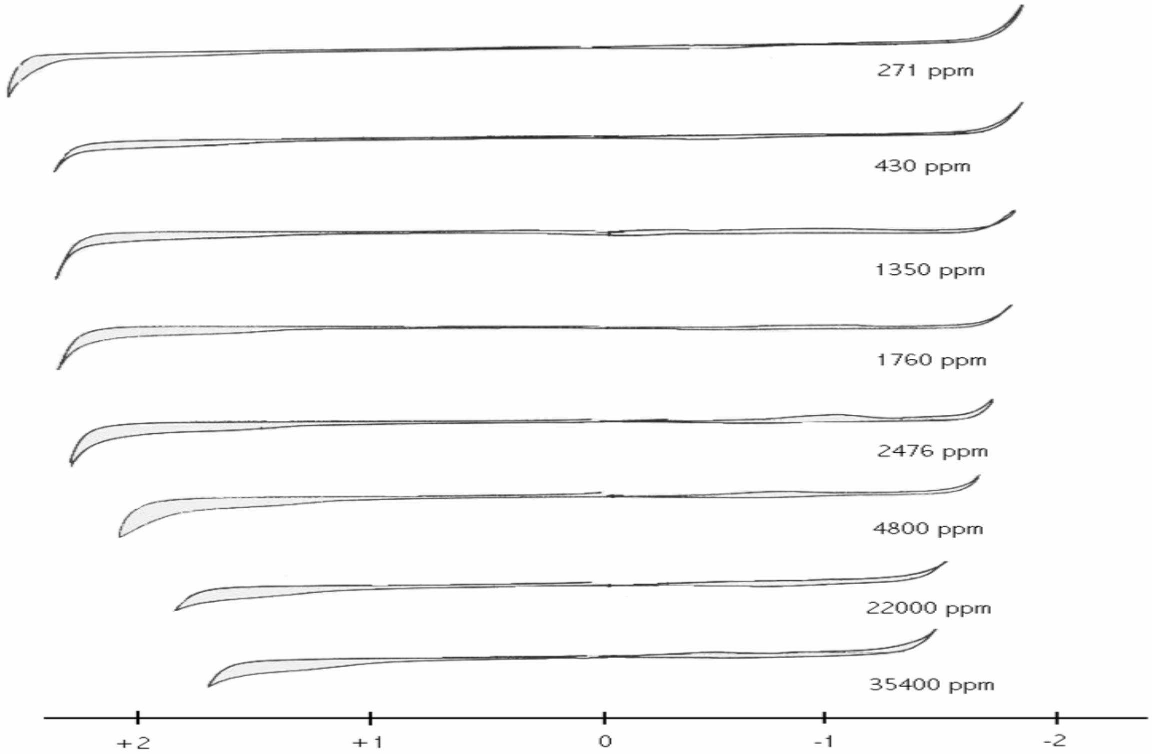
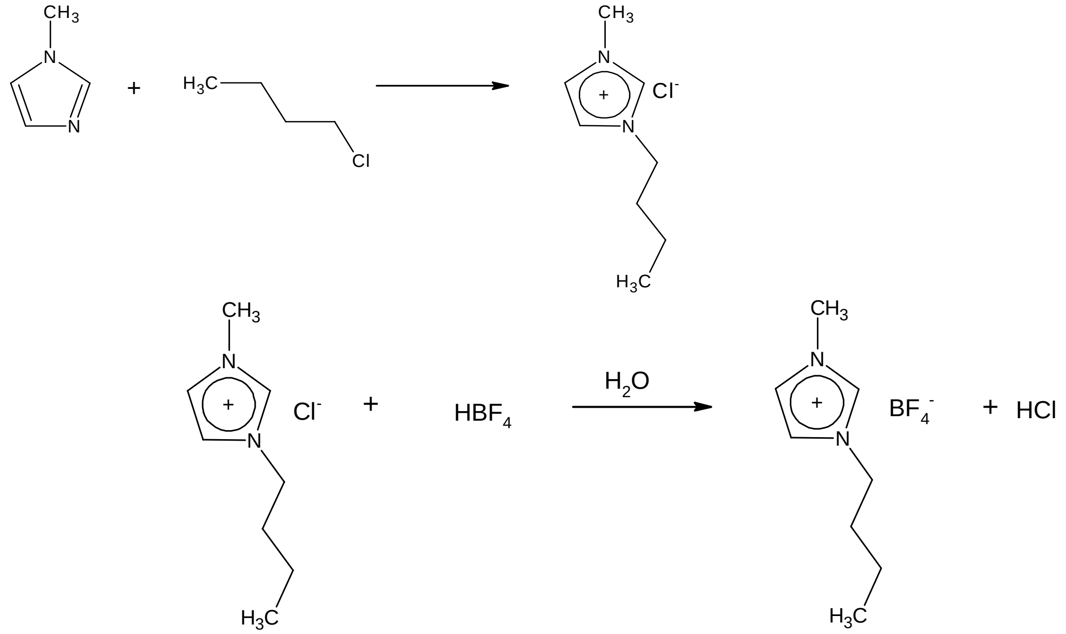


Figure 5 - Cyclic Voltammograms of $EMImBF_4$ containing different amount of Water at a Platinum Electrode

*b. 1-Butyl-3-Methylimidazolium Tetrafluoroborate ($BMImBF_4$).*-The 1-Butyl-3-Methylimidazolium Tetrafluoroborate was synthesized by a similar procedure as was $EMImBF_4$. The product was dried by evacuation on a high vacuum line ($<10^{-5}$ mmHg) for 48 hours.



The water content of BMImBF$_4$ couldn't be lowered below 4000ppm. A cyclic voltammogram containing 4000ppm of water is shown in Figure 6.

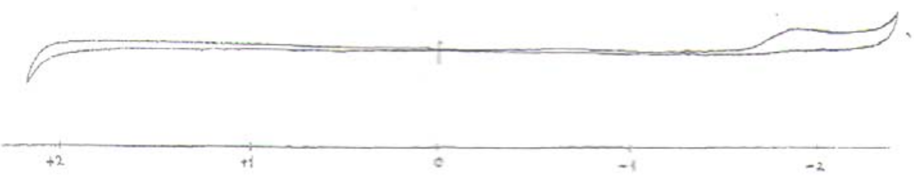


Figure 6 – CV of BMImBF$_4$ containing 4000ppm H$_2$0

Water in BMImBF$_4$ shows an irreversible reduction peak at about -1.8 V. This peak is hardly visible at water concentrations of less than 4000ppm, but increases in size as the amount of water increases as shown in Figure 7.

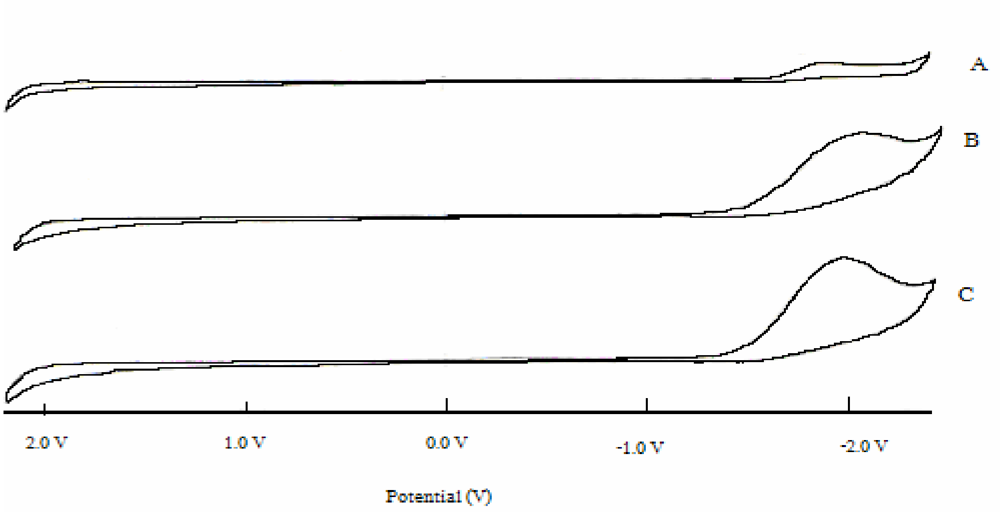
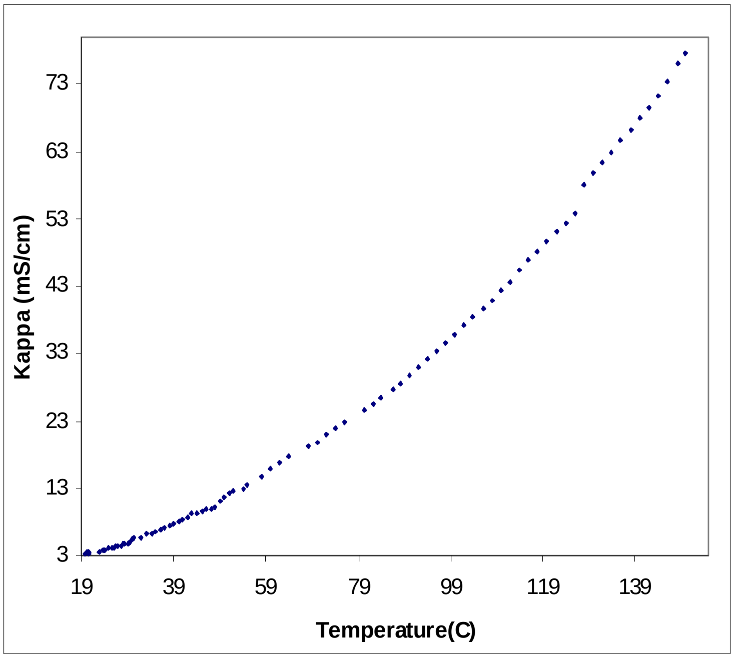


Figure 7 – CV of BMImBF$_4$ containing different amounts of water: A. 4000ppm; B. 27000ppm; C. 29700ppm

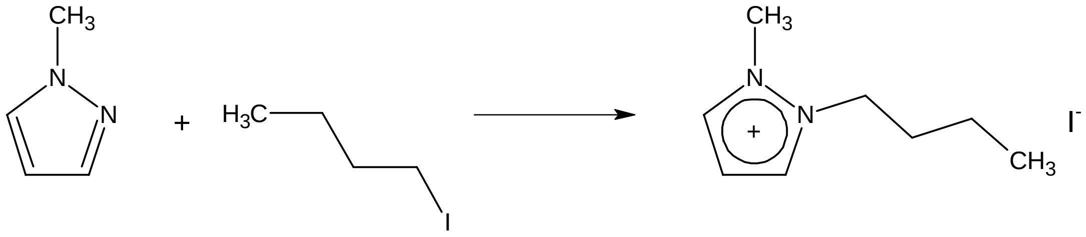
The conductivity of BMImBF$_4$ was measured in the 20-150°C temperature range and the data are shown in Figure 8. These values are about three times smaller than the conductivity of EMImBF$_4$. This could be attributed to the higher viscosity of EMImBF$_4$.



| T (°C) | Specific conductivity (mS/cm),K |
|---|---|
| 20 | 3.46 |
| 30 | 5.31 |
| 39 | 7.85 |
| 45 | 9.68 |
| 58 | 14.78 |
| 68.2 | 19.14 |
| 80.5 | 25.68 |
| 92 | 30.95 |
| 100 | 35.83 |
| 112 | 43.73 |
| 124 | 52.29 |
| 134 | 62.98 |
| 148.5 | 76.67 |

Figure 8- Conductivity of BMImBF$_4$ measured at different temperatures

*c. 1-Butyl-3-Methylpyrazolium BETI (BMPBETI).*-BMPBETI was synthesized by metathesis of BMPI with LiBETI in water. The product, BMPBETI was dried on a high vacuum, down to <50ppm of water.[3] A cyclic voltammogram of BMPBETI, shown in Figure 9, displays a potential window of about 4V. Conductivity data as a function of temperature are shown in Figure 10.



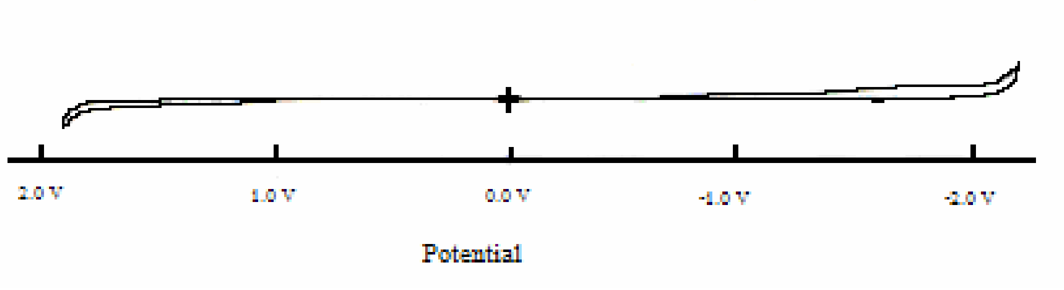


Figure 9 – Cyclitamc Volmogram of BMPBETI (<200ppm of water)

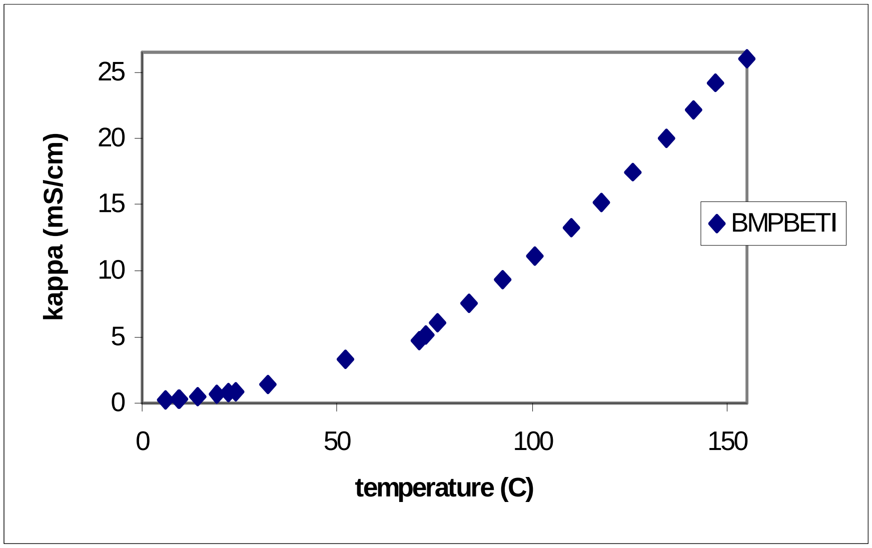


Figure 10- Conductivity of BMPBETI at different temperatures

| T (°C) | Specific Conductivity (mS/Cm), K |
|---|---|
| -0.1 | 0.154 |
| 9.5 | 0.329 |
| 19.3 | 0.679 |
| 24.2 | 0.883 |
| 32.3 | 1.397 |
| 52.1 | 3.327 |
| 71.1 | 4.736 |
| 83.8 | 7.578 |
| 92.4 | 9.329 |
| 100.6 | 11.106 |
| 117.7 | 15.084 |
| 125.9 | 17.405 |
| 134.5 | 20.009 |
| 141.3 | 22.141 |
| 147 | 24.177 |
| 155 | 26 |

**B. Electrochemistry of Ethanol in 0.1M $HClO_4$-** A cyclic voltammogram of 0.1M ethanol in 0.1M $HClO_4/H_2O$ obtained on a clean platinum electrode is shown in Figure 11. On the initial negative sweep the voltammogram displays strong reduction current which is due to the reduction of $H^+$ to $H_2$. On the reverse sweep, a peak of +0.24V corresponds to reoxidation of $H_2$ to $H^+$. On the continuous positive sweep the voltammogram displays two oxidation peaks at $E_{p,a}$ = 0.66V (peak 1) and $E_{p,a}$ = 1.1V (peak 2) vs. Ag/AgCl electrode. On the reverse sweep these two peaks do not display cathodic current, but a new

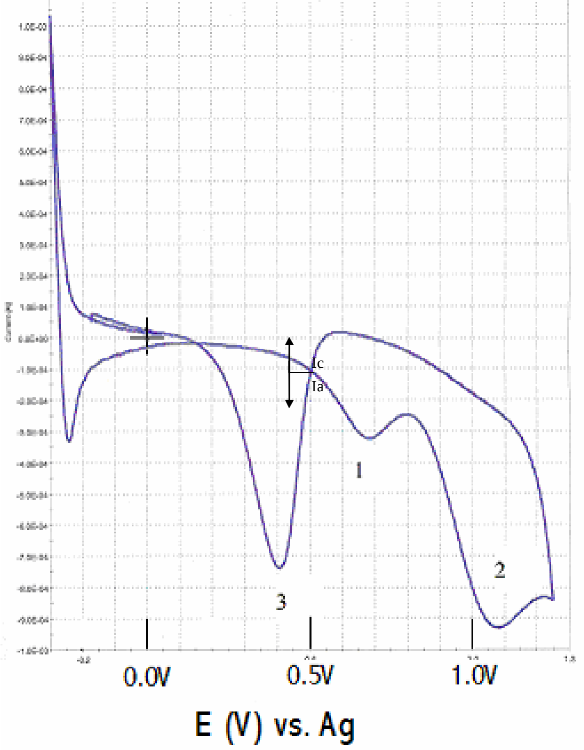


Figure 11 – CV of 0.1M EtOH / 0.1M $HClO_4$ solution on a Pt electrode

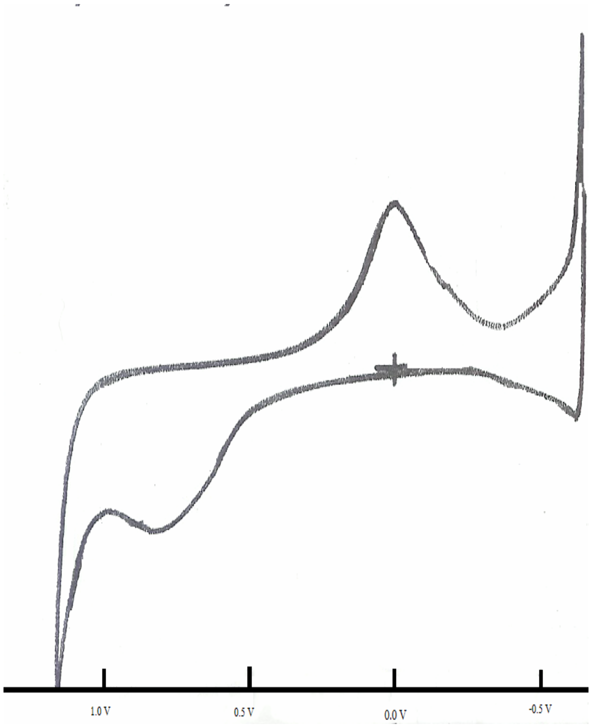


Figure 12-CV of 0.1M $HClO_4$ on a Pt electrode

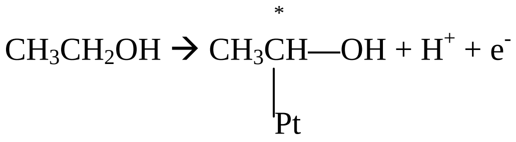
oxidation peak (3) appeared at $E_{p,a}$ = 0.4V. A background CV obtained in 0.1M $HClO_4$ without ethanol is shown in Figure 12. The background voltammogram displays only one oxidation peak at $E_{p,a}$ =0.85V. This peak has been assigned to the oxidation of Pt to PtO. Based on the previous literature data[4,5,6,7,8,9] the three oxidation peaks of EtOH in Figure 11 were assigned as follows:

Peak 1 at $E_{p,a}$ = 0.66V

This oxidation peak corresponds to a two electron oxidation of EtOH to acetaldehyde:

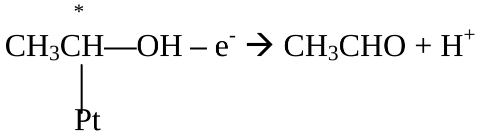
$$CH_3CH_2OH - 2e^- \rightarrow CH_3CHO + 2H^+$$

The overall process consists of two, one-electron steps. The first step involves chemisorptions of $CH_3CH_2OH$ on Pt and fast 1-electron oxidation.



$$CH_3CH_2OH \rightarrow CH_3\overset{*}{\underset{\overset{|}{Pt}}{C}}H—OH + H^+ + e^-$$

This first step is followed by a slower one electron oxidation of adsorbed species to aldehyde



$$CH_3\overset{*}{\underset{\overset{|}{Pt}}{C}}H—OH - e^- \rightarrow CH_3CHO + H^+$$

At the same potential a surface oxidation of Pt to PtO takes place. (Oxidation peak at $E_{p,a}$ =0.6V on Figure 27).

$$Pt + H_2O - e^- \rightarrow Pt(OH) + H^+$$
$$Pt(OH) - e^- \rightarrow PtO + H^+ + e-$$

Peak 2 at $E_{p,a}$ = 1.1V

The second oxidation peak at $E_{p,a}$ = 1.1V involves a slow one electron oxidation of Pt and a formation of Pt-OEt.

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

This is followed by both a one electron oxidation of Pt-($OCH_2CH_3$) to PtO and the oxidation of $PtOCH_2CH_3$ to acetaldehyde.

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

(B) $Pt\text{-}(OCH_2CH_3) - e^- \rightarrow Pt + CH_2CHO$

At this potential oxidation of $CH_3CHO$ to $CH_3COOH$ will also take place. The poisoning of the electrode occurs by the formation of PtO when the reaction A is faster than reaction B. If reaction B is faster than A, the poisoning of the electrode will not occur.

Peak 3 at $E_{p,a}$ = 0.4V

Peak three at $E_{p,a}$ = 0.4V is observed only when the potential is again reversed at 1.4V in the negative direction. This peak has been attributed to the reactivation of the platinum surface by the reduction of PtO with $CH_3CH_2OH$ to PtOH.

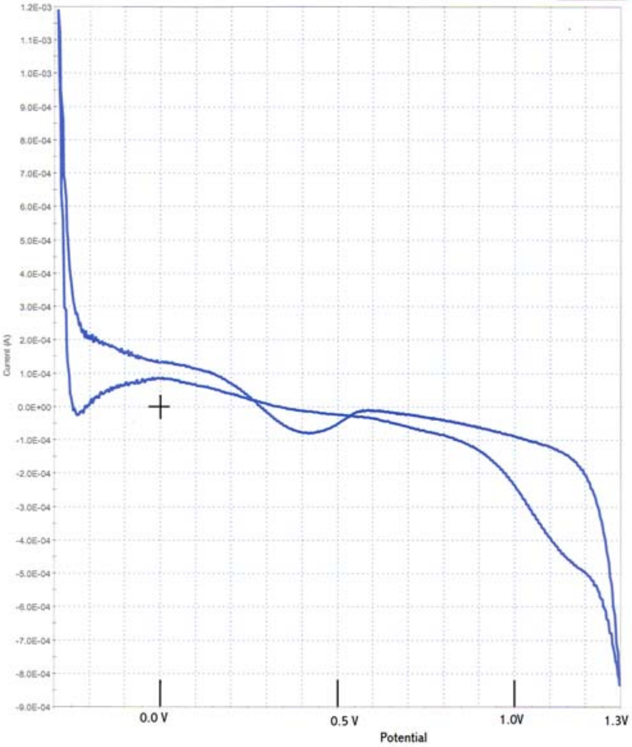
$$CH_3CH_2OH + PtO \rightarrow CH_3CHO + PtOH$$

However, the PtOH formed could be reoxidized back above 0.6V.

$$PtOH - e^- \rightarrow PtO + H^+$$

Peak three is observed because above 0.8 V the reduction of PtO with $CH_3CH_2OH$ will not occur and below 0.6 V the oxidation of PtOH to PtO will not proceed.

The shape of the cyclic voltammogram of ethanol on the platinum electrode is critically dependant upon the concentration of EtOH in $HClO_4$. While the 0.1M solution of EtOH in 0.1M $HClO_4$ gives very pronounced oxidation peaks, as shown in Figure 11, at higher ethanol concentrations, the oxidation peaks become sluggish and relatively small as shown in Figure 13. The first oxidation peak at 0.65V is not visible while the second and third peaks are much smaller. It was proposed that at higher ethanol concentration the poisoning of the Pt electrode occurs.



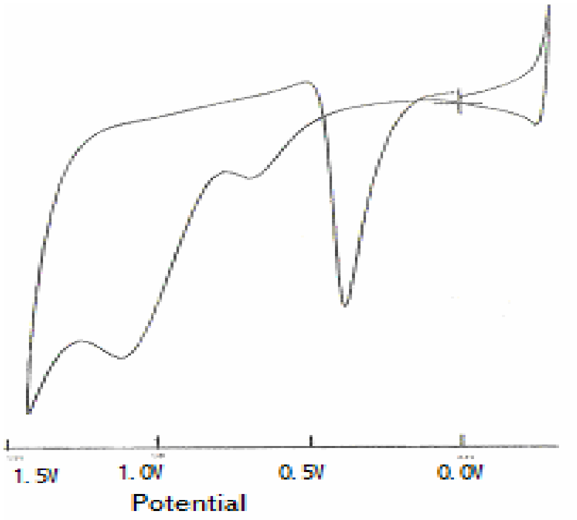
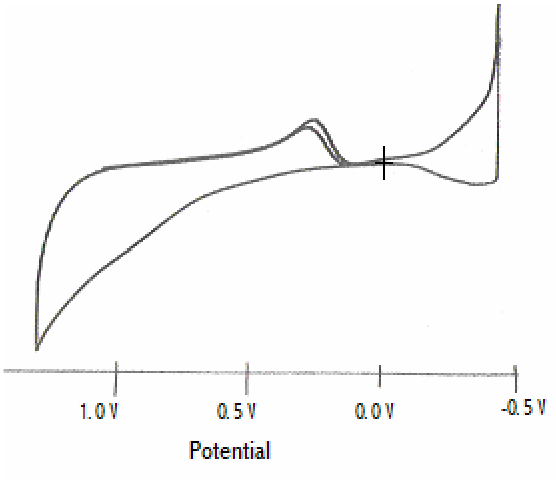


Figure 13 – CV of high EtOH concentration in 0.1M $HClO_4$ obtained on a Pt electrode

Figure 14 – CV of a 0.1M EtOH/0.1M $HClO_4$ on a new Pt electrode

Similarly, if the platinum electrode surface becomes poisoned, the oxidation of EtOH becomes sluggish and only very small oxidation peaks are observed. This is shown in Figure 14 and 15. Figure 14 shows the cyclic voltammogram of 0.1M EtOH / 0.1 $HClO_4$ on a clean/new polycrystalline platinum electrode. Three chemisorption oxidation peaks are clearly visible. For comparison, Figure 15 is a CV of the same solution concentration using a "dirty" platinum electrode, where oxidation peaks are not visible due to the deactivation of Pt electrodes.



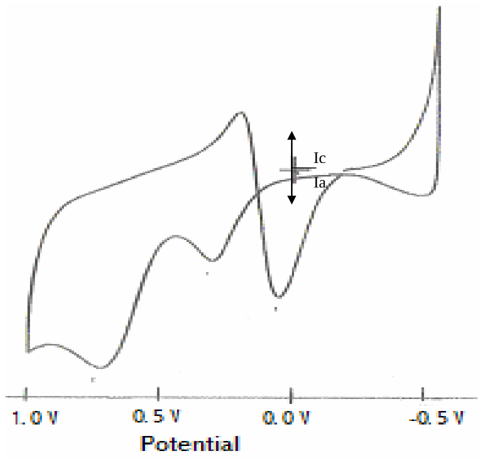


Figure 15 - CV of 0.1M EtOH/0.1M $HClO_4$ obtained on a poisoned Pt electrode (Pt electrode same was the Same as the one used in Figure 33).

Figure 16- CV of a 0.1M EtOH/0.1M HClO4 solution obtained on Pt electrode after cleaning with $H_2SO_4$

**C. Cleaning of the Poisoned Platinum Electrode.-** A polycrystalline platinum electrode is easily poisoned after multi-cycle use. This poisoning is due to the formation of PtO and or absorption of some species. Mechanical polishing using alumina suspension does not reactivate the electrode. There are several methods described in literature for cleaning platinum electrodes used for the reduction of $H^+$ to $H_2$. While these procedures are good for $H^+$ to $H_2$ reduction process they are not good for reactivation of the electrode for oxidation of ethanol in the 0.0 to -1.0V potential range. Several methods were used to clean the polycrystalline platinum and the platinum (111) electrodes.[10] Some of the techniques used were polishing with 1um Alumina suspension, cleaning in hot nitric acid, potassium dichromate solution and concentrated sulfuric acid ($K_2Cr_2O_7$ / $H_2SO_4$). The best method for removing PtO from platinum and the reactivation of Pt electrodes is cleaning in sulfuric acid.

*a. Sulfuric acid cleaning.*-We have found that the best way to reactivate the platinum electrode is to soak the electrode in concentrated sulfuric acid ($H_2SO_4$) overnight. The electrode is then placed in a sonicator, to remove any debris, and finally rinsed off by high purity water. After the electrode is cleaned, a CV of 0.1M EtOH in 0.1M $HClO_4$ is ran to make sure the electrode is clean. Three oxidation peaks of ethanol become visible, as shown in Figure 16. The CV with multiple cycles is obtained on the electrode after cleaning is shown in Figure 17.

*b. Alumina cleaning.*- Alumina suspension was used to clean platinum electrodes by removing film or layers that are formed during the oxidation of ethanol. The alumina suspension was applied to a soft cloth in which the Pt electrode was placed into the suspension and rotated in a “figure 8” fashion. The platinum with excess alumina was soaked in high purity water and inspected under a microscope to reassure removal of alumina particles. For the 7 $mm^2$ platinum polycrystalline platinum (Teflon), the cyclic voltammogram in Figure 18 shows that the third regeneration peak is present, but the first and second peaks are not defined.

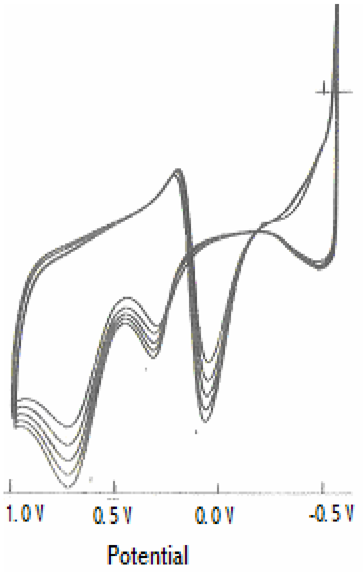


Figure 17 – Multiple cyclic voltammograms of 0.1M EtOH/0.1M $HClO_4$ solution obtained on a Pt electrode after cleaning with $H_2SO_4$

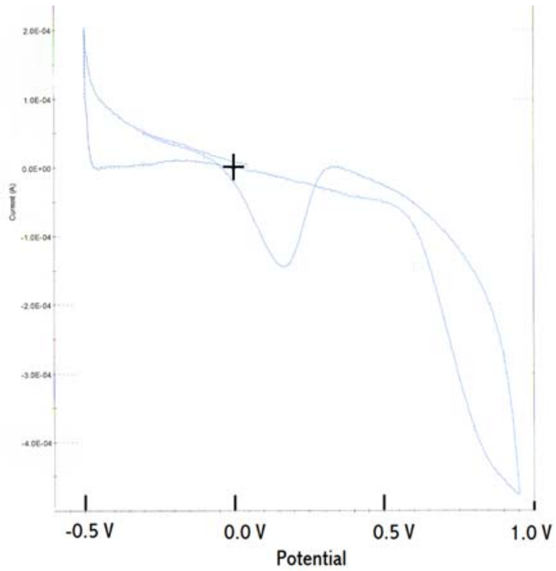


Figure 18 – CV of 0.1M EtOH/0.1M $HClO_4$ obtained on a Pt electrode after cleaning with alumina

*c. Nitric acid cleaning.*- Another cleaning technique involved hot nitric acid as the oxidant. Placing the electrode in a hot concentrated nitric acid bath for over 24 hours should oxidize the platinum oxide PtO that is formed during cyclic voltammetry of alcohols. However, in Figure 19, the first peak is not seen at all. The second peak is very small as well as the third regeneration peak. Nitric acid is not a good candidate for removing PtO on platinum electrodes.

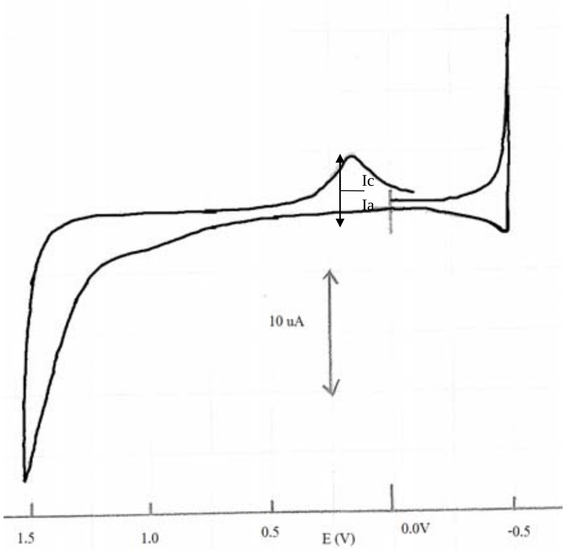


Figure 19 – CV of 0.1M EtOH/0.1M $HClO_4$ solution obtained using a Pt electrode after cleaning in hot nitric acid

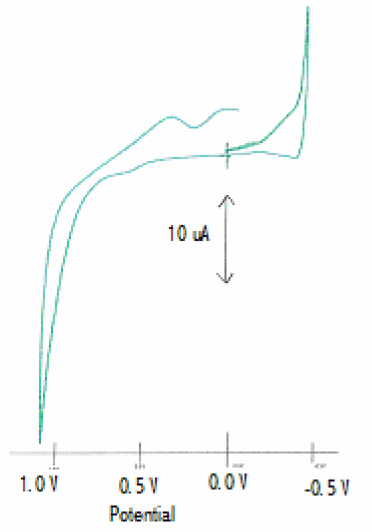


Figure 20 -CV of 0.1M EtOH/0.1M $HClO_4$ obtained on a Pt electrode after cleaning in $K_2Cr_2O_7$ / $H_2SO_4$

*d. Potassium Dichromate Cleaning.*-The electrode again is placed in potassium dichromate solution and concentrated $H_2SO_4$ and soaked for over 24 hours. The CV shown in Figure 20 show does not show oxidation peaks of EtOH, and therefore $K_2Cr_2O_7$/$H_2SO_4$ is not a suitable solution for reactivation of Pt electrodes.

**D. Construction of the Single Crystal Pt(111) Disk Electrode.**-The single crystal Pt (111) electrode was constructed from a Pt (111) disk. The disk was attached to the conducting rod using conducting epoxy and the rod was insulated from the solution with a Kynar shrink tube. However, the seal around the Pt disk would not seal tightly, and the solution would leak into the tube. The solution contacted the rod showing a large polarization current because of the large surface area, as shown in Figure 21. The proper seal was obtained using a non-conductive epoxy on the copper rod and the edges

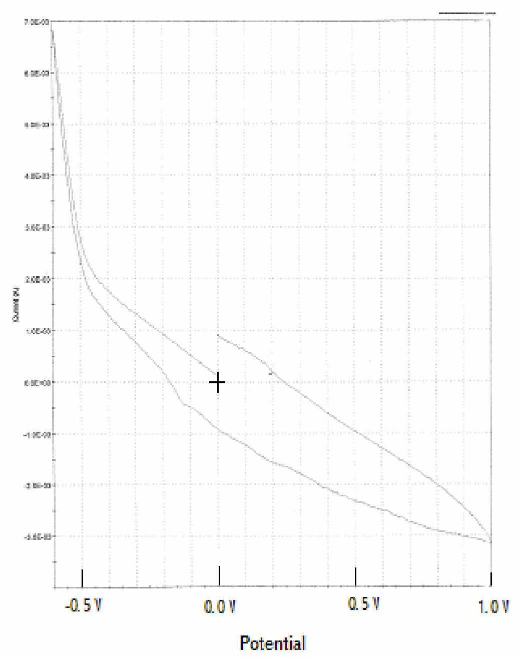


Figure 21 – CV of HClO4 obtained on a leaking Pt (111) electrode showing a large charging current

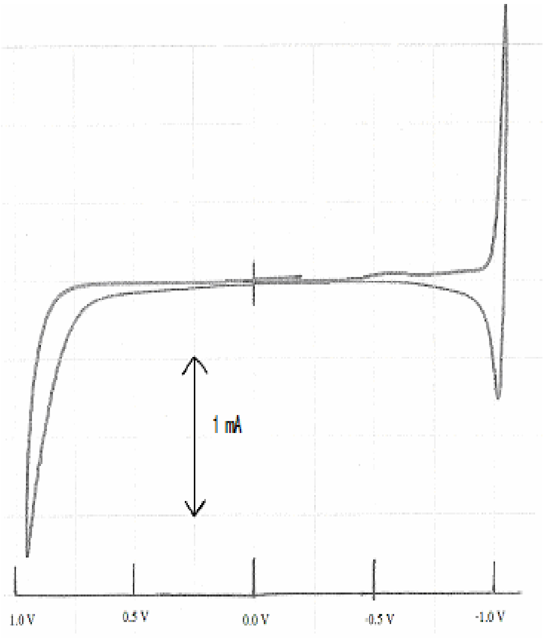


Figure 22 – Cyclic Voltammogram of 0.1M $HClO_4$ using Pt (111) electrode vs. Ag quazi reference electrode

of the platinum disk. The electrode and wet epoxy was dried in a horizontal rotating manner, for an evenly smooth surface of epoxy. Epoxy prohibits solution to have contact with the copper rod. The Kynar shrink tube was then attached to the electrode. The cyclic voltammogram of the sealed Pt (111) electrode is shown in Figure 22. It shows the characteristic E vs. I curve with a small charging current.

*a. Determination of the Surface Area of Platinum Electrodes.*-The surface area of a clean platinum electrode was determined by cyclic voltammetry using a 4 mM potassium hexacyanoferrate ($K_3Fe(CN)_6$) solution in 0.1M KCl. From the Randles-Sevcik equation, [11,12,13]

$$i_p = (2.69x10^5)n^{\frac{3}{2}}AD^{\frac{1}{2}}C\nu^{\frac{1}{2}}$$

surface area A could be obtained if n, D, C, V are known and $I_{p,a}$ is calculated from cyclic voltammograms. The diffusion coefficient of $K_3Fe(CN)_6$ in KCl was obtained from literature and has a value as $D=0.73 \times 10^{-5}$ $cm^2/M$. [10] The cyclic voltammograms of the $K_3Fe(CN)_6$ solution at different scan rates are shown in Figure 23.

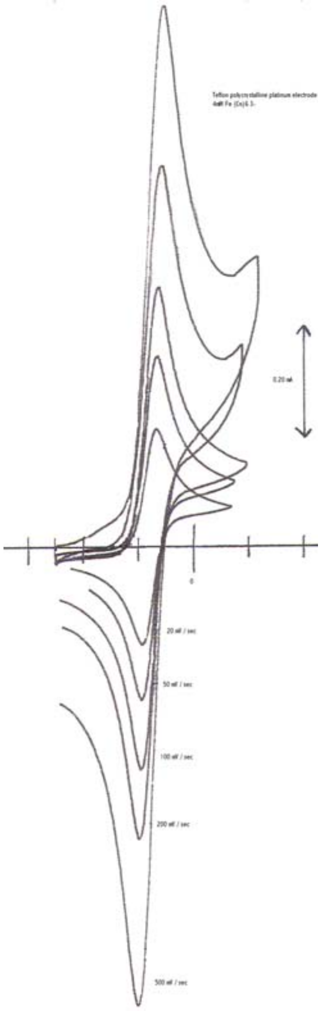


Figure 23 – Cyclic Voltammogram of 4 mM $K_3Fe(CN)_6$ in 0.1M KCl using Pt (111) disk electrode at different scan rates

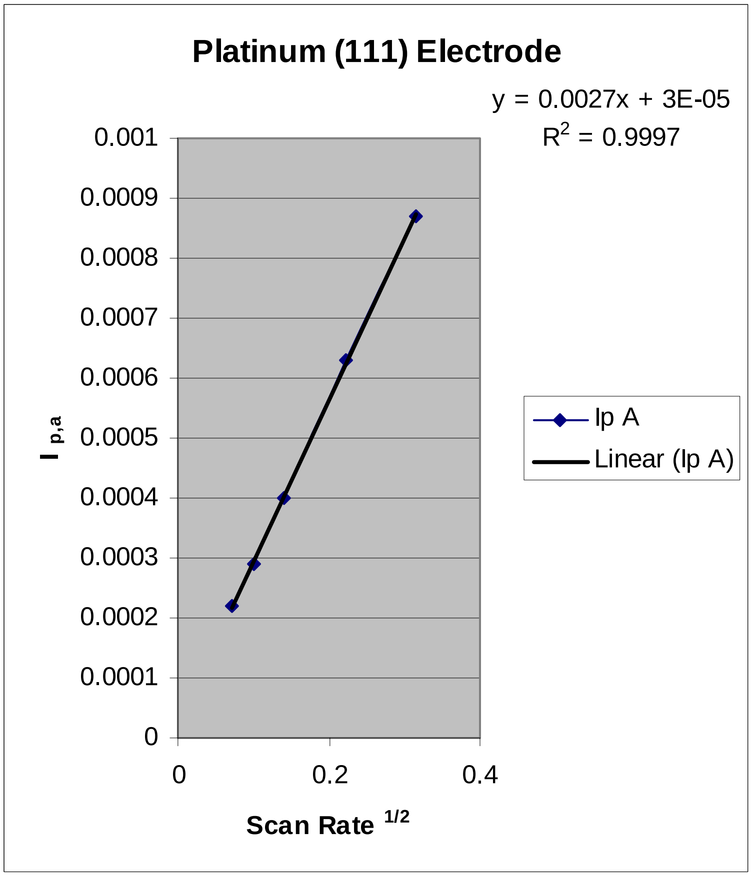


Figure 24 – Plot of $I_{p,a}$ versus (scan rate) $^{½}$ used to determine surface area for Pt (111) electrode

A plot of $I_{p,a}$ versus V $^{½}$ is shown in Figure 24, 25, and 26 for Pt (111), Pt Foil and Teflon Pt electrodes respectfully. The slope of the graphs determined the average $I_{p,a}$ for each electrode, in which the surface area of the electrode was calculated. Individual values for the graphs are given in Table 1.

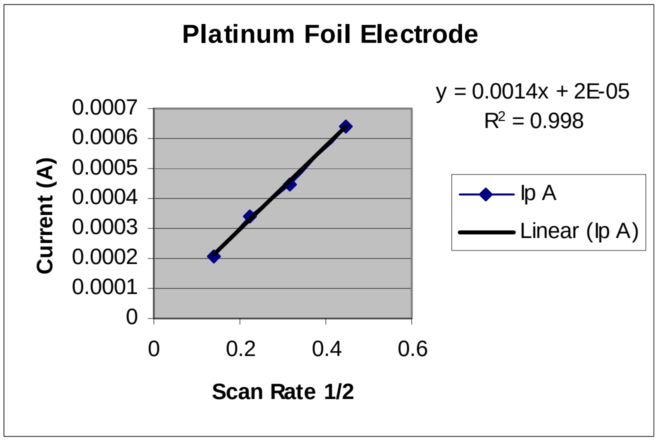


Figure 25 – Plot of $I_{p,a}$ versus (scan rate) ½ used to determine determine surface area for Pt Foil electrode

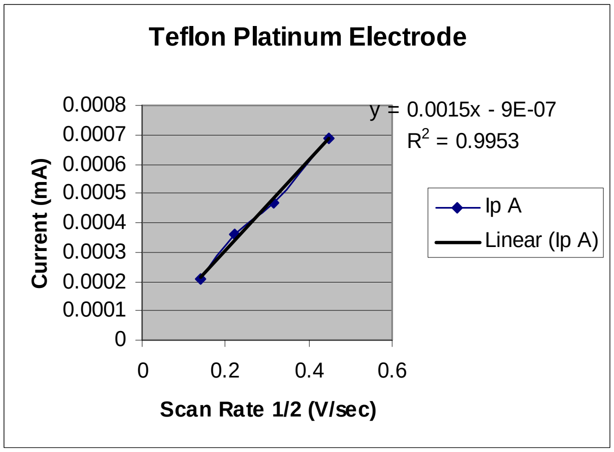


Figure 26 - Plot of $I_{p,a}$ versus (scan rate) ½ used to determine surface area for Pt Teflon electrode

Table 1 – $I_{p,a}$ values for Pt electrodes as a function of (scan rate)½

| Platinum (111) | | Teflon Platinum Electrode | | Platinum Foil | |
|---|---|---|---|---|---|
| SR $^{1/2}$ | $I_{p,a}$ | SR $^{1/2}$ | $I_{p,a}$ | SR $^{1/2}$ | $I_{p,a}$ |
| 0.0707 | 0.00022 | 0.1414 | 0.00021 | 0.1414 | 0.00021 |
| 0.1 | 0.00029 | 0.2236 | 0.00036 | 0.2236 | 0.00034 |
| 0.1414 | 0.0004 | 0.3162 | 0.00047 | 0.3162 | 0.00045 |
| 0.2236 | 0.00063 | 0.4472 | 0.00069 | 0.4472 | 0.00064 |
| 0.3162 | 0.00087 | | | | |

Results of the surface area for each platinum electrode are shown in Table 2, in which they are compared to calculated values.

Table 2 - $I_{p,a}$ and scan rate ½ values of the surface area calculation for platinum electrodes

| Surface Area ($cm^2$) | Teflon Pt | Foil Pt | Pt (111) |
|---|---|---|---|
| Diameter Calculated | 0.5024 | 0.5024 | 0.708 |
| Cyclic Voltammetry | 0.517 | 0.483 | 0.931 |

As demonstrated from the surface area results. The platinum (111) has a higher surface area, and better than when calculated from the diameter of the disk. This is due to the highly characterized surface, in which the platinum is highly active.

Pt (111) single crystal electrode is the most active and exhibits the least poisoning effects. When comparing the polycrystalline platinum electrode, platinum (111) is much active and produces larger peak current for the same concentration of ethanol in the solution (Figure 27). [14,15.16]

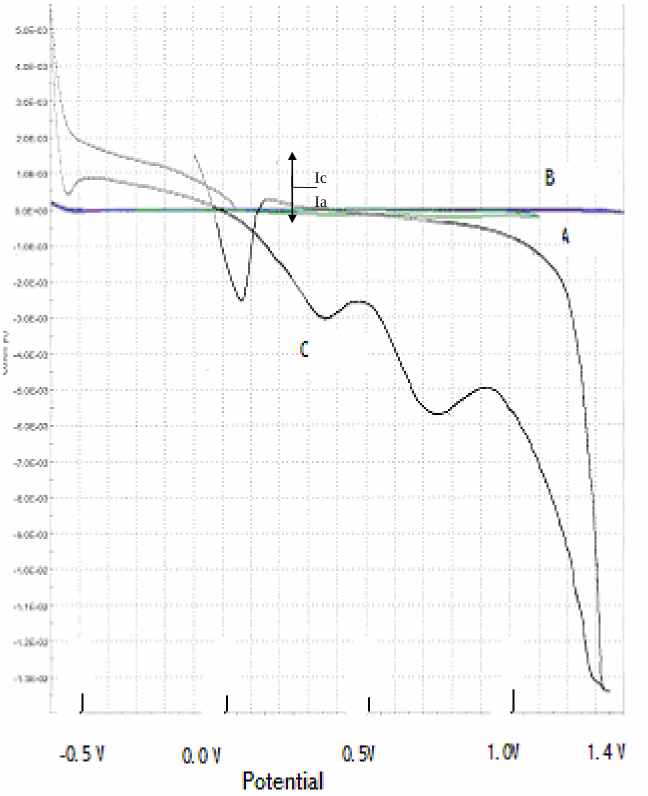


Figure 27 – CV of 0.1M EtOH/0.1M $HClO_4$ solution using A) Pt mini, B) Pt Teflon, C) Pt (111)

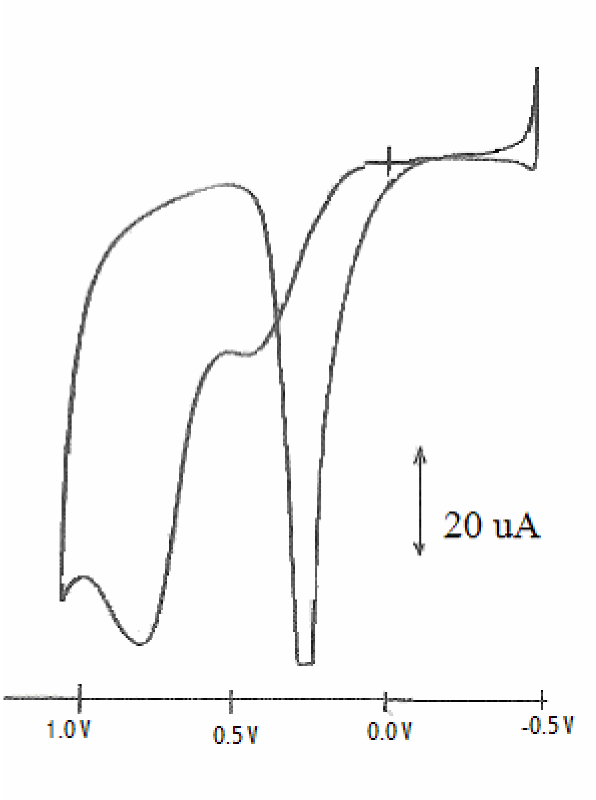


Figure 28 – CV of 0.1M EtOH /0.1M $HClO_4$ at 73°C

**E. Electrochemistry of Ethanol in Ionic Liquids.-** It is known that the oxidation of EtOH in $HClO_4$ aqueous solution is dependent on the active surface area of the electrode. At low EtOH concentrations (~0.1M) well resolved oxidation peaks are observed at E = 0.5 V and E=1.1 V. When the concentration of EtOH is increased, poisoning of the electrode takes place and the CV oxidation peaks decrease and practically disappear. We have used ionic liquids to see if the poisoning of Pt could be avoided in ionic liquids.

In the first set of experiments $EMImBF_4$ ionic liquid was added to 0.1M $HClO_4$ (0.1M EtOH solution). The small volume cell was used and the mini platinum electrode ($1mm^2$) was used as the working electrode, silver wire acted as the quazi reference electrode, and a platinum wire was the auxiliary electrode. The CV in Figure 28 was obtained in the absence of ionic liquids at 73°C shows two oxidation peaks. The voltammogram in Figure 29 is obtained after a few drops of $EMImBF_4$ were added to ~2mL of 0.1M $HClO_4$/0.1M EtOH solution. A significant decrease in the first peak for EtOH oxidation current is observed as well as a decrease of the regeneration oxidation peak 3.

Figure 30 shows a cyclic voltammogram of a 0.1M EtOH/0.1M $HClO_4$ solution in 0.1M $EMImBF_4$ obtained at 25°C. The voltammogram shows well defined oxidation peaks at Ep = 0.45V and Ep = 0.85V and a very small regeneration peak at Ep = 0.35V on the reverse scan. These peaks significantly increase in size after the temperature was raised to 78°C, shown in Figure 31. It is also noted that the first oxidation peak at 78°C becomes almost as large as the second oxidation peak. This clearly demonstrates that the presence of ionic liquids increases the rate of the oxidation process of ethanol.

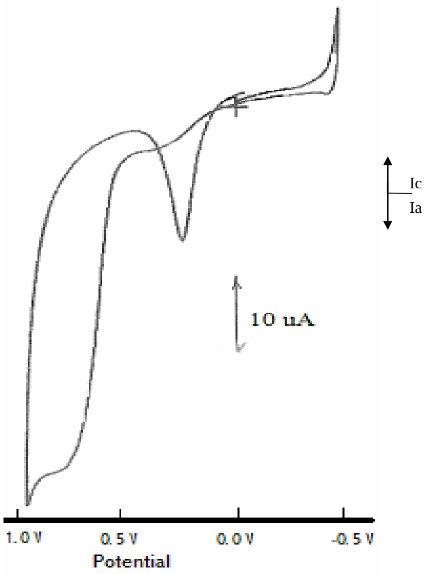


Figure 29.-CV of 0.1 M EtOH/0.1M $HClO_4$ containing a few drops of EMImBF4 at 75 $^0C$

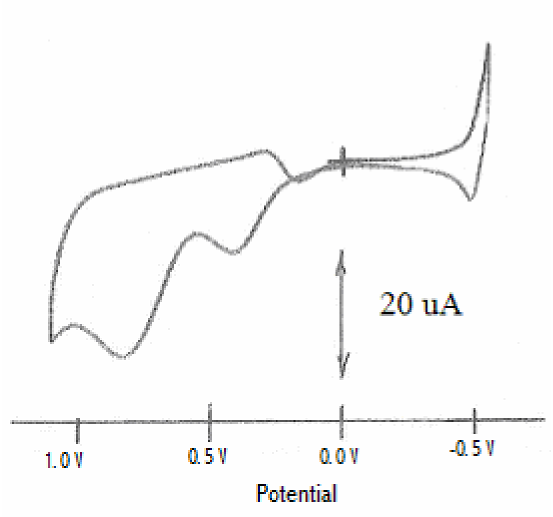


Figure 30 – CV of 0.1M $EMImBF_4$, 0.1M EtOH, in 0.1M $HClO_4$ at 25°C

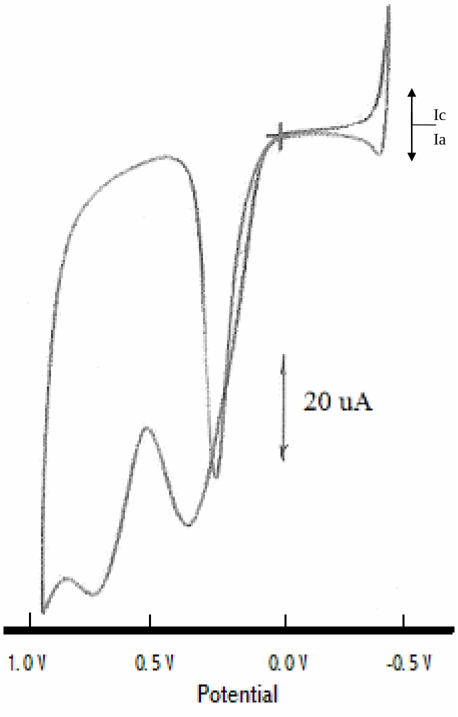


Figure 31 – CV of 0.1M $EMImBF_4$, 0.1M EtOH, 0.1M $HClO_4$ at 78°C

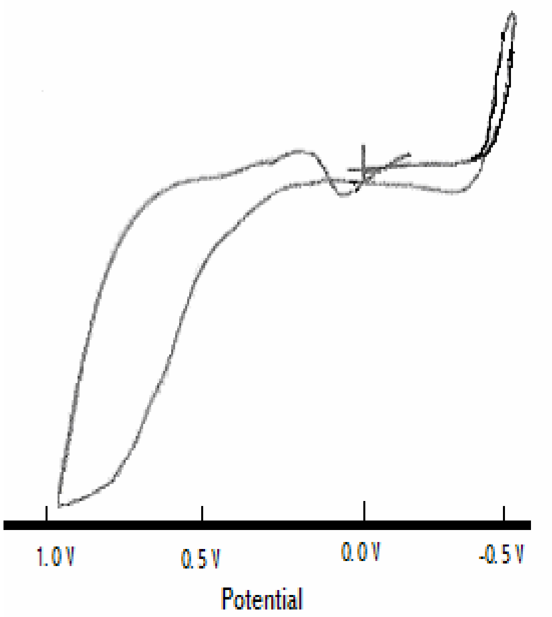


Figure 32 – CV of 0.1M EtOH in water containing 0.1M $EMImBF_4$ at 22°C

Cyclic voltammograms of EtOH in the absence of $HClO_4$ are shown in Figure 32 and 33. The solution was 0.1M EtOH and 0.1M $EMImBF_4$ in $H_2O$ (1.07 mL). The cyclic voltammograms shown in Figure 51 is obtained at room temperature (22°C). The two oxidation peaks are hardly noticeable, however, when the temperature is increased to 71°C, as shown in Figure 52, well defined oxidation peaks are observed. They are well resolved and have similar shape as the peaks observed in $HClO_4$ solutions. This indicates that $EMImBF_4$ can be used as an electrolyte in EtOH oxidation instead of corrosive $HClO_4$, $H_2SO_4$ or $Na_2CO_3$ electrolytes.

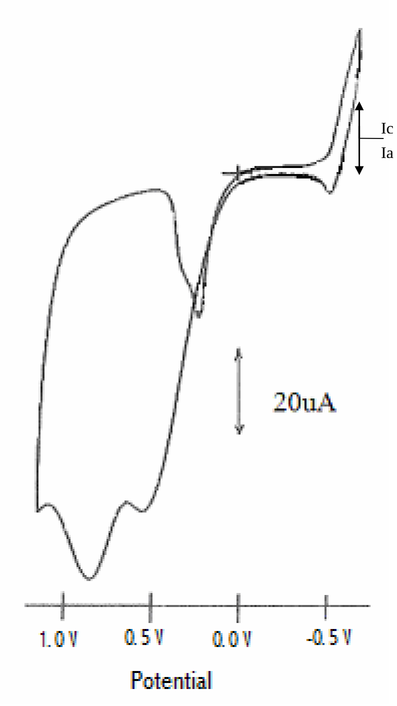


Figure 33 – CV of 0.1M EtOH in water containing 0.1M EMImBF$_4$ at 71°C

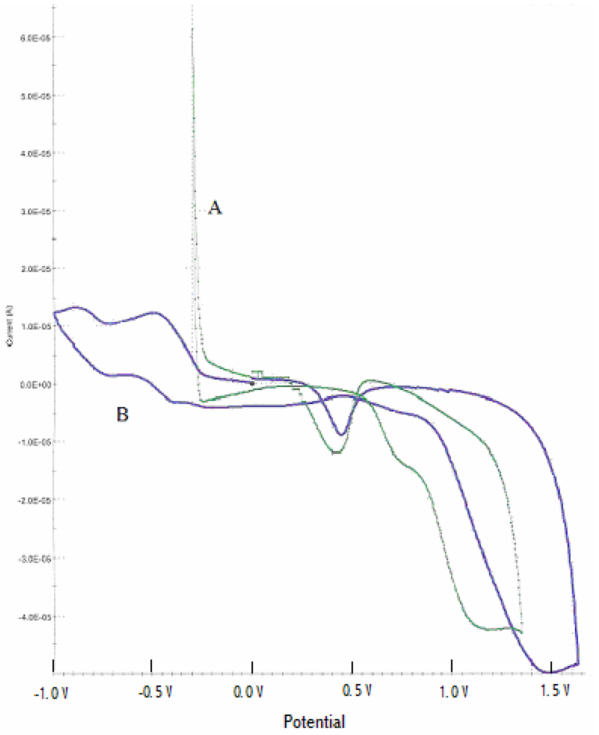


Figure 34 – CV of 1.0M EtOH obtained in A) HClO$_4$, B) EMImBF$_4$

A comparison of cyclic voltammograms of 1.0M EtOH in (0.1M) HClO$_4$ and EMImBF$_4$ is shown in Figure 34 at 25°C. The voltammograms are very similar except that the first oxidation peak is significantly smaller in ionic liquid in comparison to HClO$_4$.

Cyclic voltammograms of ethanol in pure EMImBF$_4$ are shown in Figure 35. The voltammograms display a large second oxidation peak. The first oxidation peak is present only while the concentration of EtOH is small ~1.0M. Contrary to the behavior in HClO$_4$ solution the second oxidation peak increases as the concentration of EtOH is increased from 1.0M to 10.0M. This clearly indicates that poisoning of Pt electrode does not happen in pure ionic liquid. In HClO$_4$ solution at increased concentration of EtOH > 0.1M poisoning (formation of PtO) of the electrode takes place and the electrode becomes deactivated.

**F. Oxidation of EtOH on Pt (111) electrode in EMImBF$_4$.-**It is known from previous studies that Pt (111) electrode oixdizes EtOH better than a polycrystalline Pt electrode. Comparison of CV's obtained on Pt (111) and polycrystalline Pt electrode in EMImBF$_4$ ionic liquid is shown in Figure 55. Trace A in Figure 36 is a CV obtained using a polycrystalline Pt where trace B is a CV obtained on Pt (111). It is clearly visible that the oxidation peaks of EtOH in EMImBF$_4$ are significantly larger on Pt (111) electrode.

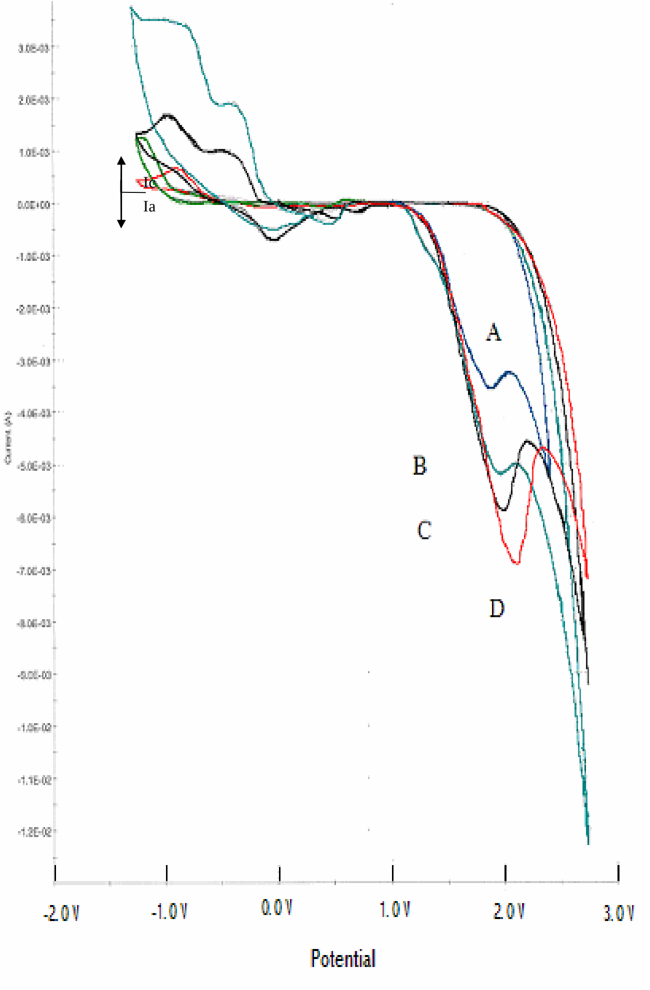


Figure 35 – CV of $EMImBF_4$ containing different amounts of EtOH; A) 1.0M EtOH, B) 2.0M EtOH, C) 5.0M EtOH, D) 10.0M EtOH

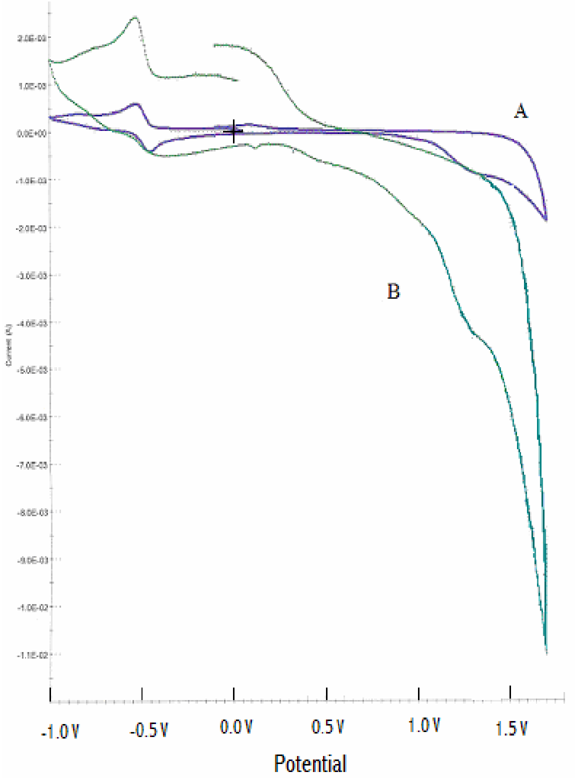


Figure 36 – CV of 1.3M EtOH in $EMImBF_4$ obtained on A) Polycrystalline Platinum electrode and B) Platinum (111) single crystal electrode

**G. Attempts to Identify the Oxidation product by IR Reflectance Spectroscopy.-** A reflectance infrared spectroscopy was used to identify the species formed by oxidation of EtOH on the surface of the platinum electrode. The polycrystalline electrode was placed in the large volume cell with a calcium fluoride ($CaF_2$) window. The $CaF_2$ window was chosen because it was transparent to the IR wavelength. The electrode is placed next to the window with approximately a 1 mm thick electrolyte solution sandwiched between the electrode and the window.

The whole cell was positioned on the IR reflectance attachment and IR reflectance spectra were measure before and after the electrolysis. The schematic of the attachment is shown in Figure 37. The background IR spectrogram was the electrolyte (ionic liquid or acid) and a 0.1M EtOH solution was the sample, shown in Figure 38. The spectral region for detection of $CO_2$ at 1920cm$^{-1}$ was monitored before and after electrolysis. No peak at 1920cm$^{-1}$ was detected after electrolysis. The IR spectrometer was not of a required sensitivity to detect small absorption of $CO_2$. This could be due to either a week IR source or not a sensitive enough IR detector.

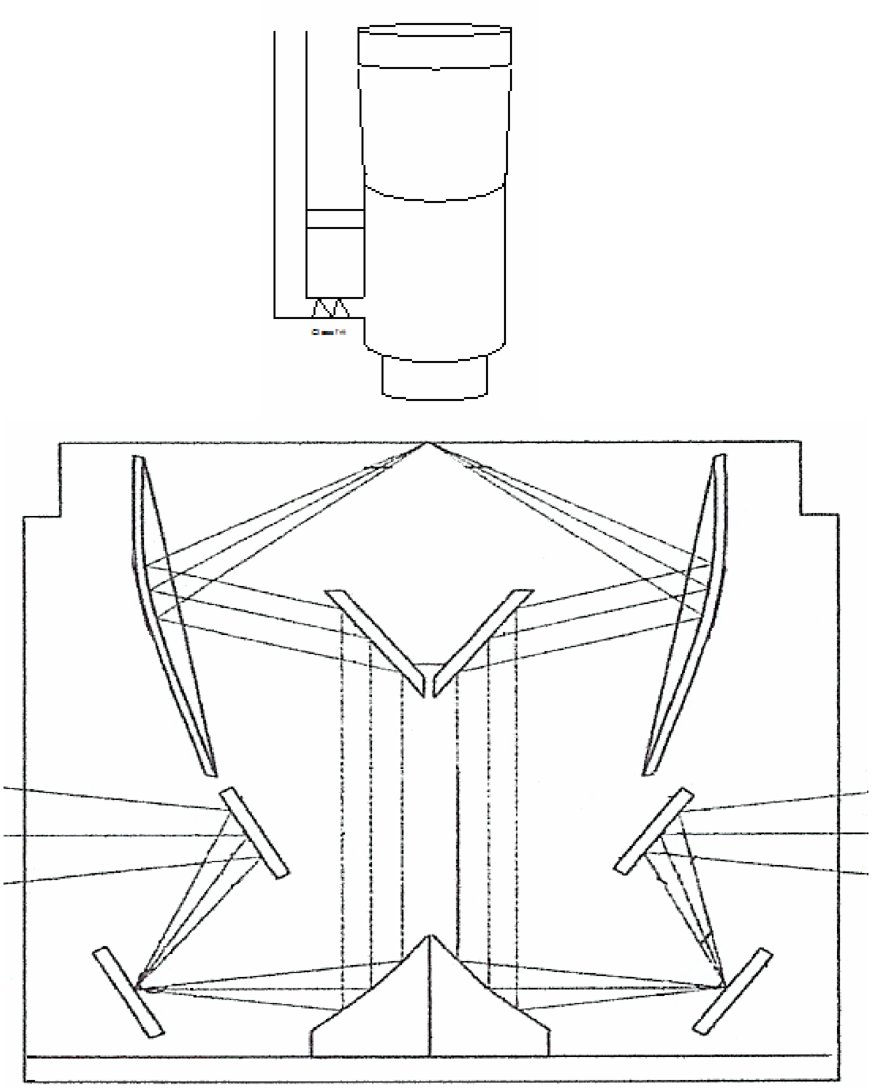


Figure 37 – Diagram of IR reflectance attachment used for detection of absorbed species on Pt working electrode

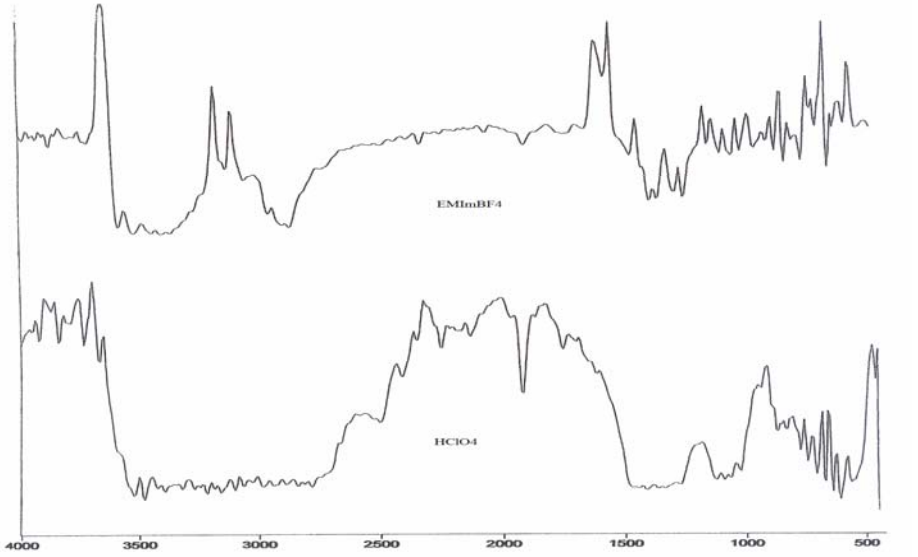


Figure 38 – Reflectance IR spectra of EtOH in EMImBF$_4$ and HClO$_4$

## REFERENCES

1. Koel, M. *Proc. Estonian Acad. Sci. Chem*. Vol. 49 No. 3, p. 145, 2000.
2. Popp, B.V. *Imidazolium and Pyrazolium Based Room Temperature Ionic Liquids*. Master Thesis, Wright State University, Dayton, OH, 2002.
3. Dancevic, A. *Synthesis and Purification of Imidazolium and Pyrazolium Based Ionic Liquids and their Application in Electrochemistry,* Master Thesis, Wright State University, Dayton, OH, 2002.
4. Rightmire, R.A., Rowland, R.L., Boos, D.L., and Beals, D.L. *J. Electrochem.* Soc., Vol. 111, No 2, February 1964.
5. Feldberg, S.W., Thesis, Princeton University, 1961.
6. Laitinen, H.A., Enke, C.G. *J.Electro Chem. Soc.* J. Vol. 107, p. 779, 1960.
7. Breiter, M.W. *J. Electro Chem. Soc.* Vol. 109, p. 42, 1961.
8. Feldberg, S.W., Enke, C.G., Bricker, E.E. Society Meeting, Los Angeles, May 7-10, 1962.
9. Knorr, C.A. WADC Technical Report 59-687, Wright Air Development Division, April, 1960.
10. Adams, R.N. *Electrochemistry at Solid Electrodes*. Marcel Dekker, Inc., NewYork, 1969.
11. Matheson, L.A., Nichols, N. *Trans. Electrochem. Soc*. Vol. 73, p. 193, 1938.
12. Randles, J.E.B. *Trans. Faraday. Soc*. Vol. 73, p.193, 1948.
13. Sevcik, A. *Coll. Czech. Chem. Commun*. Vol. 13, p.349, 1948.
14. Beden, B., Morin, M.C., Hahn, F., Lamy, C. *J. Electroanal. Chem*., Vol. 229, p. 353, 1987.
15. Chang, S., Leung, L., Weaver, M. *J. Phys. Chem.*, Vol. 94, p. 6013, 1990.
16. Schmiemann, U., Muller, M., Baltruschat, H. *Electrochimica Acta*, Vol. 40, No. 1, p. 99, 1995.