Electrochemical Window of 1-Butyl-3-Methylimidazolium Hexafluorophosphate

by

Muhd Azimey Bin Mamat

Dissertation submitted in partial fulfillment of
the requirements for the
Bachelor of Engineering (Hons)
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Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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Approved by,

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(Assoc. Prof. Dr M Azmi Bustam)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
July 2010

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

MUHD AZIMEY BIN MAMAT

ABSTRACT

Room-Temperature Ionic Liquids, RTILs are liquids that compose entirely of ions and exist in the liquid state at room temperature. 1-Butyl-3-Methylimidazolium Hexafluorophosphate, ($C_8H_{15}N_2F_6P$) or BMIM-PF_6 is one of RTILs which is used in a wide variety of applications due to its attractive physical–chemical properties such as having wide electrochemical window value. The electrochemical window of an ionic liquid is the voltage range between which the substance doesn't get oxidized or reduced. This range is important for the efficiency of an electrode. Out of this range water gets electrolyzed, spoiling the electrical energy that is intended for another electrochemical reaction. The objective of this project is to determine the electrochemical window of ionic liquid that is 1-Butyl-3-Methylimidazolium Hexafluorophosphate. The electrochemical window is measured by the reduction of the cation and the oxidation of the anion. The electrochemical window value can be obtained by running linear sweep voltammetry experiment. The electrochemical window value obtained from the experiment is about 2.3 V.

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TABLE OF CONTENTS

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Room-Temperature Ionic Liquids, RTILs are composed entirely of ions and exist in the liquid state at room temperature. RTILs as a class typically contain a bulky organic cation that is weakly coordinated to an organic or inorganic anion. Weak coordination results in a reduction in the lattice energies and crystalline structure of the salt and, hence, lowers the melting point.

RTILs possess a variety of properties that make them desirable as solvents for investigation of electrochemical processes. They often have wide electrochemical potential windows, they have reasonably good electrical conductivity and solvent transport properties, they have wide liquid ranges, and they are able to solvate a wide variety of inorganic, organic, and organometallic species.

The presence of an abundance of charge carriers means that when RTILs are used as solvents no supporting electrolyte is required for electrochemical experiments, and this minimizes waste.

One would expect that intrinsic conductivity would allow faster mass transport of the analyte to the electrode surface, but the high viscosity of RTILs results in conductivities approximately similar to traditional organic solvents with added supporting electrolyte.

The reduction and oxidation of the cations and anions accounts for the wide electrochemical window so that a window of 5 to 6 V or more is not unusual for an ionic liquid.

The ability to vary the nature of the cation and the anion allows one to tune the solvents for a specific purpose and has given them the name “designer solvents”.

This paper is concerned with the use of RTILs for electrochemistry. RTILs have been used in many electrochemical applications such as solar cells, electrochemical sensors, fuel cells, capacitors and in lithium batteries and are employed as solvents in electrochemical experiments.

Recently, electrodes modified with ionic liquids have been studied. It has been shown that it is possible to use ionic liquid formation on the electrode surface to form a liquid-liquid interface with an aqueous phase as an electroanlaytical tool for quantitative anion detection and could possibly replace previously used volatile organic solvents.

The low volatility and high thermal stability of RTILs is also advantageous for gas detection and the development of robust gas sensors. A gas sensor lifetime is determined by how quickly the electrolyte dries up, and most conventional electrolytes dry up quickly and thus cannot survive drastic temperature changes. Ionic liquids can sustain high temperature and pressure changes and remain physically and chemically unchanged.

1-Butyl-3-Methylimidazolium Hexafluorophosphate, $C_8H_{15}N_2F_6P$ or BMIM-PF_6 is an example of RTILs, which is used in a wide variety of applications due to its attractive physical–chemical properties. These properties include viscous, colourless, hydrophobic, non-water soluble ionic liquid and has wide electrochemical window. It is one of the most widely studied ionic liquids and is commercially available from most of the major international suppliers of chemicals. It is known to very slowly decompose in the presence of water. As a result, RTILs have found important applications in research fields like synthetic chemistry, catalytic processes, electrochemistry, and material science.

1.2 PROBLEM STATEMENT

The electrochemical window of an ionic liquid is the voltage range between which the substance doesn't get oxidized or reduced. An electrochemical window of ionic liquid is measured by the reduction of the cation and the oxidation of the anion. 1-Butyl-3-Methylimidazolium Hexafluorophosphate is one of the Room-Temperature Ionic Liquids, RTILs that has been reported to have wide electrochemical window. In this final year project we would like to know how to determine electrochemical window of an ionic liquid? What are the significant after knowing its electrochemical windows?

1.3 OBJECTIVE

The objective of this project is to determine the electrochemical window of ionic liquid. The ionic liquid being studied is 1-Butyl-3-Methylimidazolium Hexafluorophosphate.

1.3 SCOPE OF STUDY

This project focuses on electrochemical properties of 1-Butyl-3-Methylimidazolium Hexafluorophosphate. The electrochemical window value can be obtained by running linear sweep voltammetry experiment.

CHAPTER 2

LITERATURE REVIEW

The early history of ionic liquid research is dominated by their application as electrochemical solvents. F. H. Hurley and T. P. Wier (1951) stated that one of the first recognized uses of ionic liquids is as a solvent system for the room-temperature electrodeposition of aluminium. In addition, much of the initial development of ionic liquids was focused on their use as electrolytes for battery and capacitor applications. Electrochemical studies in the ionic liquids have until recently been dominated by work in the room-temperature haloaluminate molten salts. This work has been extensively reviewed by H. L. Chum and R. A. Osteryoung (1981). Development of non-haloaluminate ionic liquids over the past ten years has resulted in an explosion of research in these systems. However, recent reviews by T. Welton (1999) have provided only a cursory look at the application of these “new” ionic liquids as electrochemical solvents.

A. Fry and W. E. Britton (1984) state that a key criterion for selection of a solvent for electrochemical studies is the electrochemical stability of the solvent. This is most clearly manifested by the range of voltages over which the solvent is electrochemically inert. This useful electrochemical potential “window” depends on the oxidative and reductive stability of the solvent. In the case of ionic liquids, the potential window depends primarily on the resistance of the cation to reduction and the resistance of the anion to oxidation. (A notable exception to this is in the acidic chloroaluminate ionic liquids, where the reduction of the heptachloroaluminate species $[A_{l2}C_{l7}]^-$ is the limiting cathodic process). In addition, the presence of impurities can play an important role in limiting the potential windows of ionic liquids.

P. C. Trulove and R. A. Mantz (2002) state that the most common method used for determining the potential window of an ionic liquid is cyclic voltammetry (or its digital analogue, cyclic staircase 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 ionic liquid, respectively. The oxidative and reductive potential limits are assigned when the background current reaches a threshold value. The electrochemical potential window is the difference between these anodic and cathodic potential limits. Since the choice of the threshold currents is somewhat subjective, the potential limits and corresponding electrochemical window have a significant uncertainty associated with them. Normally this is in the range of ± 0.2 V.

K. R. Seddon, A. Stark and M. J. Torres (2000) state that 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 of the non-haloaluminate ionic liquids, residual halide 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 ionic liquids. Consequently, the observed anodic potential limit can be appreciably reduced if significant concentrations of halide ions are present. Contamination of an ionic liquid with significant amounts of water can affect both the anodic and the cathodic potential limits, as water can be both reduced and oxidized in the potential limits of many ionic liquids.

Recent work by U. Schroder, J. D. Wadhawan, R. G. Compton, F. Marken, P. A. Z. Suarez, C. S. Consorti, R. F. de Souza and J. Dupont (2000) demonstrate considerable reduction in both the anodic and cathodic limits of several ionic liquids upon the addition of 3 % water by weight. For example, the electrochemical window of ‘dry’ $[BMIM][BF_4]$ was found to be 4.10 V, while that for the ionic liquid with 3 % water by weight was reduced to 1.95 V.

In addition to its electrochemistry, water can react with the ionic liquid components (especially anions) to produce products that are electroactive in the electrochemical potential window. This has been well documented by C. L. Hussey (1983) in the chloroaluminate ionic liquids, in which water will react to produce electroactive proton-containing species (e.g., HCl and $[\mathrm{HC}_{\mathrm{l2}}]^{-}$).

In addition, water appears to react with some of the anions commonly used in the nonhaloaluminate ionic liquids. A. E. Visser, R. P. Swatloski, W. M. Reichert, S. T. Griffin and R. D. Rogers (2000) show in their work that the $[\mathrm{PF}_6]^{-}$ anion, for example, is known to react with water to form HF.

Glassy carbon (GC), platinum (Pt), and tungsten (W) are the most common working electrodes used to evaluate electrochemical windows in 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. For example, R. T. Carlin and T. Sullivan (1992) in their work show that W gives a 0.1 to 0.2 V greater oxidative limit for $[\mathrm{EMIM}]\mathrm{Cl/AlC}_{\mathrm{l3}}$ ionic liquids than Pt, due to a greater overpotential for the oxidation of the chloroaluminate anions. In addition, GC and to a lesser extent W exhibits a large overpotential for proton reduction. Under normal circumstances, the electrochemistry of protonic impurities (i.e., water) will not be observed in the ionic liquid electrochemical window with GC. Pt, on the other hand, exhibits good electrochemical behavior for proton. Consequently, protonic impurities will give rise to a reduction wave(s) at Pt positive of the cathodic potential limit. Interestingly, comparison of the background electrochemical behavior of an ionic liquid at both Pt and GC working electrodes can be an excellent qualitative tool for determining if significant amounts of protonic impurities are present.

S. Zhang (2006) reports that wide electrochemical window makes ionic liquid as a promising electrolyte for electrochemical power applications. Most ionic liquids have a wide electrochemical window above 4 V. It has been found for some ionic liquids the potential of anode limit proportionally decreases with increasing highest occupied molecular orbit energy calculated for the anion.

S. Zhang (2006) also reports that ionic liquids, ionic liquids as green solvents, have been studied extensively. They have tempting properties such as negligible vapor pressure, large liquidus range, high thermal stability, high ionic conductivity, large electrochemical window, and ability to solvate compounds of widely varying polarity. Utilizing ionic liquids is one of the goals of green chemistry because they create a cleaner and more sustainable chemistry and are receiving increasing interest as environmental friendly solvents for many synthetic and catalytic processes. An intriguing characteristic is to fine tune the physical-chemical properties by suitable choice of cations and anions. Therefore, ionic liquids have been recognized as “designer-solvents.”

J. S. Wilkes (2002) define in his study that ionic liquids may be viewed as a new and remarkable class of solvents, or as a type of materials that have a long and useful history. In fact, ionic liquids are both, depending on your point of view. It is absolutely clear though, that whatever “ionic liquids” are, there has been an explosion of interest in them. Entries in Chemical Abstracts for the term “ionic liquids” were steady at about twenty per year through 1995, but had grown to over 300 in 2001. The increased interest is clearly due to the realization that these materials, formerly used for specialized electrochemical applications, may have greater utility as reaction solvents.

J. S. Wilkes (2002) also states that there are many synonyms used for ionic liquids, which can complicate a literature search. “Molten salts” is the most common and most broadly applied term for ionic compounds in the liquid state. Unfortunately, the term “ionic liquid” was also used to mean “molten salt” long before there was much literature on low-melting salts. It may seem that the difference between ionic liquids and molten salts is just a matter of degree (literally); however the practical differences are sufficient to justify a separately identified niche for the salts that are liquid around room temperature. That is, in practice the ionic liquids may usually be handled like ordinary solvents. There are also some fundamental features of ionic liquids, such as strong ion–ion interactions that are not often seen in higher-temperature molten salts.

John S. Wilkes (2002) suggests that for purposes of discussion in this volume we will define ionic liquids as salts with a melting temperature below the boiling point of water. That is an arbitrary definition based on temperature, and says little about the composition of the materials themselves, except that they are completely ionic. In reality, most ionic liquids in the literature that meet our present definition are also liquids at room temperature. The melting temperature of many ionic liquids can be problematic, since they are notorious glass-forming materials. It is a common experience to work with a new ionic liquid for weeks or months to find one day that it has crystallized unexpectedly. The essential feature that ionic liquids possess is one shared with traditional molten salts: a very wide liquidus range. The liquidus range is the span of temperatures between the melting point and boiling point. No molecular solvent, except perhaps some liquid polymers, can match the liquidus range of ionic liquids or molten salts. Ionic liquids differ from molten salts in just where the liquidus range is in the scale of temperature.

In Journal of Chemical & Engineering Data, Vol. 53, No. 12, 2008 (2885) it is reported that Room Temerature Ionic Liquids,RTILs whether they are hydrophobic or hydrophilic in nature, can absorb considerable amounts of water, which changes their physical and chemical properties. This is of particular interest where electrochemical sensing is concerned. RTILs have been particularly well documented as solvents for gas sensing for gases.The uptake of water from any source reduces the wide electrochemical windows of RTILs and can limit their use as sensing solvents. RTIL-modified electrodes at a liquid-liquid interface with aqueous solution have also been studied over the last number of years to substitute volatile organic solvents with more thermally stable RTILs. The effects of water on RTILs would be of particular interest in this field. In this work, we will show the extent of water uptake of several RTILs, as well as its effect on the electrochemical window of ionic liquids. This provides information to aid the selection of RTILs as solvents for electrochemical experiments.

CHAPTER 3

METHODOLOGY

3.1 GANTT CHART

No.	Title/Weeks	1	2	3	4	5	6	7/8	9	10	11	12	13	14	15	16	17	18	19	20
1	Project Work	🟩	🟩	🟩	🟩	🟩	🟩	MID SEMESTER BREAK	🟩	🟩	🟩	🟩	🟩	🟩						
2	Submission Progress Report 1					🟩														
3	Submission Progress Report 2										🟩									
4	Poster /Pre-EDX										🟩									
5	EDX											🟩								
6	Submission of Final Report (CD & Softbound)													🟩						
7	Final Oral Presentation																	🟩	🟩	
8	Submission of Hardbound Copies																			🟩

3.2 TOOLS REQUIRED

Instrument: A computer with installed appropriate software. The software has a provision for carrying out Linear Sweep Voltammetry, storing, overlaying and printing graphs. In this experiment we use WEIS software.

Electrodes: Working electrode: glassy carbon. Counter electrode: Pt electrode; Reference electrode: Ag/AgCl

Chemicals: 10mL 1-Butyl-3-Methylimidazolium Hexafluorophosphate

3.3 EXPERIMENTAL PROCEDURE

In order to determine electrochemical window of ionic liquid, linear sweep voltammetry experiment has been carried out. Voltammetric measurements are carried out using an electrochemical cell made up of three electrodes immersed in a solution containing 1-Butyl-3-Methylimidazolium Hexafluorophosphate.

One of the three electrodes is the working electrode, which is glassy carbon. The redox process occurs at this electrode. Its dimensions are kept small in order to enhance its tendency to become polarized. The second electrode is the reference electrode, which provides calibration for the applied potential. The reference electrode used in this experiment is Ag/AgCl electrode. The third electrode is the counter electrode, which is platinum wire that simply serves to conduct electricity from the signal source through the solution to the other electrodes.

The voltammetric setup is shown in Figure 1. In linear sweep voltammetry experiment, the potential of the reference electrode is varied and the current between the working and reference electrodes is measured.

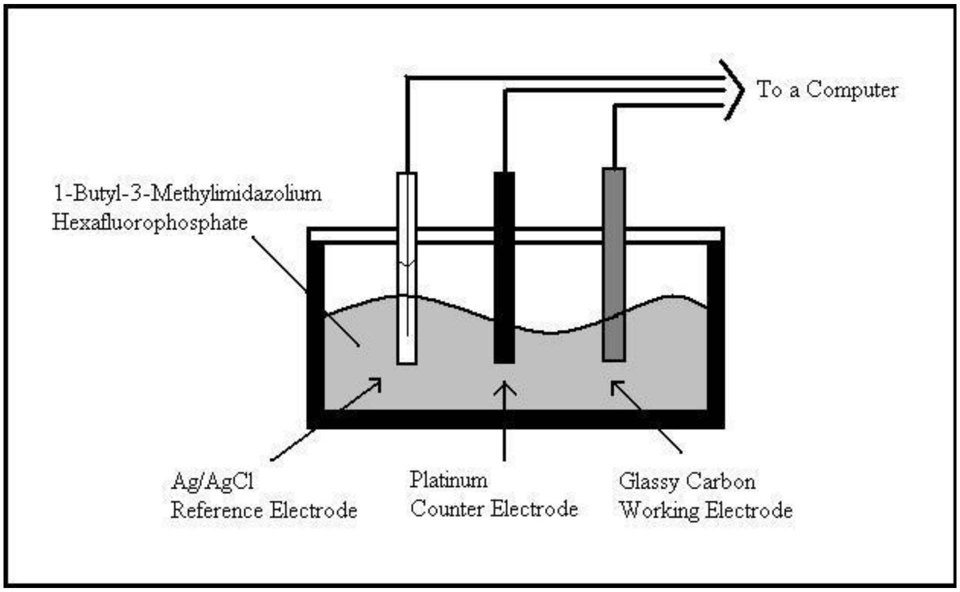
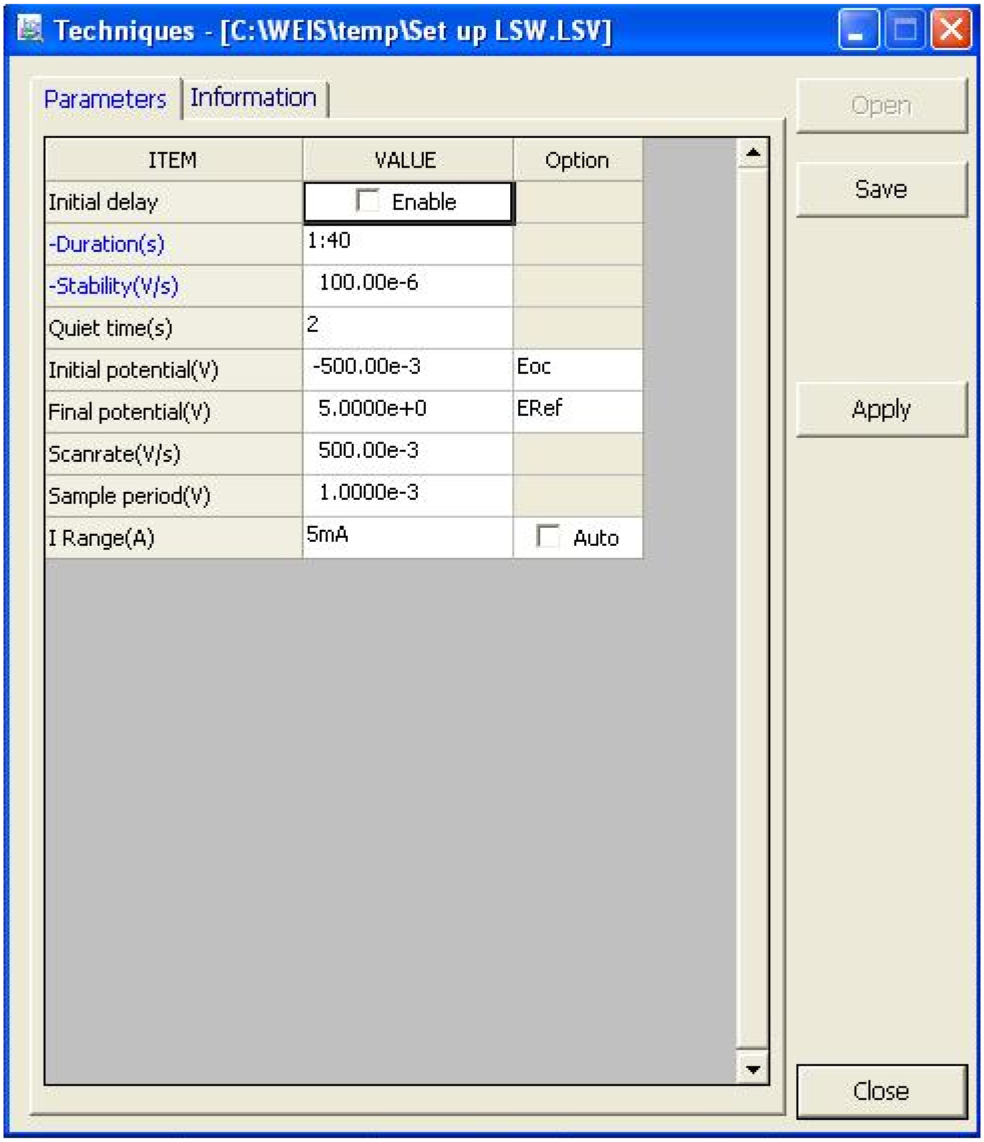


Figure 1: Experimental Setup.

3.3.1 PARAMETERS SETTING



ITEM	VALUE	Option
Initial delay	☐ Enable	
-Duration(s)	1:40	
-Stability(V/s)	100.00e-6	
Quiet time(s)	2	
Initial potential(V)	-500.00e-3	Eoc
Final potential(V)	5.0000e+0	ERef
Scanrate(V/s)	500.00e-3	
Sample period(V)	1.0000e-3	
I Range(A)	5mA	☐ Auto

Figure 2: Parameters setting for the experiment.

Figure 2 shows parameters setting for the experiment. Initial potential is set to -0.5 V and final potential is set to 5.0 V. The scan rate is set to 0.5 V/s. This means that the potential will be applied to the liquid being experimented about 0.5 V per second started from -0.5 V until 5.0 V. The current versus potential graft will be plotted.

CHAPTER 4

RESULT AND DISCUSSION

4.1 CURRENT, A Vs POTENTIAL, V

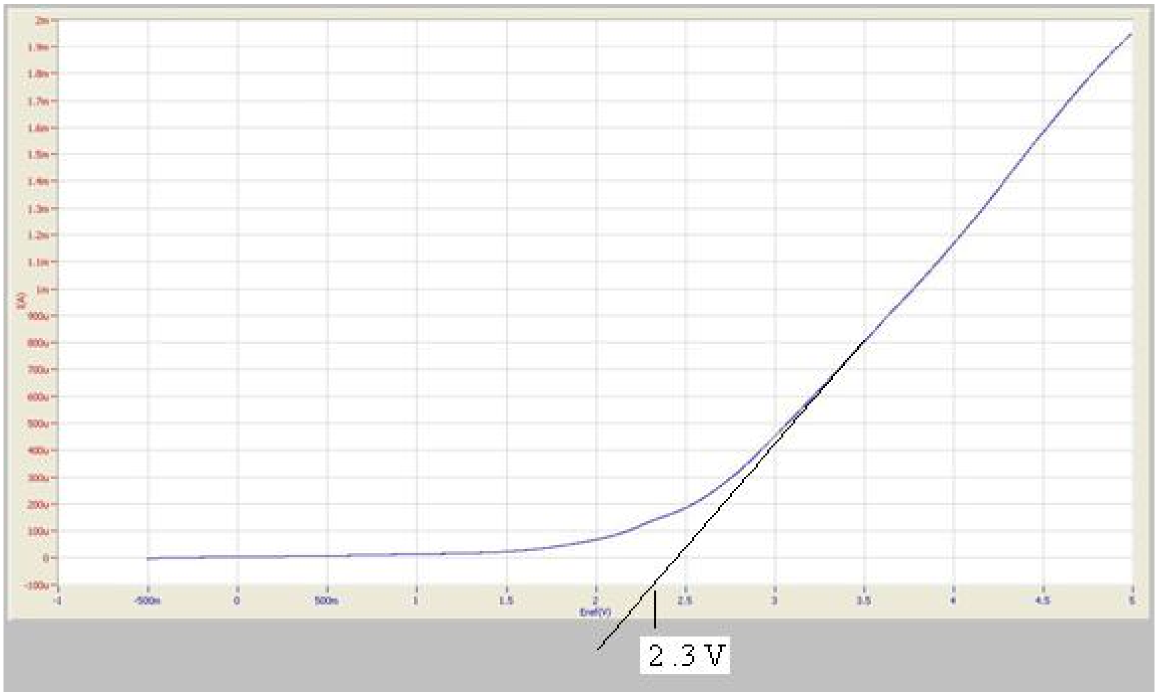


Figure 3: Current vs. Potential Graph.

Figure 3 above shows current versus graph of experiment linear sweep voltammetry of 1-Butyl-3-Methylimidazolium Hexafluorophosphate. Initial potential is scanned start from -0.5V and end at 5.0 V. The value of potential limit is about 2.3 V.

4.2 DISCUSSION

The electrochemical window of an ionic liquid is the voltage range between which the substance doesn't get oxidized or reduced. The graph shows that $BMIMPF_6$ has potential limit of 2.3 V. Above this value the current rises dramatically means that there is oxidation occur inside the ionic liquid. This means $BMIMPF_6$ is still stable and does not get oxidized if we apply potential below this value.

According to literature review of recent work by U. Schroder, J. D. Wadhawan, R. G. Compton, F. Marken, P. A. Z. Suarez, C. S. Consorti, R. F. de Souza and J. Dupont (2000) demonstrate considerable reduction in both the anodic and cathodic limits of several ionic liquids upon the addition of 3 % water by weight. For example, the electrochemical window of 'dry' $[BMIM][BF_4]$ was found to be 4.10 V, while that for the ionic liquid with 3 % water by weight was reduced to 1.95 V. In addition to its electrochemistry, water can react with the ionic liquid components (especially anions) to produce products that are electroactive in the electrochemical potential window.

The recent work by P. C. Trulove and R. A. Mantz in the book of ionic liquid in synthesis (2002) shows that $BMIMPF_6$ has potential limit of 4.2 V. Therefore the potential limit that we obtain in this experiment may be affected by impurities (water content) inside the ionic liquid.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

Electrochemical windows of 1-Butyl-3-Methylimidazolium Hexafluorophosphate can be determined by using linear sweep voltammetry. The proposed working electrode to be used is glassy carbon and the counter electrode is Platinum, Pt electrode while the reference electrode suggested to be used is Ag/AgCl wire. The 1-Butyl-3-Methylimidazolium Hexafluorophosphate can be obtained in UTP laboratory or directly purchased front chemical shop. Safety cautions must be considered while handling this material because it is classified as harmful and corrosive material.

According to literatures, electrochemical window of ionic liquid can be varied by other factors such as impurities. So it is recommended to investigate further about the factors that can influence the electrochemical value of ionic liquid. Furthermore the value we obtain above is not exact value which means the value we got may be influenced by impurities.

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