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Electrosynthesis of hydrogen peroxide in room temperature ionic liquids and *in situ* epoxidation of alkenes

A Thesis

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in

Partial Fulfilment of the Requirements

for

the Degree of Master of Philosophy

at

The Hong Kong Polytechnic University

by

Michael Chi Yung TANG

May, 2005

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Declaration

I hereby declare that the thesis summarizes my own work carried out since my registration for the Degree of Master of Philosophy in September, 2003, and that it has not been previously included in a thesis, dissertation or report submitted to this or any other institution for a degree, diploma or other qualification.

Michael Chi Yung TANG

May, 2005

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Abstract

Hydrogen peroxide is advocated as green oxidant and widely applied on academic and industrial applications since it only leaves oxygen and water in the reaction stream after reaction. Industrial production (AQ process) and *in situ* electrogeneration of hydrogen peroxide is the major production route of hydrogen peroxide. The former requires huge amount of organic solvents, metal catalysts and energy input to produce highly concentrated hydrogen peroxide. The latter only needs oxygen, carbon cathode and electricity in aqueous media to give diluted hydrogen peroxide by electroreduction of oxygen. Nevertheless, the electrogeneration of hydrogen peroxide in aqueous media limits its applications in organic synthesis because of the immiscibility between aqueous medium and the organic compounds. Recently, ionic liquids are considered as clean solvents as they are non-volatile, easily recycled and able to dissolve compounds with different polarities. In addition, they have been explored in electrochemistry because they usually possess a wide electrochemical window. We believed that the ionic liquids can act as promising and effective electrolyte for the electrosynthesis of hydrogen peroxide from oxygen electroreduction when compared with the aqueous electrolytes (Chapter 2). Based on the unique properties of ionic liquids, the usefulness of the electrogenerated hydrogen peroxide in the ionic liquids can be enhanced because it can be applied in organic oxidation. In Chapter 3, a simple epoxidation system was developed to epoxidize electrophlic alkenes with electrogenerated hydrogen peroxide in the ionic liquid-water mixtures. The ionic liquid itself can be easily recovered and re-used.

The work presented in this thesis aims to develop a simple, environmentally friendly and effective method to electrochemically generate hydrogen peroxide in the recyclable ionic liquids and subsequently *in situ* to epoxidise alkenes.

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Chapter 1 Introduction

1.1 Hydrogen Peroxide

Hydrogen peroxide is a strong oxidizing agent. It exists as a clear, colourless, and odorless liquid in room temperature. It is completely miscible with water and soluble in a range of organic solvent, such as carboxylic esters, when it is highly concentrated aqueous solution (> 65 wt%). It is a slightly stronger acid than water. The dissociation constant (pKa) of hydrogen peroxide is 11.62 at 25°C [1] (Equation 1.1).

$$\mathbf{H_2O_2 \rightleftharpoons H^+ + HOO^-}$$

Equation 1.1 *The dissociation constant of hydrogen peroxide at 25°C is 11.62*

The first discovered and industrial manufacture of hydrogen peroxide can be traced back to 1818 by L.J.Thenard [2]. Thenard reacted barium peroxide with nitric acid to produce a very diluted aqueous hydrogen peroxide (Equation 1.2); however, this process had limitation due to high production costs, low hydrogen peroxide content and high levels of impurities present in the isolated hydrogen peroxide. This made the stability of hydrogen peroxide was poor. The barium peroxide process was continuously improved until 1901.

$$\mathbf{BaO_2 + 2HCl \longrightarrow BaCl_2 + H_2O_2}$$

Equation 1.2 *Thernard's route to the production of aqueous hydrogen peroxide*

Manchot made a significant breakthrough in 1901 in the industrial production of hydrogen peroxide. He made use of autoxidizable compounds like hydroquinones or hydrazobenzenes to react quantitatively under alkaline conditions with oxygen to form peroxides [3]. Subsequently, further development of the process by Pfleiderer using alkaline autoxidation of hydrazobenzenes in which sodium peroxide was obtained, and sodium amalgam was used to reduce the azobenzene. Based on the work done and improvement by Pfleiderer, the anthroquinone process (so-called AQ process) was emerged between 1935 and 1945, with a monthly production from 30 metric tones to 2000 metric tones per annum. Until 1996, industrial production of hydrogen peroxide by anthroquinone process was continuously increasing to 1.3 x 10^6 metric tones 100% concentrated hydrogen peroxide.

The anthraquinone process is shown in Figure 1.1 which involves the hydrogenation of a 2-alkyl-9,10-anthraquinone with hydrogen to the hydroquinone and oxidation of the hydroquinone with oxygen back to 2-alkyl-9,10-anthraquinone in order to regenerate hydrogen peroxide.

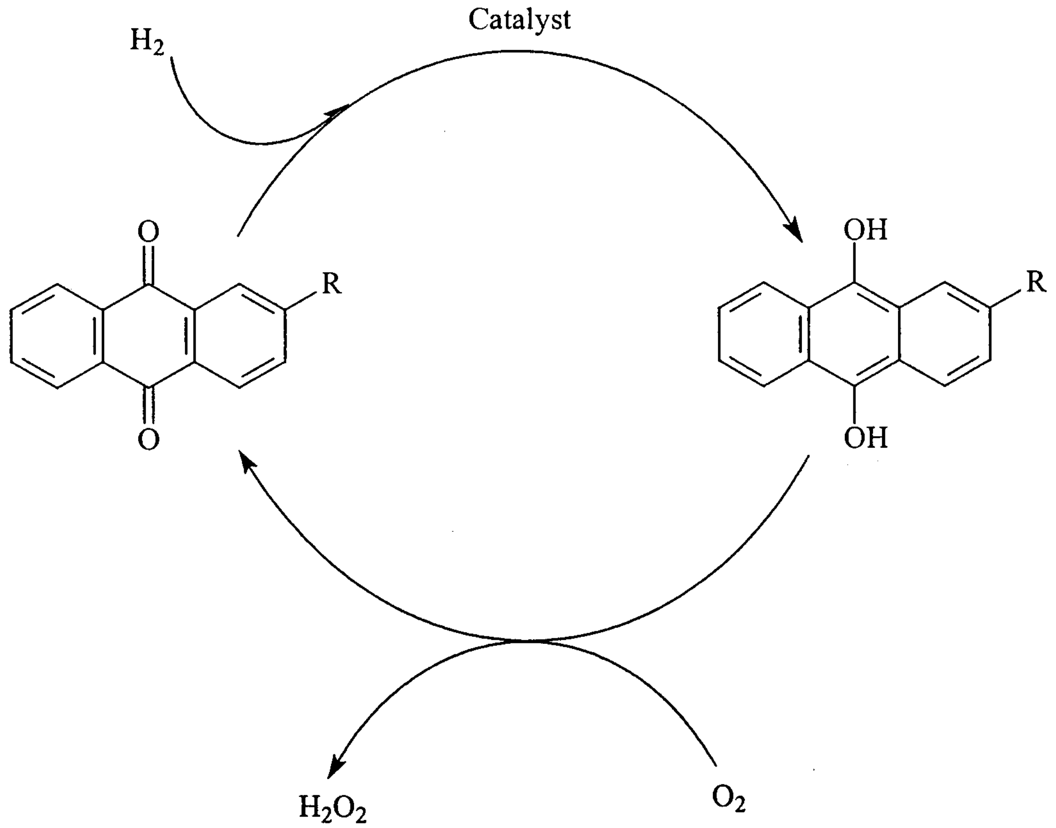


Figure 1.1 Anthrahyroquinone process for the industrial manufacture of hydrogen peroxide

Hydrogen peroxide has drawn increased attention on its applications in past decades. The use of hydrogen peroxide has become an attractive option based on the environmental and economic grounds. It has recently been recognized as an environmentally friendly oxidant since it is relatively less toxic, readily available and cheap when compared with traditional organic oxidizing agents such as, *tert*-butyl hydroperoxide and *tert*-butyl cyclohexenyl peroxide. The most significant advantage of hydrogen peroxide is that it leaves no hazardous residues in reaction stream, only with oxygen and water as by-products after reaction. Therefore, the increased use of this green oxidant, hydrogen peroxide, in pulp bleaching[4], chemical synthesis [3, 5, 6] and aqueous effluent treatment [7, 8] are well documented. It is believed that the world demand for hydrogen peroxide is expected to grow 10% per annum. The global hydrogen peroxide demand by applications for the year 1995 was shown in Figure 1.2 [4].

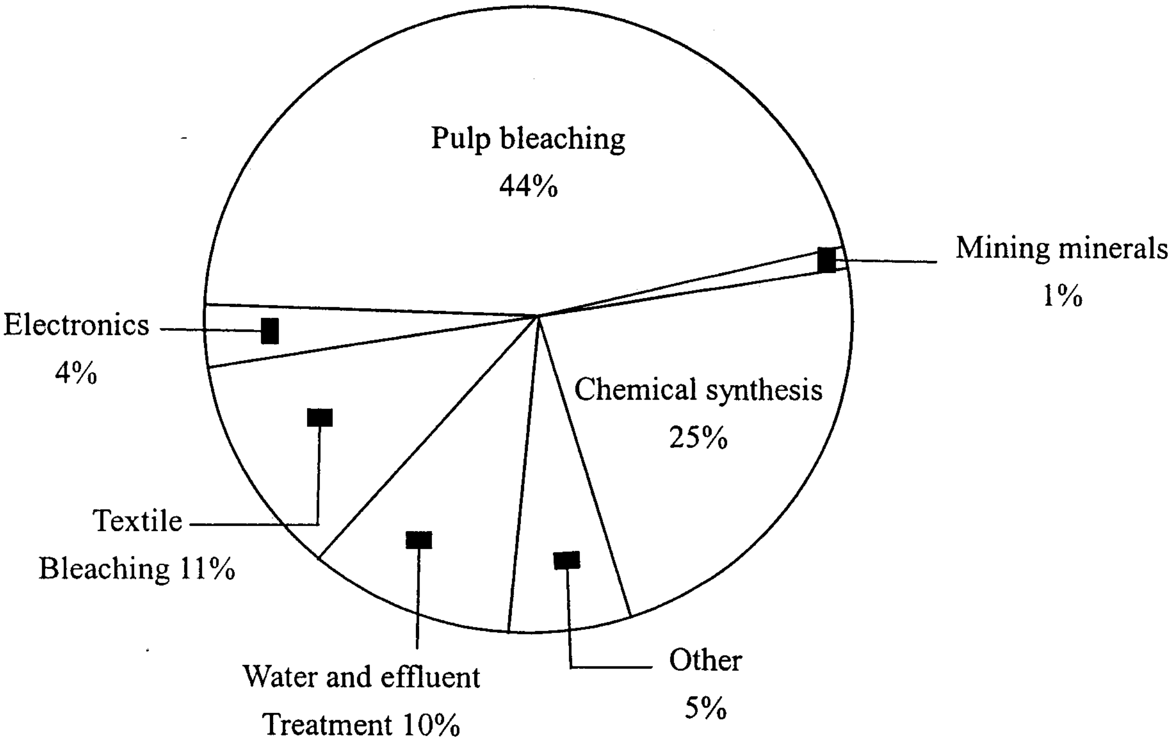


***Figure 1.2** Global hydrogen peroxide demand by applications*
(1995, total = 1.2×10^6 metric tones)

Nevertheless, hydrogen peroxide produced from the anthraquinone process employs large scale use of non-aqueous organic solvents, consumption of alkylated anthraquinones and catalysts and requires significant energy input. Furthermore, because of the potential hazards of neat or highly concentrated aqueous hydrogen peroxide (50 ~ 70 wt %), it is generally used as a 30 wt % aqueous solution, which adds to high transportation and storage costs. The AQ process is unsuited for small-scale or on-site production of hydrogen peroxide. For these reasons, methods for the alternative production of hydrogen peroxide are being actively explored [9, 10]. Interest has recently focused on the manufacture of hydrogen peroxide by the electrochemical method, using cathodic reduction of oxygen (Equation 1.3). The process requires only oxygen and electricity as feedstock. The on-site electrogeneration of hydrogen peroxide usually produces as a dilute aqueous solution (10mM ~100mM) which greatly reduces the safety hazards associated with hydrogen peroxide.

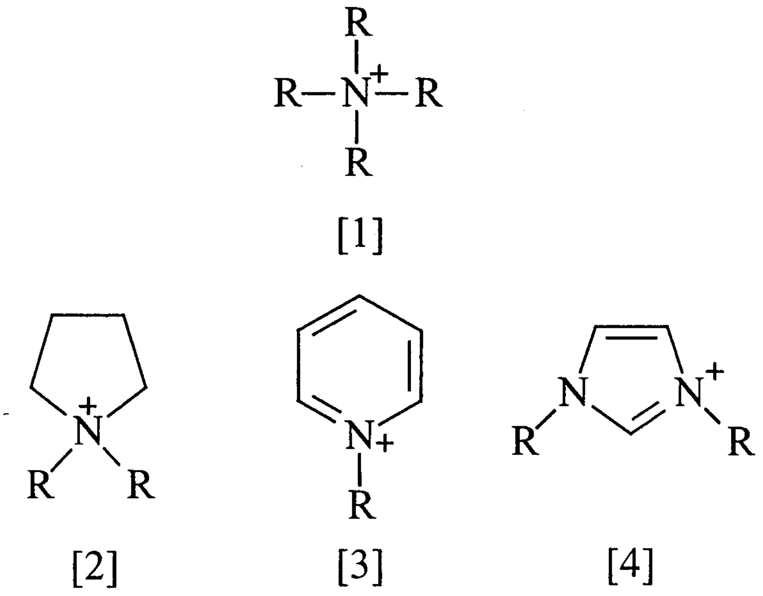
$$\mathbf{O_2 + 2H_2O + 2e^- \longrightarrow H_2O_2 + 2OH^-}$$

Equation 1.3 *Cathodic reduction of oxygen to hydrogen peroxide*

Electrosynthesis of hydrogen peroxide has an extensive history [10]; the hydrogen peroxide which is usually generated in acidic (e.g. H_2SO_4) or alkaline (e.g. NaOH and Na_2CO_3) aqueous solutions has been widely applied in various aspects, such as organic degradation [11, 12], chemical electrosynthesis [13, 14], and removal of low level organics in effluent treatment [15, 16]. It is apparent that electrogenerated hydrogen peroxide plays an important role for chemical synthesis and effluent treatment. Nevertheless, the hydrogen peroxide produced is not highly concentrated in the aqueous media because of the low oxygen solubility in aqueous solution. This diminishes the application of electrochemically generate hydrogen peroxide in aqueous media.

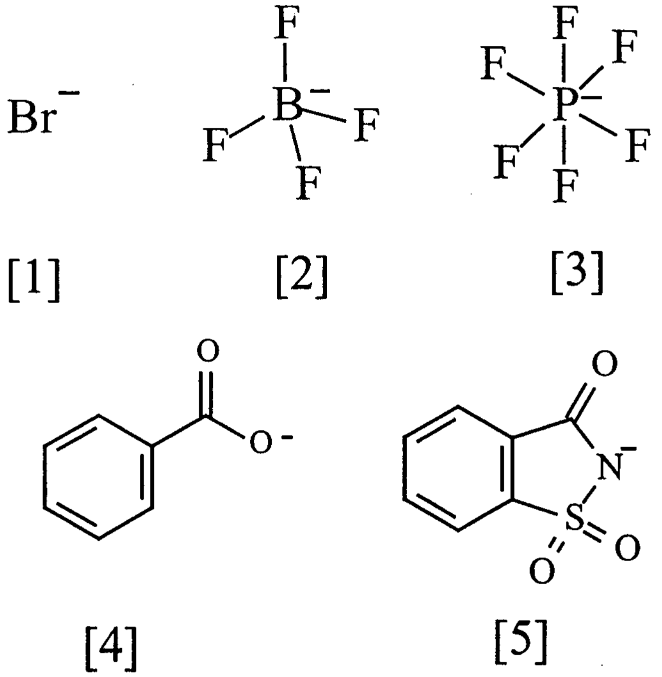
1.2 Ionic Liquids

Room temperature ionic liquids are molten salts that exist in liquid form at and below room temperature, and they are regarded as useful solvents in chemical synthesis. The first report on the preparation of ionic liquids dated back to 1914, where ethylammonium nitrate was synthesized [17]. They have been identified as one of the new classes of neoteric and environmentally friendly solvents that offer opportunities to bring the traditional chemical processes to novel and clean platform. Ionic liquids typically composed of a cation and an anion. The most common ionic liquids of cations are tetraalkylammonium, N,N'-dialkypyrrolidinium, N-alkylpyridinium, and N,N'-dialkylimidazolium (Figure 1.3). The corresponding counterion can be inorganic or organic anions, for example, bromide, tetrafluoroborate, hexafluorophosphate, benzoate and saccharinate (Figure 1.4).



[1] [2] [3] [4]

Figure 1.3 *Tetraalkyammonium [1], N,N-dialkypyrrolidinium [2], N-alkypyridinium [3], and N,N'-dialkylimidazolium [4] cations*



[1] [2] [3] [4] [5]

Figure 1.4 *Bromide [1], tetrafluoroborate[2], hexafluorophosphate [3], benzoate [4], saccharinate [5] anions*

Over the past few years, there has been a dramatic increase in the number of publications in the field of ionic liquids. In 2004 alone, more than 450 publications related to ionic liquids have been released (Figure 1.5). The increasing trend of the publications indicates the importance and attractiveness of ionic liquids in chemistry.

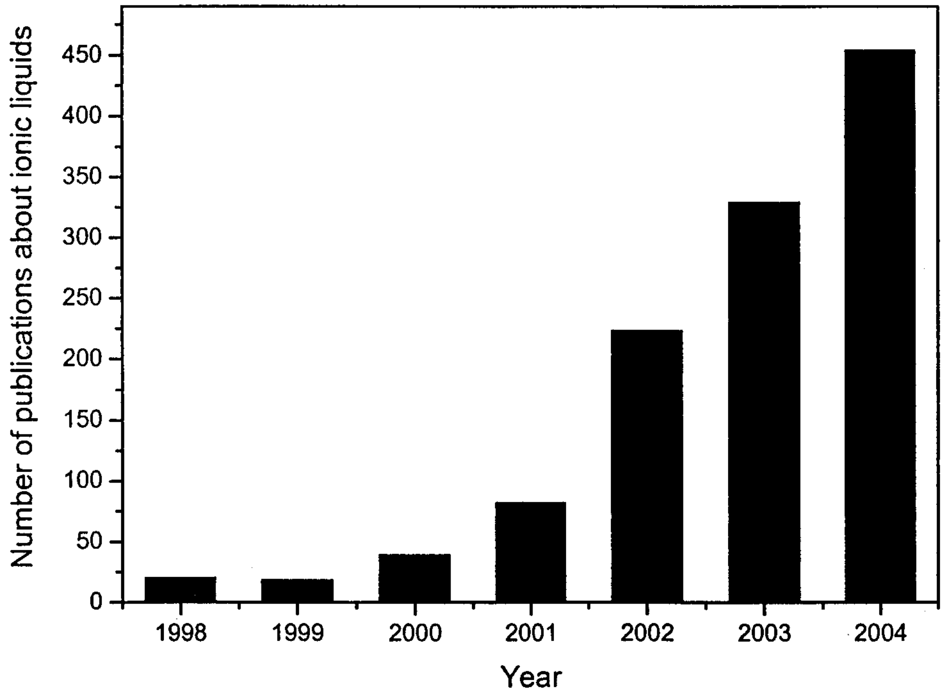


Figure 1.5 A bar chart showing the number of research papers published involving ionic liquids, complied using SciFinder Scholar 2004

Ionic liquids are recognized as potential green solvents or media for chemical reactions, especially in organic synthesis. They offer numerous advantages over conventional organic solvents for carrying out organic reactions, such as, product recovery is easier, catalysts can be recycled, and the ionic liquids can be reused. Some of the classical organic reactions have already been successfully carried out in these ionic liquids. These include Diels-Alder [18], alkylation of aldehydes [19], Suzuki coupling reaction [20], allylation of carbonyl compounds[21], and epoxidation [22]. The interest is mainly due to their peculiar properties [17, 23, 24], such as thermal stability, high loading capacity, negligible vapour pressure, recyclable, air and moisture resistant and a wide electrochemical window. Based upon their unique properties, ionic liquids have been advocated as green solvents and as an alternative recyclable and environmentally benign reaction media to replace traditional volatile molecular solvents.

1.3 Electrosynthesis of Hydrogen Peroxide in Ionic Liquids

Even though it is generally recognized that ionic liquids have a high intrinsic conductivity, thermally stable, and wide electrochemical window [25]. Electrochemical window depends on the oxidative and reductive stability of the solvent. For ionic liquids, the potential window depends primarily on the resistance of the cation to reduction and the resistance of the anion to oxidation. Table 1.1 illustrated the electrochemical window of some common ionic liquids [23].

Table 1.1 *The room-temperature electrochemical window for common ionic liquids*

Ionic Liquid	Working electrode	Window (V)
1-butyl-3-methylimidiazolium tetrafluoroborate	Platinum	4.1
1-butyl-3-methylimidiazolium hexafluorophosphate	Platinum	4.2
1-ethyl-3-methylimidiazolium trifluoromethansulfonate	Platinum	4.1
1-buyt-1-methyl-pyrrolidinium bis(trifluoromethansulfon)imide	Glassy carbon	5.5
N-butylpyridinium tetrafluoroborate	Platinum	3.4

Electrochemical applications of ionic liquids to organic synthesis have not been extensively explored. Some recent examples include cycloaddition of carbon dioxide to epoxide [26], dimerisation of PhBr and $PhCH_2Br$ [27], reduction of dimethyl maleate and benzaldehyde [28], and preparation of functionalized siloxanes [29].

Recently, the one electron reduction of oxygen to superoxide (Equation 1.4) in 1-butyl-3-methylimidazolium hexafluorophosphate, [bmim][PF_6] has been reported by Weidner and his co-workers [30, 31]. They shown that the generated superoxide species is stable in [bmim][PF_6] at glassy carbon electrode from the cyclic voltammoagram

$$O_2 + e^- \rightleftharpoons O_2^{\bullet -}$$

***Equation 1.4** One electron transfer reversible reaction between oxygen and superoxide*

However, the irreversibility of the oxygen and superoxide couple in [bmim][PF_6] is due to trace amount of water in [bmim][PF_6] which may act as a proton source and further react with the generated superoxide (Equation 1.5). The overall reaction of oxygen electroreduction in the presence of an excess of water is derived from Equation 1.4 and Equation 1.5 and expressed by Equation 1.6. Some studies have indicated that ionic liquids process higher gas solubility (carbon dioxide, oxygen) [23, 32] than aqueous solution. On this basis, we think that hydrogen peroxide can be generated by electroreduction of oxygen in water-containing ionic liquids with a good yield when compared with aqueous media.

$$\mathbf{O_2^{\bullet -} + H_2O + e^- \longrightarrow HOO^- + OH^-}$$

Equation 1.5 *Two electrons irreversible reaction in the presence of water*

$$\mathbf{O_2 + H_2O + 2e^- \longrightarrow HOO^- + OH^-}$$

Equation 1.6 *Two electrons oxygen reduction to generate hydroperoxide and hydroxide ion*

1.4 Epoxides

Epoxides, which are cyclic ethers with three-membered rings, are highly useful intermediates for the manufacture of a range of modern commercial products, namely epoxy resins, textiles, surface coatings, and biological chemicals [3, 33], owing to the large range of reactions they undergo (Figure 1.6). Their synthetic routes are subjects of considerable academic and industrial interest. Epoxidation of alkenes is one of the important routes which lead to the production of epoxides on both laboratory and industrial scales.

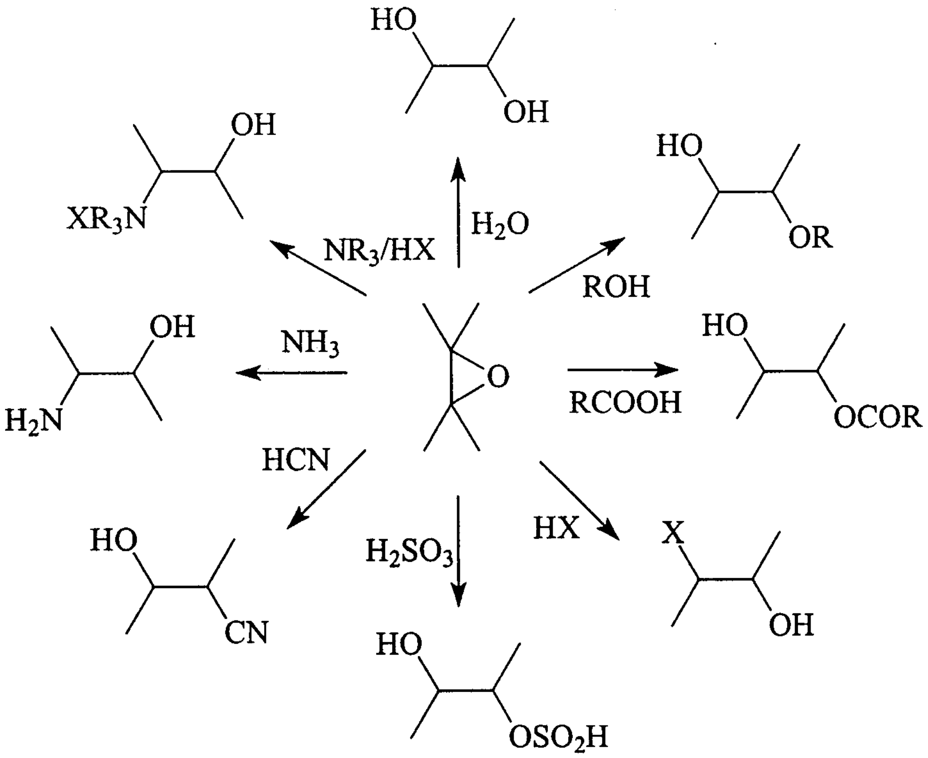


Figure 1.6 Ring opening reactions of epoxides

Recently, the conversion of alkenes into an epoxide is performed by using hydrogen peroxide in conjunction with transition metal catalysts in organic solvents. Aqueous hydrogen peroxide is possibly the best terminal oxidant from environmental and economic considerations [34]. The catalysts are usually transition metal complexes, such as molybdenum [35], methyltioxorhenium [36], silicotungstate [37] compound catalysts. However, these catalysts are often toxic and expensive. Moreover, the solvent systems are often the volatile molecular solvents, such as acetonitrile, DMF, dichloromethane, or less toxic t-BuOH. These volatile molecular solvents contribute to the volatile organic contaminants (VOC) in the environment. In this regard, there is a strong need for the development of new epoxidation methods that produce little waste, without using volatile molecular solvents. Recently, the use of the less toxic simple manganese salt with aqueous hydrogen peroxide in bicarbonate solutions has been reported to catalyse the epoxidation of a range of disubstituted alkenes with good yields [38]. However, the need to use of organic solvents (DMF and t-BuOH) in that system for hydrophobic alkenes is a major drawback for a clean epoxidation system. Thus, our research group has recently replaced the use of molecular solvent system with room temperature ionic liquid, [bmim][BF_4], a non-volatile and recyclable solvent, combined with tetramethylammonium hydrogen carbonate and aqueous hydrogen peroxide to achieve a relatively clean epoxidation system [22]. In this system, the need to use aqueous hydrogen peroxide at 30% concentration still imposes certain limitations on the reaction.

One way to circumvent the usage of commercial aqueous hydrogen peroxide for epoxidation is to use our proposed system – electrosynthesis of hydrogen peroxide in ionic liquids and *in-situ* epoxidation of alkenes.

1.5 Aim of project

From the discussion summarized in the previous sections, hydrogen peroxide is a green oxidant for a wide range of commercial applications. However, the problems of using huge amount of organic solvents, energy, and metal catalyst in the anthraquinone process (AQ process) render the hydrogen peroxide less environmentally friendly. The electrogenerated hydrogen peroxide is an attractive and green route since only oxygen and electricity are required in aqueous medium. But the aqueous medium used for the electrosynthesis of hydrogen peroxide will hinder its usefulness in organic oxidation. The immiscibility between the electrogenerated hydrogen peroxide in aqueous medium and the organic compounds in organic solvent is a great challenge in chemistry. In Section 1.2, references were made to the advantages of using ionic liquids as reaction media; especially in bringing the compounds with different polarities altogether. Investigations also showed that the stable superoxide can be electrogenerated in ionic liquids; we reasoned that hydrogen peroxide can be electrochemically generated from oxygen in water-containing ionic liquids and the hydrogen peroxide in water-containing ionic liquids can be coupled to *in situ* organic oxidation, for example, epoxidation of alkenes, without isolation or extraction of the hydrogen peroxide. After extraction and isolation of the product epoxide from the water-containing ionic liquid, the water-containing ionic liquid can be recovered and recycled for regeneration of hydrogen peroxide and epoxidation.

In our study, we will probe into the electrosynthesis of hydrogen peroxide from oxygen in ionic liquid and the *in-situ* epoxidation of alkenes in the recyclable ionic liquids (Figure 1.7).

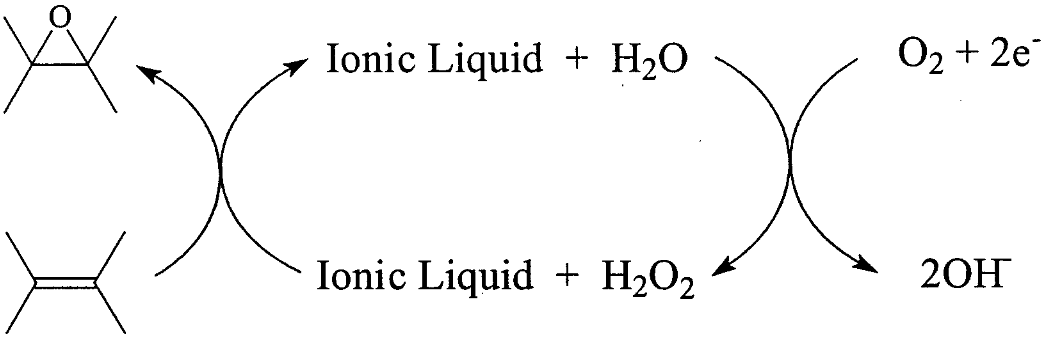


Figure 1.7 *Electrosynthesis of hydrogen peroxide in ionic liquids and in situ epoxidaiton of alkenes*

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Chapter 2 Electrosynthesis of hydrogen peroxide in room temperature ionic liquids

2.1 Introduction

The use of ionic liquids as environmentally benign solvents for a wide range of chemical processes has seen a fast growth during recent years. This is due to a number of beneficial properties of ionic liquids, such as, non-volatile, non-flammable, thermally stable, good solvating properties and good electrochemical stability [1-3]. Hydrogen peroxide is regarded as a green oxidant because it leaves no hazardous residues, only oxygen and water, after reaction. It has been widely applied in industrial processes. However, the industrial production of hydrogen peroxide (AQ process) involves the use of huge amounts of organic solvents and the consumption of alkylated anthraquinones. Furthermore, because of the potential hazards of neat hydrogen peroxide, it is generally used as a 30% aqueous solution, which adds to high transportation costs. In situ electrogeneration of hydrogen peroxide is attracting much interest because it utilizes only oxygen, water and electricity on the carbon cathode. This provides an environmental friendly and convenient way to generate hydrogen peroxide.

Recently, Weidner *et al.* demonstrated that the stable superoxide ion can be electrogenerated from oxygen in the ionic liquid, 3-butyl-1-methylimidazolium hexafluorophosphate, [bmim][PF_6] [4, 5]. It is well known that the superoxide will readily be reduced in water to give hydrogen peroxide [6, 7]. The work described in this chapter discusses our attempts to develop and optimize an electrochemical system for the generation of hydrogen peroxide in water-containing ionic liquids.

2.2 Electrochemical studies on ionic liquid

It has been demonstrated that stable superoxide ions can be generated electrochemically in ionic liquid, [bmim][PF$_6$] [4, 5], by a single electron reduction of dissolved oxygen gas (Equation 1). In the presence of proton source, such as water, the superoxide ion will undergo the second electron reduction (Equation 2) to generate hydroperoxide ion, HOO$^-$, and hydroxide ion, OH$^-$. As a result, the oxygen reduction is expected to follow a two electrons reduction pathway in ionic liquids in the presence of proton sources (Equation 3).

$$\begin{array}{lr} O_2 + e^- \rightleftharpoons O_2^{\bullet -} & [1] \\ O_2^{\bullet -} + H_2O + e^- \longrightarrow HOO^- + OH^- & [2] \\ \hline O_2 + H_2O + 2e^- \longrightarrow HOO^- + OH^- & [3] \end{array}$$

In our proposed system, the ionic liquid that is chosen for the electrosynthesis of hydrogen peroxide is [bmim][BF$_4$] instead of [bmim][PF$_6$] because [bmim][PF$_6$] undergoes hydrolysis in contact with moisture or water, forming the volatile HF [8]. In addition, the ionic liquid [bmim][BF$_4$] was known to be stable towards relatively high concentration of hydrogen peroxide [9]. Therefore, we have investigated the electrochemical characteristics of the [bmim][BF_4] in the following sections.

2.2.1 Effect of impurities on the electrochemical characteristics of [bmim][BF_4]

Generally, the presence of impurities can seriously affect the usefulness of the ionic liquids as solvents for a given chemical reaction. The presence of impurities such as halide ions, molecular solvents, and water can greatly influence the results of an electrochemical investigation. For the electroreduction of oxygen in ionic liquids, the presence of impurities, such as water and halide, can have a dramatic effect on the stability of the superoxide ion in the ionic liquids. Weidner *et al.* [5] and Ohsaka *et al.* [10] reported that only 3% impurities in [bmim][PF_6] or the presence of 2.64M of water in [emim][BF_4] can prevent the reverse reaction of oxygen to superoxide ion (Equation 1) to occur. The halide impurities, such as bromide ion and chloride ion, will generate additional anodic background signals which may interference with the electrochemical process under investigation. Durazo and co-workers also believed that the halides impurities will catalyze the disproportionation of hydrogen peroxide to molecular oxygen and water [11]. Therefore, additional purification steps of [bmim][BF_4] are necessary especially in electroreduction of oxygen to superoxide ion and electrogeneration of hydrogen peroxide

The crude [bmim][BF_4] was prepared by simple metathesis reactions from [bmim][Br] and $NaBF_4$. After filtration of the NaBr, the crude [bmim][BF_4] was dissolved in dichloromethane and filtered by silica gel and Celite. The solvent was removed *in vacuo* overnight to yield pure [bmim][BF_4]. Figure 2.1 shows the cyclic voltammograms (CVs) of [bmim][BF_4]. Reduction currents are shown as negative throughout this thesis. The crude and purified [bmim][BF_4] were saturated with argon before recording the CVs. Two oxidation and reduction peaks can be observed in [bmim][BF_4] before purification. This showed that the crude [bmim][BF_4] contained bromide impurities because the CV was consistent with the CV of bromide ion in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, ([bmim][NTf_2]) and acetontrile [12, 13]. From the experiments, when we increased bromide concentration in [bmim][BF_4], the first anodic oxidation peak current at 600mV vs FcH^+/FcH also increased. It indicated that this peak is bromide oxidation to bromine (Equation 4). The literatures also showed that the potentials corresponding to the first anodic peak are due to the formation of bromine from bromide as well as the formation of the tribromide anion from reaction of bromide with bromine (Equation 5). At the higher potentials, the driving force is sufficient to induce the dissociation of tribromide to bromide and bromine and facilitate the oxidation of bromide to bromine again (Equation 4). Thus, the cathodic peaks are due to the reverse processes of anodic peaks. On the other hand, the purified [bmim][BF$_4$] shows only negligible background currents thus confirming its purity and showing that it is electrochemically stable for the electrochemical generation of superoxide ion.

$$2Br^- \longrightarrow Br_2 + 2e^- \qquad [4]$$

$$Br_2 + Br^- \rightleftharpoons Br_3^- \qquad [5]$$

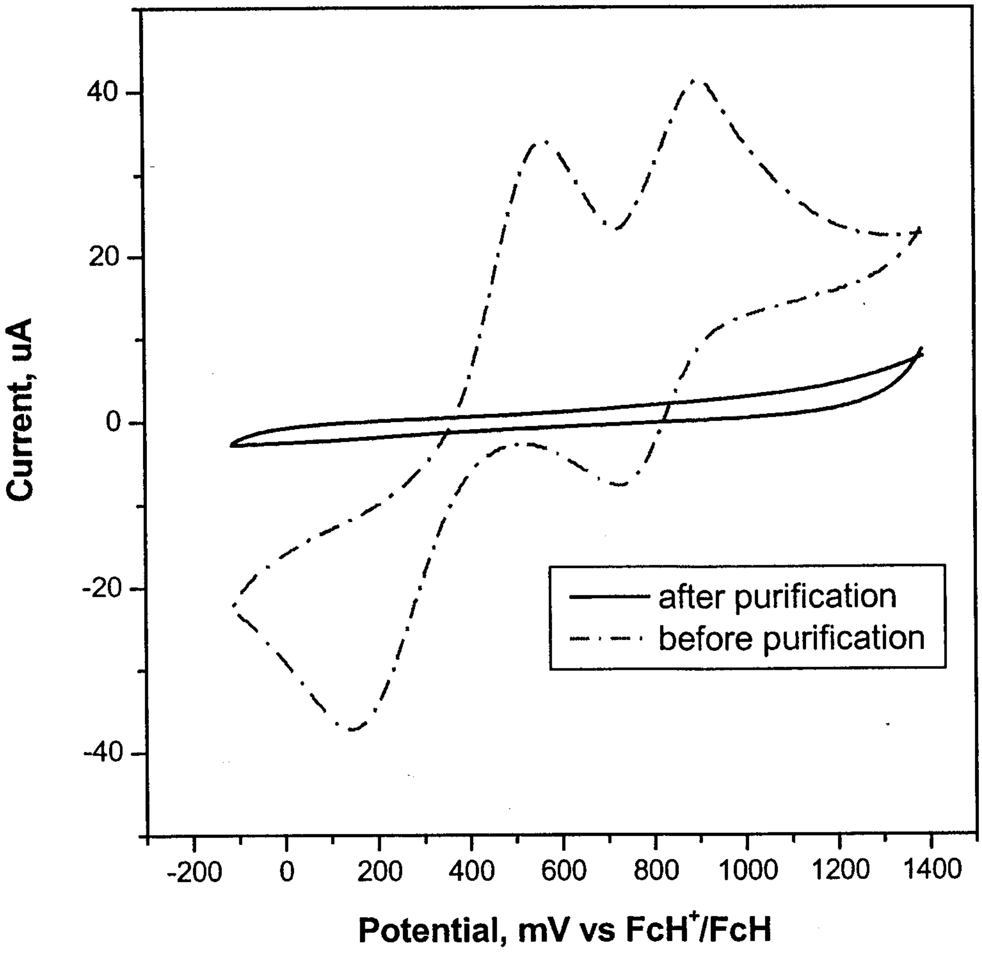

Figure 2.1 *CVs in purified and crude [bmim][BF$_4$] purged with argon. All scans used a platinum working electrode at a scan rate of 100mV/s*

2.2.2 Cyclic voltammeteric study of oxygen reduction in [bmim][BF_4]

Figure 2.2 shows CVs in pure [bmim][BF_4] run with argon and oxygen. The negligible background current in the presence of argon indicates that the [bmim][BF_4] is electrochemical stable under these condition. The presence of water in [bmim][BF_4] only has a remarkable narrowing in the potential window available for voltammetric studies while the background currents is almost the same [14]. This indicates that water in [bmim][BF_4] is not electrochemically active. In [bmim][BF_4], the presence of oxygen results in a reduction and oxidation peaks at – 1100mV and -900mV vs FcH^+/FcH, respectively. The reduction peak is due to the generation of superoxide ions according to Equation 1 and the oxidation peak is due to the reverse of Equation 1. However, the reduction current is much larger than the oxidation current (the ratio of cathodic and anodic currents is not unity). In addition to the Karl-Fischer titration measurements, in the presence of small amount of water (0.48M) in [bmim][BF_4] will consume the superoxide ions quickly and facilitate the second electron reduction (Equation 2). The second electron reduction is easier to reduce than the first electron reduction of oxygen. Hence, the reduction peak consists of two reduction process (Equations 1 and 2) while only those free superoxide ions that have not been reacted with water can be oxidized back to oxygen (Equation 1). Thus, an irreversible reaction can be observed and the oxidation current depends on the amount of water in [bmim][BF_4].

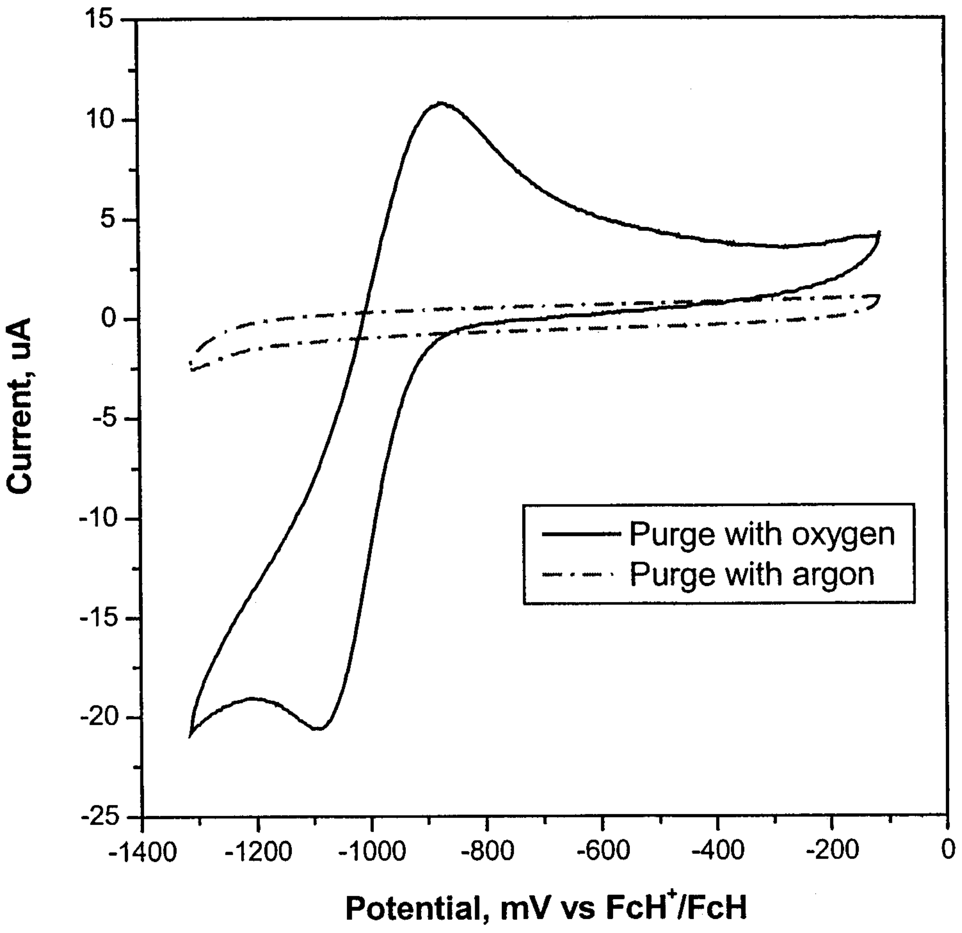

Figure 2.2 *CVs of [bmim] [BF$_4$]. One was purged with argon and the other with oxygen. All scans used a glassy-carbon working electrode at a scan rate of 100mV/s*

2.3 Electrosynthesis of hydrogen peroxide in ionic liquid using a batch cell

Based on the above electrochemical studies on [bmim][BF_4], the stable superoixde ion can be generated from oxygen in dried [bmim][BF_4] and the superoxide ion reacts readily with water to give hydroperoxide ion and hydroxide ion (Equation 3). We believed that hydrogen peroxide can be electrosynthezied by electroreduction of oxygen in water-containing ionic liquids, [bmim][BF_4].

For preparative electrogeneration of hydrogen peroxide, a batch glass H-cell was used (Figure 2.3). The dissolved oxygen is saturated and electrochemically reduced to hydroperoxide ion and hydroxide ion at the reticulated vitreous carbon cathode (Equation 3), while at the anode, the oxidation of H_2O releases oxygen gas and protons (Equation 8). Equation 9 gives the overall reaction for the electrogeneration of hydrogen peroxide in water-containing ionic liquid.

$$O_2 + H_2O + 2e^- \rightarrow HOO^- + OH^- \qquad [3]$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad [8]$$

$$O_2 + 2H_2O \rightarrow 2H_2O_2 \qquad [9]$$

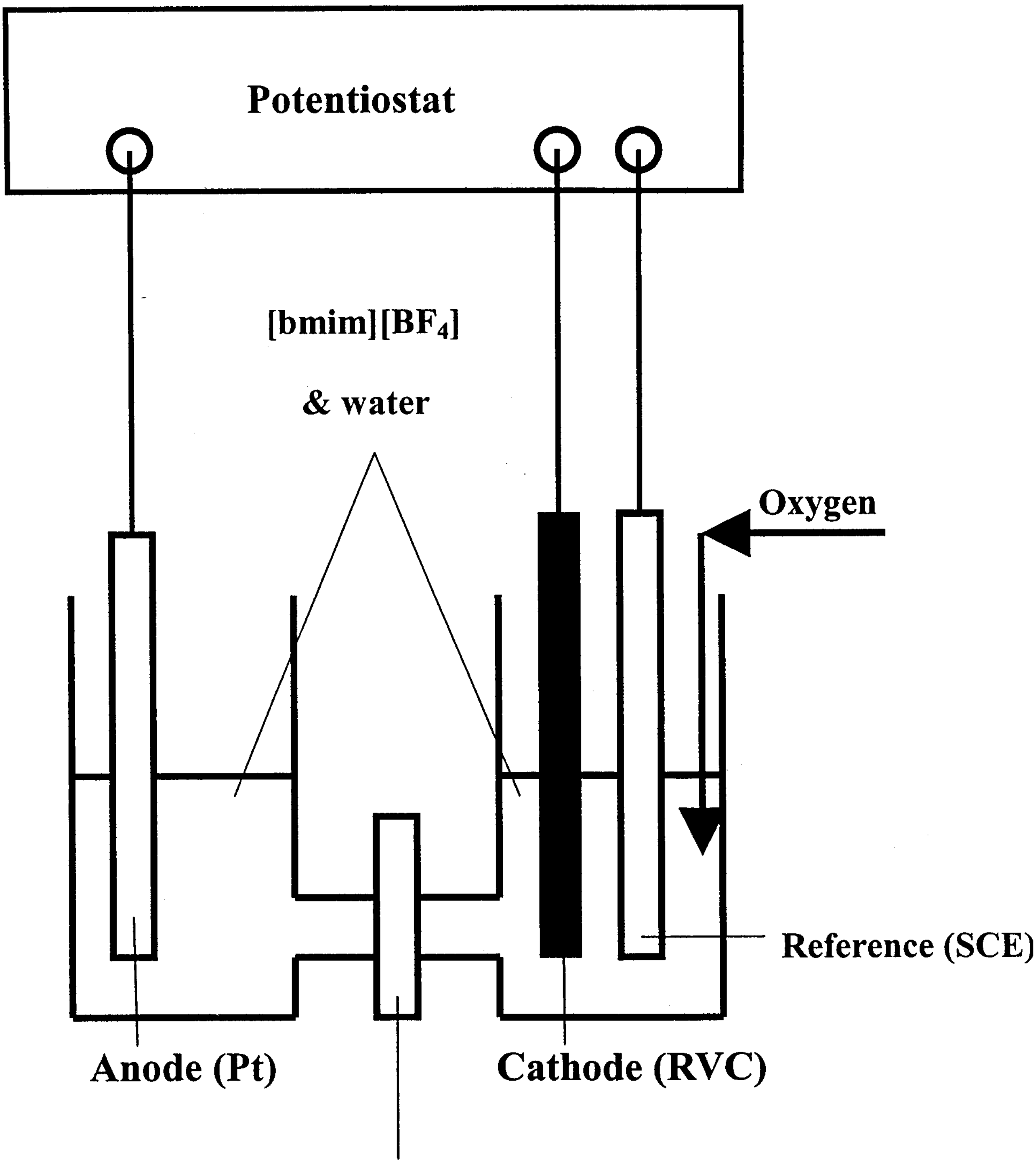

Figure 2.3 The electrochemical cell for batch electrolysis of oxygen in [bmim][BF_4] with water

According to Equation 3, when oxygen is saturated in [bmim][BF_4]-water mixture, the amount of electrons (applied potential) and water are the major factors affecting the yield of electrogeneration of hydrogen peroxide. Therefore, the optimal applied potential and volume ratio of [bmim][BF_4] to water were investigated in order to obtain the highest yield of hydrogen peroxide. Investigations into these optimal operational parameters (optimal applied potentials and volume ratios of [bmim][BF_4] to water) were performed in a electrochemical H-cell (Figure 2.3). The concentration of electrogenerated hydrogen peroxide was determined by differential pulse voltammetry, based on the oxidation of hydrogen peroxide at a platinum electrode (Equation 10) [15, 16]. It was continuously carried out after the electrochemical cell had consumed a certain amount of charge. After hydrogen peroxide generation, a known volume of catholyte was extracted and a series of known amount of commercial hydrogen peroxide was added. The differential pulse voltammetry was recorded again to produce the calibration curve; and the hydrogen peroxide concentration could be determined by back extrapolation.

$$HOO^- + OH^- \rightarrow O_2 + H_2O + 2e^- \qquad [10]$$

2.3.1 Optimal operational parameters investigations

A series of constant potential from -600mV to -750mV vs SCE was applied to the [bmim][BF_4] with water (80:20 v/v) (Figure 2.4). The concentration of hydrogen peroxide was only 11.3mM when -600mV (vs SCE) was applied. This cathodic potential is not negative enough; therefore oxygen reduction takes place slowly. At -650mV, the hydrogen peroxide concentration could be obtained up to 64mM. However, further increase in the cathodic potential lowered the yield of hydrogen peroxide. This may be due to the further reduction of hydroperoxide ion to hydroxide ion (Equation 11) or decomposition by disproportionation (Equation 12) [17, 18]. It has also been proposed that four electron oxygen reduction may occurs readily on vitreous carbon surfaces (Equation 13) without hydroperoxide ion as a discrete intermediate [18]. Moreover, protons generated at the anode (Equation 4) will be electrically driven to the catholyte, partially supplementing the protons consumed for hydrogen peroxide synthesis. Those protons may consume the electron to evolve hydrogen gas (Equation 14) instead of generating hydroperoxide ion in the catholyte [19].

$$HOO^- + H_2O + 2e^- \rightarrow 3OH^- \quad [11]$$

$$2HOO^- \rightarrow 2OH^- + O_2 \quad [12]$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad [13]$$

$$2H^+ + 2e^- \rightarrow H_2 \quad [14]$$

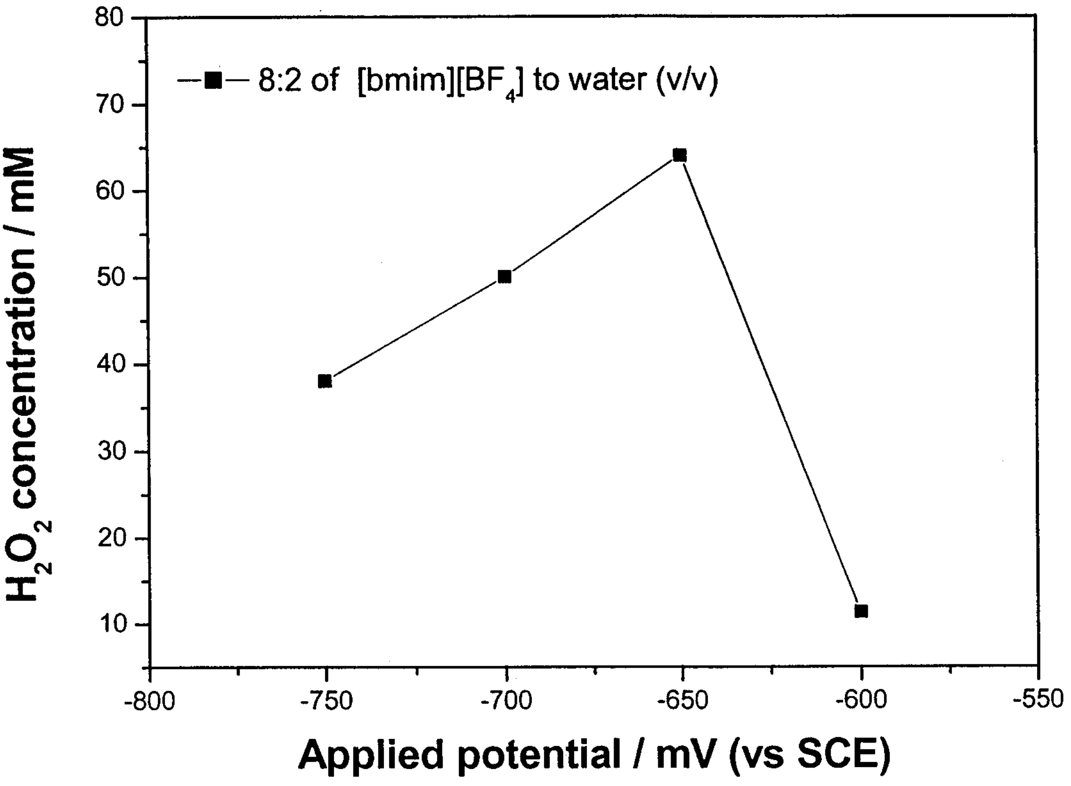

Figure 2.4 *Influence of applied potentials on the electrosynthesis of hydrogen peroxide in [bmim][BF$_4$] with water (80:20 v/v)*

Having found out the optimal applied potential for the generation of hydrogen peroxide in [bmim][BF_4]-water mixture (-650mV vs SCE), several different [bmim][BF_4] to water volume ratios were also investigated. Figure 2.5 shows that increasing the volume of [bmim][BF_4] from 60% to 80% can largely increase the hydrogen peroxide concentration from 21mM to 64mM. Two competing factors may contribute to the observation. One factor is attributed to the increase in the conductivity of the media due to decreased amount of water. On the other hand, the gaseous saturated solubility of oxygen is 2.8mM in [bmim][BF_4] at 41°C and it is higher than in water which only has 1.0mM at 41°C [2, 20, 21]. Larger proportion of water may hinder the dissolution of oxygen in the media to generate hydrogen peroxide according to Equation 3. The balance of these two factors seems to lead to increased hydrogen peroxide production as the amount of water declined. However, when the amount of water further declined as the volume of [bmim][BF_4] was larger than 80%, the generation of hydrogen peroxide was suppressed. It is because water is the reactant needed to provide proton source for generating hydrogen peroxide (Equation 3).

In conclusion, the optimal applied potential and optimal volume ratio for electrogenerated hydrogen peroxide was found to be -650mV vs SCE and 80:20 (v/v) for [bmim][BF_4] to water respectively. Under such conditions, hydrogen peroxide can be generated at a concentration of 64mM and with a current efficiency of 57% after 4 hours electrolysis.

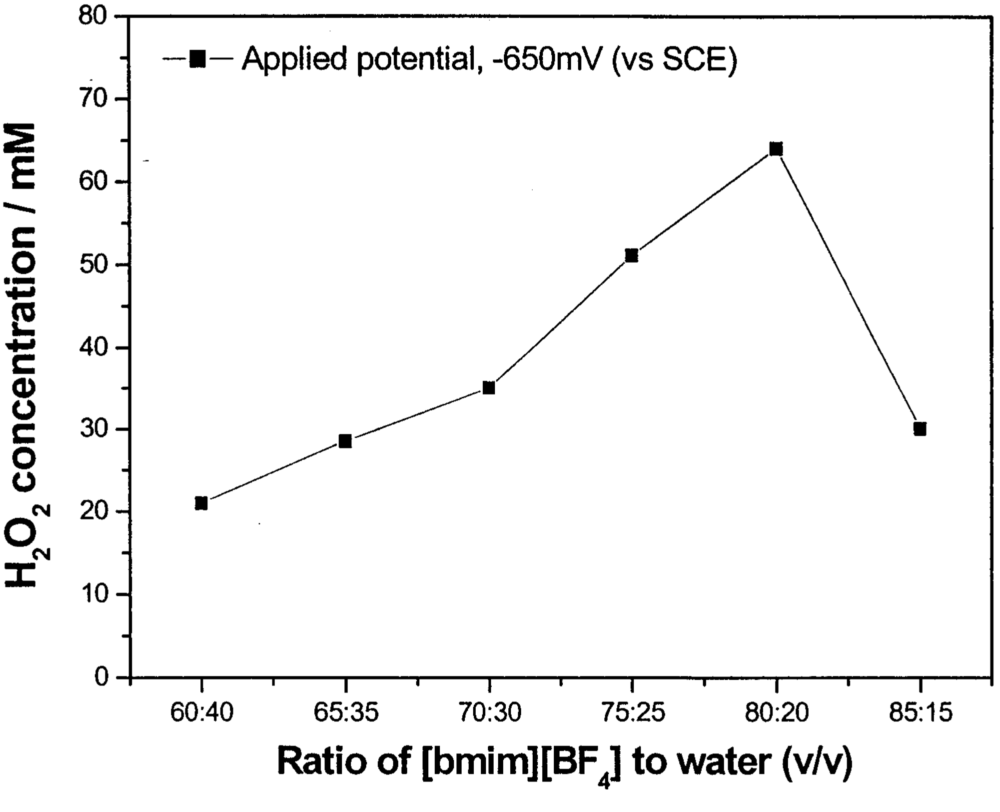

Figure 2.5 *Influence of different volume ratios of [bmim][BF$_4$] to water on the electrosynthesis of hydrogen peroxide in [bmim][BF$_4$] with water*

2.3.2 Comparison of yield of hydrogen peroxide between [bmim][BF_4]-water mixture and aqueous media in batch electrolysis

Electroreduction of oxygen to hydrogen peroxide in various aqueous electrolytes, such as Na_2CO_3, H_2SO_4, KOH, and NaOH has been extensively investigated [19, 22-26]. However, there has been no report on using ionic liquids as the electrolyte. In this work we have successfully employed [bmim][BF_4]–water mixture as electrolyte to generate hydrogen peroxide in batch electrolysis. Table 2.1 shows the comparison of the yield of electrogenerated hydrogen peroxide in aqueous media and [bmim][BF_4]–water mixture. Based on similar electrochemical setups (Figure 2.3), the use of 0.1M aqueous Na_2CO_3 and 0.1M aqueous H_2SO_4 as electrolytes would only generate 14mM and 40mM of hydrogen peroxide with 7% and 20% current efficiencies respectively [23]. Obviously, using [bmim][BF_4]–water mixture as the electrolyte, higher yield of hydrogen peroxide can be generated than that of the aqueous media as electrolyte.

Table 2.1 Comparison of the yield of electrogeneration of hydrogen peroxide and current efficiencies using different electrolytes

	Electrolyte		
	0.1M Na_2CO_3[23]a	**0.1M H_2SO_4[23]a**	**$[bmim][BF_4] - H_2O$ (80:20 v/v)^a**
$[H_2O_2]$, mM	**14 mM**	**40 mM**	**64mM**
Current efficiency, %	7 %	**20 %**	57 %^{b}
Time consumed, hr	**4 hrs**	**4 hrs**	**4 hrs**

[a] The configuration of the electrochemical setup is similar to our system and the current density is $300 Acm^{-2}$, our system is $375 Acm^{-2}$

[b] The current efficiency is calculated based on the mole of hydrogen peroxide generated from the experimental electrolysis over the theoretical mole of hydrogen peroxide generated times 100%

2.4 Electrosynthesis of hydrogen peroxide in ionic liquid in continuous flow cell

Electrogeneration of hydrogen peroxide in [bmim][BF_4]-water mixture has been successfully demonstrated in the batch electrochemical cell equipped with reticulated vitreous carbon cathodes. The results warranted the investigation of mediated system in a continuous flow electrochemical cell under conditions closer to potential industrial applications [24, 27-29]. It is therefore desirable to study our system in a continuous flow system. Based on the preliminary electrolysis conducted in [bmim][BF_4]-water mixture (80:20 v/v) at -650mV vs SCE, it is expected that the hydrogen peroxide concentration and current efficiency can be further increased when using continuous flow electrolysis system.

2.4.1 Comparison of yield of hydrogen peroxide in batch electrolysis and continuous flow electrolysis

Figure 2.6 shows the arrangement of the continuous flow cell system. The continuous flow electrolysis experiments were performed under galvanostatic conditions at 60mA. The major difference between the batch electrolysis and the continuous flow electrolysis is that continuous flow electrolysis use precise pump to circulate the electrolyte continuously and constantly throughout the experiment. The fresh electrolyte saturated with oxygen can flow through the whole system and undergo oxygen electroreduction on the reticulated vitreous carbon. As a result, the hydroperoxide ion will not be confined on the surface of the reticulated vitreous carbon cathode and not be further reduced to hydroxide ion easily (Equation 10). Table 2.2 shows that the yield of hydrogen peroxide concentration in continuous flow electrolysis is higher than that of the batch electrolysis.

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Table 2.2 *Comparison of the yield of electrogeneration of hydrogen peroxide and current efficiencies between the batch and continuous flow electrolytsis*

	Batch	**Continuous**
	[bmim][BF$_4$] – H_2O	**[bmim][BF$_4$] – H_2O**
[H_2O_2], mM	**64 mM**	**102mM**
Current efficiency, %	**57 %**	**62 %**
Time consumed, hr	**4 hrs**	**4 hrs**

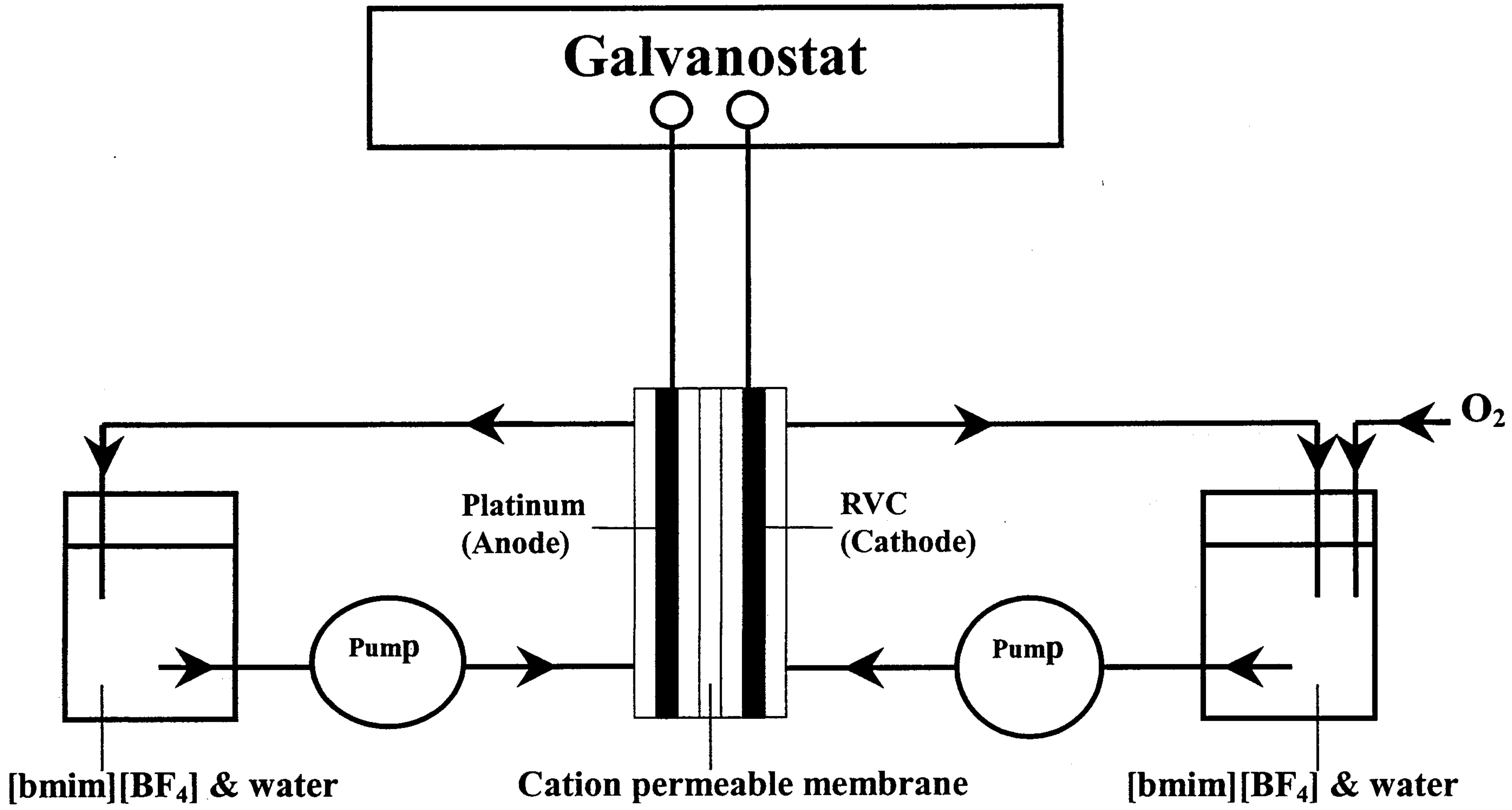


Figure 2.6 *The electrochemical cell for continuous flow electrolysis of [bmim][BF$_4$]-water mixture*

2.4.2 Comparison of yield of hydrogen peroxide in [bmim][BF$_4$] with different additives and aqueous media in continuous flow electrolysis

It is well known that hydrogen peroxide is a slightly stronger acid than water ($pK_a = 11.64$ at $25.0^{O}C$) [19, 30]. Under alkaline medium, it would be dissociated to proton, H^+, and hydroperoxide ion, HOO^- (Equation 15).

$$H_2O_2 \rightarrow H^+ + HOO^- \qquad [15]$$

Thus, the formation of hydroperoxide ion will be more favored under alkaline condition. By changing the proton source from water to aqueous Na_2CO_3, and aqueous NaOH in [bmim][BF$_4$], the yield of electrogenerated hydrogen peroxide is expected to increase. Table 2.3 shows the comparison of generation of hydrogen peroxide under [bmim][BF$_4$] with water, 0.05M Na_2CO_3, and 0.04M NaOH solutions. Using 0.05M Na_2CO_3 and 0.04 M NaOH solutions to replace water can improve the hydrogen peroxide production from 102 mM to 120mM and 124 mM respectively. Using the 0.3M tetraethyammonium sulfate solution as a proton source, the yield of hydrogen peroxide and current efficiency are almost the same as using water as proton source. Tetraethyammonium sulfate solution which is a weak acid will not favor the formation of hydroperoxide ion at the beginning of the electrolysis.

By comparison, according to the literature [28], under similar electrochemical setup (Table 2.4), the yield of electrogenerated hydrogen peroxide in 2.0 M aqueous NaOH electrolyte is lower than that of [bmim][BF_4]–water or [bmim][BF_4]–NaOH mixture. This may be attributed to the low oxygen solubility in aqueous solution [2, 20]. Another explanation may be that the control current (1370mA) used in the 2.0M aqueous NaOH system may be too high and, as a result, the hydroperoxide ion was further reduced to hydroxide ion (Equation 7). In the literature, another system, 11% (v/v) of organic solvent (tributyphosphate and diethyl benzene) mixed with 89% of 2M NaOH solution, was also used for the electrosynthesis of hydrogen peroxide. It was found that the yield of hydrogen peroxide in this system was higher than that of [bmim][BF_4]–NaOH. The higher concentration may be due to the possibility that the hydroperoxide ion can be extracted into the aqueous phase and prevented from further reduction to hydroxide ion (Equation 11). On the other hand, the [bmim][BF_4]–NaOH offers a better current efficiency, and avoids the use of volatile organic solvents completely.

Table 2.3 Comparison of the yield of electrogeneration of hydrogen peroxide and current efficiencies in [bmim][BF_4] with different additives under continuous flow electrolysis

	Electrolyte			
	[bmim][BF_4] & H_2O	**[bmim][BF_4] & 0.3M $(Et_4N)_2SO_4$[a]**	**[bmim][BF_4] & 0.05M Na_2CO_3**	**[bmim][BF_4] & 0.04M NaOH**
[H_2O_2], mM	**102mM**	**106mM**	**120mM**	**124mM**
Current efficiency, %	**62 %**	**63 %**	**65 %**	**71%**
Time consumed, hr	**4 hrs**	**4hrs**	**4hrs**	**4hrs**

All electrosynthesis of hydrogen peroxide were performed under the same condition as Table2.2. The volume ratio of [bmim][BF_4] to different additives is 80:20 (v/v)

[a] Tetraethyammonium sulfate $(Et_4N)_2SO_4$

Table 2.4 *Comparison of the yield of electrogeneration of hydrogen peroxide and current efficiencies in different electrolytes under continuous flow electrolysis*

	Electrolyte			
	[bmim][BF$_4$] & H$_2$O	**[bmim][BF$_4$] & 0.04M NaOH**	**2M NaOH[a]**	**11% TBP/DEB + 89% 2M NaOH[a,b]**
[H$_2$O$_2$], mM	**102mM**	**124mM**	**50mM**	**150mM**
Current efficiency, %	**62 %**	**71 %**	**40 %**	**60%**
Time consumed, hr	**4 hrs**	**4hrs**	**4 hrs**	**4 hrs**

[a] The configuration of the electrochemical setup is similar to our system and the current density is 22.5mAcm^{-2} for projected area, our system is 6.7 mAcm^{-2} for projected area

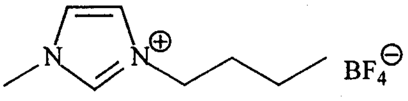
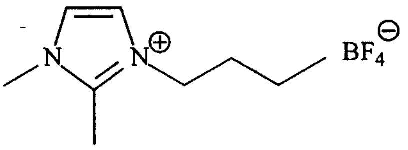
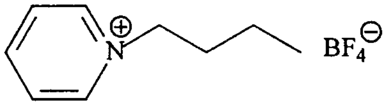
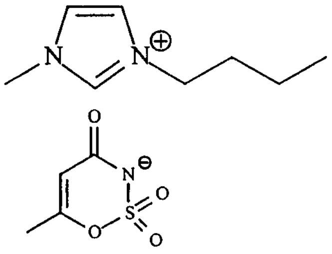
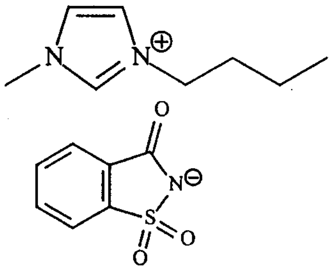
[b] 30mL Tributyphosphate (TBP) and diethyl benzene (DEB) (15:85 v/v) were added to 250mL 2M NaOH to form two-phase system.

2.4.3 Various ionic liquids for electrosynthesis of hydrogen peroxide

The electrochemical windows of the ionic liquids have been extensively investigated [2, 14, 31, 32]. The electrochemical window of an ionic liquid indicated the electrochemical stability of the ionic liquids. The electrochemical window is influenced by the stability of the cation against electrochemical reduction processes and the stability of the anion against oxidation processes. For the electrosynthesis of hydrogen peroxide, oxygen reduction takes place in the catholyte. The choice of the cation will influence the result of electrosynthesis of hydrogen peroxide. Table 2.5 showed the yield of hydrogen peroxide under different ionic liquids-water or NaOH mixture. For a given anion $[BF_4]^-$ with a range of cations (Entry 1, 2 and 3), the N-methyl-N-butylpyrrolidinium ions obtained a slightly higher yield of hydrogen peroxide than 1-butyl-3-methylimidazolium ions and 1-butyl-2,3-dimethylimidazolium ions. The 1-butyl-3-methylimidazolium ions are less stable to reduction than N-methyl-N-butylpyrrolidinium ions. The decreased of stability to reduction of these 1-butyl-3-methylimidazolium cations may be attributed to initial attack on the acidic proton attached to the ring C(2) carbon atom between the two heteroatoms [7, 33]. The 1-butyl-2,3-dimethylimidazolium ions (Entry 2) can solve this problem, but this ionic liquid has a relatively lower conductivity [31] and the yield of hydrogen peroxide is almost the same as 1-butyl-3-methylimidazolium cations. N-butylpyridinium cations (Entry 4) can not generate any hydrogen peroxide even it is mixed with water or aqueous NaOH solution after 3 hours electrolysis. Welton *et al.* illustrated that the N-butylpyridinium cation is the least stable for electrochemical process and the general trend in the electrochemical stabilities of the types of ionic liquids cations is: pyridinium < pyrazolium ≤ imidazolium ≤ sulfonium ≤ ammonium [2].

To study the effect of anion, we have examined two new ionic liquids: 1-butyl-3-butylimidiazolium acesulfammate (Entry 5) and 1-butyl-3-butylimidiazolium saccharinate (Entry 6). They were recently reported as non-fluorous anions [34] and claimed as non-toxic ionic liquids. This study is the first report of the above ionic liquids applied in electrosynthesis. According to our experiments, 1-butyl-3-butylimidiazolium saccharinate and 1-butyl-3-butylimidiazolium acesulfammate were not suitable for electrosynthesis of hydrogen peroxide. The former is a highly viscous liquid although it mixed with water at room temperature. The latter existed as solid state and can be completely well-dissolved in water or aqueous NaOH solution. However, we observed that the potential difference between the cathode and anode of the electrochemical system is unexpectedly higher than entry 1, 2, and 3. This implied the electrical conductivity of 1-butyl-3-butylimidiazolium acesulfammate is poor when compared with entry 1, 2, and 3. The unusual high voltage will readily decompose the hydrogen peroxide even though the hydrogen peroxide can be electrogenerated in 1-butyl-3-butylimidiazolium acesulfammate.

Table 2.5 Comparison of the yield of electrogeneration of hydrogen peroxide in different ionic liquids

Entry	**Ionic Liquids**	**$[H_2O_2]$, mM**	**Current efficiency, %**	**Time, hr**
1		97	74	2.5
2		95	70	2.5
3[a]		103	79	2.5
4		0	0	>3
5[b]		0	0	>3
6[c]		N.A	N.A	N.A

Electrosynthesis of hydrogen peroxide from entry 1 to 6 were carried out under continuous flow electrolysis with the same condition as in Table 2.2

[a] N-methyl-N-butylpyrrolidinium tetrafluorborate exists as a solid state in room temperature. The ratio of N-methyl-N-butylpyrrolidinium tetrafluorborate to water is 75:25 w/w

[b] 1-butyl-3-butylimidiazolium acesulfammate exists as a solid state in room temperature and it is well-dissolved in water or aqueous NaOH solution (80:20 v/v)

[c] 1-butyl-3-butylimidiazolium saccharinate exists as a very viscous liquid at room temperature.

2.5 Conclusion

To conclude, we showed that the [bmim][BF_4] is electrochemically stable and suitable for the electroreduction of oxygen to generate hydrogen peroxide. The optimal operation parameters (optimal applied potential and volume ratio of [bmim][BF_4] to water) were investigated in batch electrolysis of [bmim][BF_4]-water mixture so as to obtain the best yield of hydrogen peroxide This gave the preliminary results for further investigation of continuous flow electrolysis in [bmim][BF_4]-water and [bmim][BF_4]-NaOH mixtures. The electrogeneration of hydrogen peroxide in [bmim][BF_4]-water mixture or [bmim][BF_4]-NaOH mixture can give a good yield of hydrogen peroxide when compared to aqueous medium only in continuous flow electrolysis. But the yield of hydrogen peroxide is relatively lower when compared with the two phase system from literature.

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Chapter 3 *In situ* epoxidation of alkenes by electrogenerated hydrogen peroxide in ionic liquid

3.1 Introduction

Epoxides are an important class of industrial chemicals that have been used as chemical intermediates for the manufacture of a range of modern commercial products. Epoxidation of alkenes is one of the important routes, which leads to the production of epoxides on both laboratory and industrial scales. Traditionally, the conversion of alkenes into an epoxide is performed by using peroxides or peracids in conjunction with transition metal catalysts in organic solvents [1]. Because of the environmental consideration, combination of using green oxidants, less toxic catalysts and clean solvents to replace the traditional epoxdiation system become great challenges in academic and industry. Recently, our research group has developed an efficient system to catalytically epoxidize lipophilic alkenes by commercially available hydrogen peroxide and simple manganese salt in recyclable ionic liquid without any organic solvents [2]. However, usage of the commercially available hydrogen peroxide from industrial production (AQ process) rendered a major drawback of this clean epoxidation system. From the previous section, we reported that the hydrogen peroxide is successfully electrogenerated from oxygen in ionic liquid-water mixture. We believed that our developed system can be coupled to the epoxidation of alkenes. After removing the epoxides, the whole reaction mixtures can be recovered and reused to regenerate hydrogen peroxide and epoxidaiton of alkenes in order to achieve a totally clean epoxidation system.

3.2 *In situ* epoxidation of alkenes by electrogenerated hydrogen peroxide in ionic liquids

Traditionally, alkenes in which the double bond is in conjugation with an electron-withdrawing group (α,β-unsaturated ketones) may readily be epoxidized with a nucleophilic reagent, such as hydrogen peroxide under alkaline conditions [3, 4], by a mechanism which is shown in Figure 3.1[5]. In alkaline medium, the hydroperoxide ion, HOO^-, the conjugated base of hydrogen peroxide (pK_a = 11.64 at 25.0^{O}C) [6, 7], will be predominant and acts as a strong nucleophile for epoxidation of α,β-unsaturated ketones. In the previous chapter, we demonstrated that under continuous flow electrolysis in [bmim][BF_4]-NaOH mixture, the hydroperoxide ion can readily be electrogenerated under alkaline medium and should therefore act as a powerful nucleophile to epoxidize the α,β-unsaturated ketones. However, high concentration of base added to [bmim][BF_4] would trigger the formation of diol instead of epoxide by a base-catalysed ring-opening mechanism (Figure 3.2). The effect of substrate to sodium hydroxide molar ratio has been investigated and the optimal molar ratio of substrate to NaOH has been reported [8]. Therefore, the [bmim][BF_4] with 0.04M NaOH (80:20 v/v) was the optimal condition for epoxidation of

α,β-unsaturated ketones based on the above literature. The alkaline hydrogen peroxide generated in [bmim][BF_4]-NaOH mixture was used successfully for the epoxidation of a number of α,β-unsaturated ketones. The results are summarized in Table 3.1 showing that several different electrophilic alkene substrates have been converted to epoxides with yields ranging from fair to good after isolation by extraction with diethyl ether. Entries 1 to 5 exhibit the epoxidation of different substituted α,β-unsaturated ketones. 2-Cyclohexen-1-one (entry 1) is more active than the other substrates investigated. An increase of number of electron-donating methyl groups (entry 2, 3 and 4) reduces the reactivity and yield of the epoxides because the electron-donating effect lowers the electrophilicity of C-C double bond. The lowest reactivity of isophorone (entry 5) may be due to the hindrance of the β-substituted methyl group and *gem*-dimethyl groups at the C-5 carbon atom.

The yields of epoxides were compared with those in the literature [9] using 2M commercially available hydrogen peroxide in [bmim][BF_4] (Table 3.2). The yields of epoxides (entry 1 and 5) from 78mM electrogenerated hydrogen peroxide compare well with those using 2M commercially available hydrogen peroxide. This indicated that the lower concencration of hydrogen peroxide generated from ionic liquid can exhibit the same function as the higher concentration of the commercially available hydrogen peroxide.

For the extraction and isolation of the epoxyketones, diethyl ether was used. It is presumed that the epoxyketones can be extracted by supercritical carbon dioxide in place of diethyl ether [9]. In the event that carbon dioxide would react with the sodium hydroxide in the electrolyte, sodium carbonate instead of sodium hydroxide can be used for the electrosynthesis of hydrogen peroxide. In previous section 2.4.2., [bmim][BF_4]-Na_2CO_3 can electrogenerate the hydrogen peroxide up to 120mM in 4 hours. Table 3.3 showed that the hydrogen peroxide in [bmim][BF_4]-Na_2CO_3 mixture can successfully epoxidize the α,β-unsaturated ketones with similar yields as the [bmim][BF_4]-NaOH system.

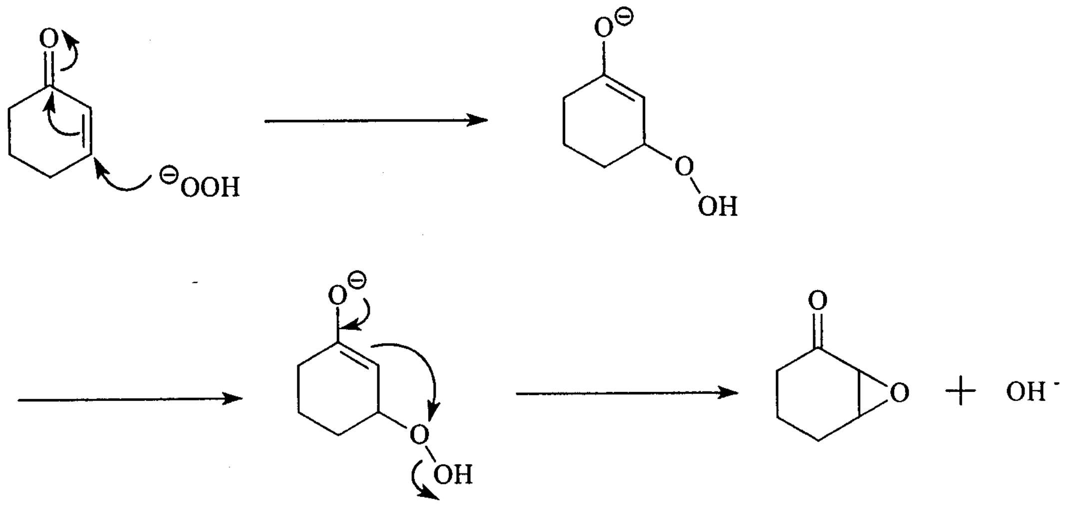


Figure 3.1 Mechanism of epoxdation of electrophilic alkenes by hydroperoxide ion

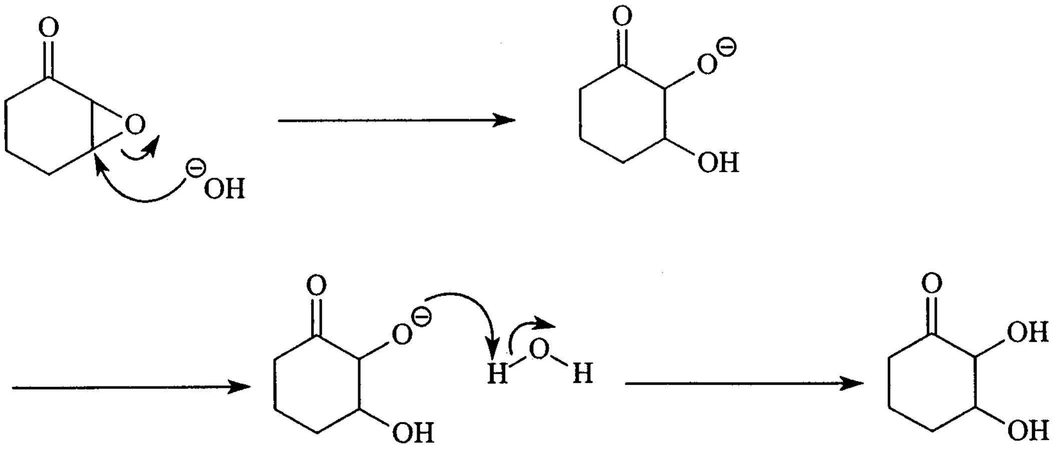
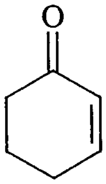
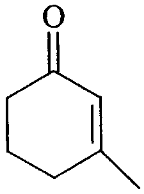
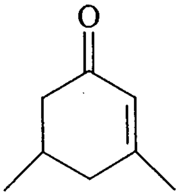
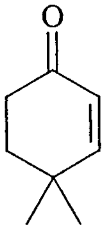
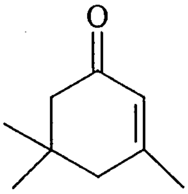


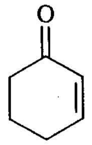
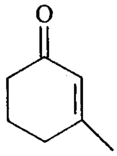
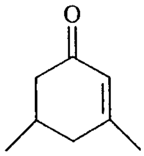
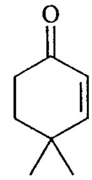
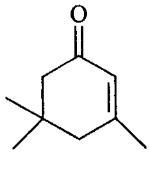
Figure 3.2 Mechanism of formation of diol from epoxide by hydroxide ion

***Table 3.1** Epoxidation of electrophilic alkenes*

Entry	Substrate	Time/min	Conversion (%)	Yield (%)
1		1	> 99	92
2		5	> 99	91
3		8	94	92
4		8	92	85
5		120	88	74

Reaction conditions: 0.37 mmol substrate, 78mM of electrogenerated hydrogen peroxide in 12mL [bmim][BF_4]-NaOH mixture, room temperature. Epoxides yield was calculated on the basis of converted alkenes and determined by GC-MS *versus* internal standard. Products were identified by ^{1}H and ^{13}C NMR after isolation by extraction with diethyl ether.

Table 3.2 *Comparison of the yield of epoxide from electrogenerated hydrogen peroxide with the commercially available hydrogen peroxide in ionic liquid.*

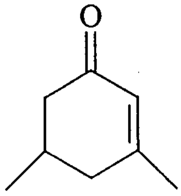
Entry	**Substrate**	**Epoxide yield, % (time, min)**	
		[bmim][BF$_4$] & 0.04M NaOH (80:20 v/v)[a]	**[bmim][BF$_4$]**[b]
1		92 (1)	98 (5)
2		91 (5)	97 (5)
3		92 (8)	*c*
4		85 (8)	*c*
5		74 (120)	Trace (120)

[a] Reaction conditions: 0.37 mmol substrate, 78mM of electrogenerated hydrogen peroxide in 12mL [bmim][BF$_4$]-NaOH mixture, room temperature. Epoxides yield was calculated on the basis of converted alkenes and determined by GC-MS verus internal standard. Products were identified by ^{1}H and ^{13}C NMR after isolation by extraction with diethyl ether.

[b] 1mmol of the substrate was dissolved in 1mL [bmim][BF$_4$] at 25°C. Water (4mmol), 2mmol of solid NaOH, and 0.3mL of commercially available aqueous solution of H_2O_2 (30% w/w) 3mmol were added with stirring.

[c] These reactions were not performed because of the observed low stability of [bmim][BF$_4$] at longer reaction times.

Table 3.3 Comparison the yield of epoxide in different electrolytes

Substrate	**Epoxide yield % (time, min)**	
	[bmim][BF$_4$]-0.04M NaOH	**[bmim][BF$_4$]-0.05M Na$_2$CO$_3$**
	**86 (8)**	**84 (8)**

3.3 Recovery and reused of [bmim][BF_4]-NaOH mixture

With [bmim][BF_4]-NaOH mixture as the electrolyte, the electrophilic alkenes and epoxides were easily extracted by diethyl ether. Since the ionic liquid is likely to be the most expensive among all the components in the reaction system, we have to find an effective way to recycle the electrolyte for the regeneration of hydrogen peroxide and epoxidation.

The loss of water in the course of extraction is the crucial factor to affect the yield of regeneration of hydrogen peroxide in the next cycle. Compensation of water was necessary in order to retrieve the optimized volume ratio of [bmim][BF_4] to NaOH for the next cycle. We first attempted to recover all [bmim][BF_4]-NaOH mixture from the electrochemical micro flow cell by washing the micro flow cell thoroughly with 100mL ethanol (10mL x 10 times). In the recovery process, several milliliters of ionic liquids would be lost in the course of recovery from the micro cell. After removing ethanol and water from the washings, the recovered [bmim][BF_4] was combined with the [bmim][BF_4]-NaOH mixture used for epoxidation to regenerate the hydrogen peroxide by electrolysis. The suitable ratio of [bmim][BF_4] to 0.04M NaOH

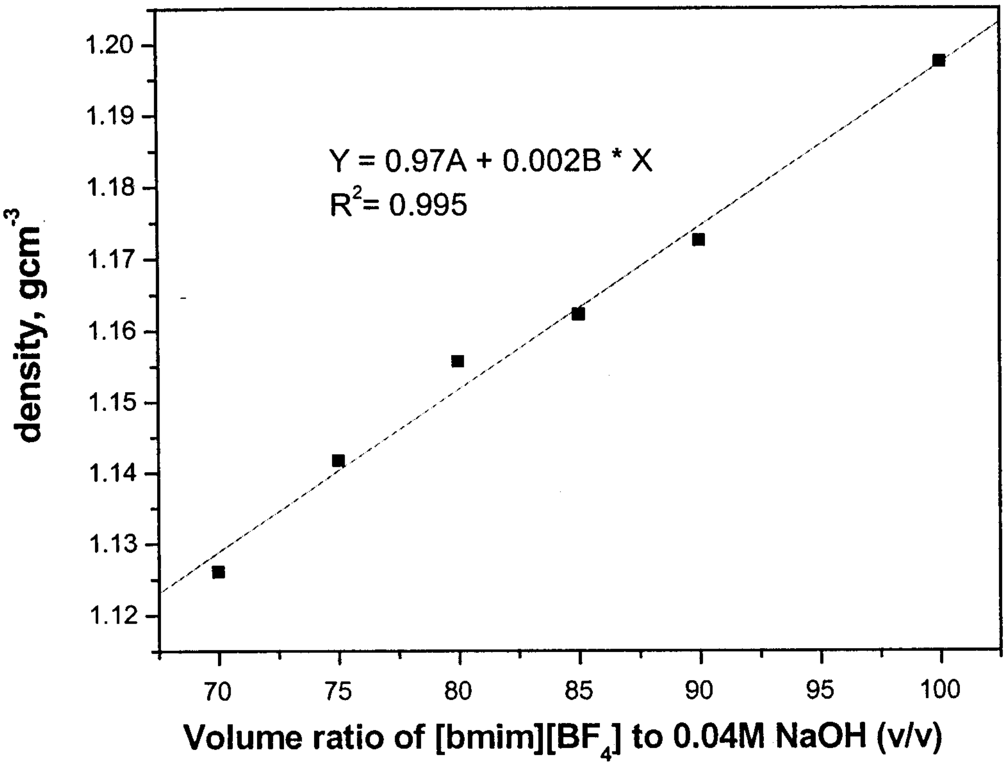
(80:20 v/v) was retrieved by adding a calculated amount of 0.04M NaOH to the recovered [bmim][BF_4] for the electrosynthesis of hydrogen peroxide in the second cycle. Table 3.4 shows the comparison of the yields of hydrogen peroxide between the first and the second cycle. Although regeneration of hydrogen peroxide was successful, the yield of hydrogen peroxide in the second cycle could not reach to the same amount as in the first cycle. The discrepancy is believed to be due to the unknown amount of NaOH remained in the reused [bmim][BF_4]. This approach of ethanol extraction is therefore considered unsatisfactory. Moreover, usage of a large amount of organic solvent (ethanol) and the loss of ionic liquid in the recovery steps will dramatically increase the cost in the reaction system.

Table 3.4 *Comparison of the yield of hydrogen peroxide between the fresh [bmim][BF_4]-NaOH mixture and reused [bmim][BF_4]-NaOH mixture*

Cycle	**1**	**2**
[H_2O_2], mM	**78**	**65**
Time consumed, hr	**2**	**2**

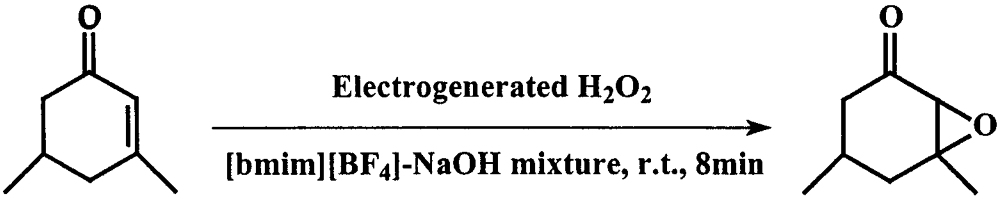
A simpler method to regenerate the same amount of hydrogen peroxide and without any loss of ionic liquid in the next cycle is necessary in order to enhance the usefulness of this system. Both aqueous NaOH and [bmim][BF_4] are the major components for the electrosynthesis of hydrogen peroxide and the *in situ* epoxidation of alkenes. Provided that we can determine the exact volume ratio of the [bmim][BF_4] and aqueous NaOH in the recovered ionic liquid after diethyl ether extraction of the epoxides, there is actually no need to remove the aqueous NaOH and water from [bmim][BF_4]-NaOH mixture to obtain pure [bmim][BF_4] for the next cycle. We therefore developed a method to determine the volume ratio of [bmim][BF_4] to 0.04M NaOH solution in the recovered ionic liquid [bmim][BF_4]-NaOH mixture. First, a calibration curve of the density of ionic liquid solution *versus* the volume ratio of [bmim][BF_4] to NaOH was generated using known standard solutions (Graph 3.1). We found that the volume ratio of [bmim][BF_4] to 0.04M NaOH is directly proportional to the density of the solution. After measuring the density of the recovered [bmim][BF_4]-NaOH mixture, and with the aid of the calibration curve, it was possible to deduce the volume ratio of [bmim][BF_4] to 0.04M NaOH in the recovered mixture. An appropriate volume of water was then added to the recovered mixture to give the optimized 80:20 v/v ratio according to this calibration curve. The mixture was then reused for the electrochemical generation of hydrogen peroxide, and used *in situ* again for the epoxidaiton.

The results are summarized in Table 3.5. It can be seen that the [bmim][BF_4]-NaOH mixture can be recycled for at least four cycles with similar yields of hydrogen peroxide. The slight decline in the yield of epoxide in the 4th cycle was attributed the formation of side products as the alkene substrate was completely converted [10].



Graph 3.1 The calibration curve for determination of volume ratio of [bmim][BF_4] to 0.04M NaOH in [bmim][BF_4]-NaOH mixture

***Table 3.5** Recovery and reuse of [bmim][BF_4] for the epoxidation of 3,5-dimethylcyclohexen-1-one*[a]



Cycle	**1**	**2**	**3**	**4**
[H_2O_2], mM	**78**	**79**	**79**	**80**
Time, hr[b]	**2**	**1.5**	**1.5**	**1.5**
Epoxide Yield, %[c]	**86**	**84**	**83**	**80**

[a] A situable amount of water was added to optimized the volume ratio of [bmim][BF_4] to NaOH in cycles 2 to 4.

[b] Time for electrolysis under the same conditions as in Section 2.3.3.

[c] Epoxidation was carried out under the same conditions as in Table 3.1. Epoxides yield was calculated on the basis of converted alkenes and determined by GC-MS verus internal standard. Products were identified by ^{1}H and ^{13}C NMR after isolation by extraction with diethyl ether.

3.4 Conclusion

In summary, we have showed that the [bmim][BF_4]-water or NaOH mixtures can be used as promising electrolytes for effective electrogeneration of hydrogen peroxide which is subsequently used for the epoxidation of alkenes. Based on the relationship between the density and the volume ratio of [bmim][BF_4] to NaOH, the [bmim][BF_4]-NaOH mixture can be reused without any loss for at least four cycles after electrosynthesis of hydrogen peroxide and epoxidation of alkenes. The whole process can be regarded as a totally clean system because only oxygen, water, and electricity are consumed in the recyclable ionic liquid to achieve electrosynthesis of hydrogen peroxide and *in situ* epoxidation of alkenes.

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Chapter 4 Experimental Section

4.1 General Protocols

Materials

All chemicals were purchased from Aldrich and high purity oxygen (>99.7%) was provided by Hong Kong Oxygen Co. The working electrode was reticulated vitreous carbon (RVC) with 60 pores per inch. Nafion® 424 cation permeable membranes were purchased from ERG Materials & Aerospace Cooperation.

Instrumentation

Proton (^{1}H) and carbon (^{13}C) NMR spectral measurements were carried out on a Bruker DPX-400MHz NMR spectrometer.

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were carried out on a Bioanalytical System (BAS) model 100B electrochemical analyzer interfaced to a computer. EG&G Princeton Applied Research Potntiostat/Galvanostat (Model 273A) was used for batch and continuous flow electrolysis.

The water content of ionic liquids was determined by Karl Fischer coulometry using a 'METROHM 756KF' apparatus. Anolyte and catholyte were "coulomat AG' purchased from Hydranal.

An unmodified housedhold microwave oven (SHARP R342D M/OVEN 34L 1100W T; microwave frequency 2450MHz) was used for preparation of [bmim][BF_4].

GC-MS was conducted on a Hewlett-Packard model G1800C gas chromatograph equipped with an electron ionization detector. A HP-5MS (30 m X 0.25 mm X 0.25 mm) stainless steel column was employed in the analysis with helium as the carrier gas. The injection volume was 2 μL.

4.2 Experimental-Chapter 2

Preparation of 1-butyl-3-methylimidazolium bromide [bmim][Br]

[bmim][Br] was prepared according to literature procedure [1] using the water-moderated microwave process. A mixture of 1-bromobutane (1.2mol, 164.4g) and 1-methylimidazole (1.0mol, 82.1g) was placed in a 500mL round bottom flask equipped with a drying tube. The reaction flask was put in a 2L beaker containing 500mL of water. The mixture was heated in microwave oven (SHARP R342DM/OVEN 34L 1100W T; microwave frequency 2450MHz) according to literature schedule. The pale yellow reaction mixture was then washed with ether (3 x 50ml) and dried under vacuum at 80^0C to give the crude [bmim][Br].

Preparation of 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF_4]

To prepare the [bmim][BF_4], the [bmim][Br] (0.5mole) was added to a suspension of $NaBF_4$ (1.1equiv, 0.55mol) in acetone (300ml). After the mixture was stirred for 48hours at room temperature, the sodium bromide precipitate was removed by filtration and purified by addition of 1g neutral alumina stirred for 2 hours. The filtrate was concentrated to oil by rotary evaporation.

Purification of 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF$_4$]

The [bmim][BF$_4$] (60g) was diluted with dichloromethane (200ml) and filtered through silica gel (~100g) and celite (~20g). The resulting solution was dried overnight with anhydrous magnesium sulfate. The filtrate was concentrated to oil.

Preparation of N-methy-N-butylpyrrolidinium bromide [N$_{14}$][Br]

[N$_{14}$][Br] was prepared according to the literature [2]. An amount of 1-methyl pyrrolidine (57.3g, 0.673mol) was mixed with acetonitrile (150mL); Bromobutane (110.7g, 0.808mol) was added dropwise into the pyrrolidine solution, and nitrogen bubbling was used. The mixture was stirred at room temperature overnight. The solvent was removed by distillation, and the solid product was dried under vacuum at room temperature for more than 48hours.

Preparation of N-methy-N-butylpyrrolidinium bromide [N$_{14}$][BF$_4$]

To prepare the [N$_{14}$][BF$_4$], the [N$_{14}$][Br] (0.5mole) was added to a suspension of NaBF$_4$ (1.1equiv, 0.55mol) in acetonitrile (300mL). After the mixture was stirred for 48hours at room temperature, the sodium bromide precipitate was removed by filtration and purified by addition of 1g neutral alumina stirred for 2 hours. The filtrate was concentrated to oil by rotary evaporation.

Preparation of 1-butyl-3-methylimidiazolium acesulfammate [bmim][Ace] and 1-butyl-3-methylimidiazolium saccharinate[bmim][Sac]

Each ionic liquid was prepared from [bmim][Br] by the combination of equimolar amounts of the potassium acesulfammate or sodium saccharinate [3].

Superoxide ion generation in [bmim][BF$_4$]

CV experiments were performed on 3mL purified [bmim][BF$_4$]. [Bmim][BF$_4$] was dried for 3 hours in a vacuum oven at room temperature. The glass electrochemical cell contained a three-electrode arrangement with two platinum wires; the working electrode was glassy carbon electrode, one being used as a counter electrode and the other serving as a pseudo-reference electrode. Prior to superoxide generation, argon was purged to obtain a background voltammogram. Oxygen was then bubbled to the system for 30 minutes for saturation. Between consecutive CV runs, oxygen was bubbled to saturate the system with oxygen to prevent the development of concentration gradients. The purge of argon or oxygen was stopped during CV data acquisition.

Hydrogen peroxide generation and determination for the batch electrolysis

Figure 2.3 shows the electrochemical H-cell of RVC (25mm x 10mm x 12.5mm) with 60 pores per inch. The reference electrode was a saturated calomel electrode (SCE) and the counter electrode was platinum gauze placed in the anodic compartment, separated by a Nafion® 424 cation permeable membrane. Constant applied potential was applied to the electrochemical cell by potentiostat. The cathodic and anodic compartments had the same volume of 5mL [bmim][BF_4] containing same proportion of water. The catholyte was bubbled with oxygen for 30 minutes to allow sufficient solubilization before the experiments. The oxygen was continuously passed through catholyte throughout the experiments. During the experiments, both catholyte and anolyte were completely stirred by magnetic stirrers. The concentration of electrogenerated hydrogen peroxide was determined by DPV, based on the oxidation of hydrogen peroxide at a platinum electrode[4, 5]. It was continuously carried out after the electrochemical cell had consumed a certain amount of charge. After the experiment, a known volume of catholyte was extracted and a series of known amount of hydrogen peroxide was added. The differential pulse voltammetry was recorded again to produce the calibration curve; and the hydrogen peroxide concentration could be determined by back extrapolation.

Hydrogen peroxide generation and determination for the continuous flow electrolysis in [bmim][BF_4]-water or 0.04M NaOH

Fig 2.4 shows the electrochemical micro flow cell (ElectroCell AB, Sweden) of the continuous electrolysis in [bmim][BF_4] with water. The working electrode was a RVC (5mm x 27mm x 33mm) with 60 pores per inch mounted on a solid graphite support. The RVC was glued onto the graphite support by conducting glue made of epoxy adhesive and graphite fine powder. The counter electrode was a platinum plate placed in the anodic compartment, separated by a Nafion® 424 cation permeable membrane. Both compartments were circulated by precision Masterflux pump with constant flow rate connecting with Telfon tubings. The cathodic and anodic compartments had the same volume of 20mL [bmim][BF_4] each containing same proportion of water or 0.04M NaOH. Both cathodic and anodic electrolytes were circulated by pump throughout the experiment. The catholyte was continuously bubbled with oxygen in electrogenerated hydrogen peroxide. At certain time intervals during electrosynthesis typically a 0.1mL reaction mixture was withdrawn from the micro flow cell and the hydrogen peroxide content of the reaction mixture was determined by standard titration with $KMnO_4$ [6, 7].

Hydrogen peroxide generation and determination for the continuous flow electrolysis in [bmim][BF_4]-Na_2CO_3 and $(Et_4N)_2SO_4$

Experimental conditions, procedures and electrochemical setup were the same as the continuous flow electrolysis in [bmim][BF_4]-water or 0.04M NaOH. Both cathodic and anodic compartments had the volume of 20mL [bmim][BF_4] each containing 0.05M Na_2CO_3 or 0.3M $(Et_4N)_2SO_4$ (8:2 v/v). The hydrogen peroxide concentration in [bmim][BF_4]-Na_2CO_3 was also determined by standard titration with $KMnO_4$.

4.3 Experimental-Chapter 3

Typical procedure for the epoxidation of alkene with electrogenerated hydrogen peroxide in [bmim][BF$_4$]

Electrophilic alkene (0.35mmole) was added to 12mL of [bmim][BF$_4$]–NaOH mixture with electrogenerated hydrogen peroxide. The reaction mixture was stirred vigorously at room temperature. When the reaction was completed, the mixture was extracted by diethyl ether (5 x 5ml), dried over sodium sulfate and the solvent was removed by rotary evaporator to give the desired product. The desired products were identified by ^{1}H and ^{13}C NMR. The percentage yields were determined by GC-MS with internal standard.

Recovery and reuse of [bmim][BF$_4$]

After diethyl ether extraction of the epoxides in the first cycle, the recovered [bmim][BF$_4$]-NaOH mixture was put under vacuum to remove the diethyl ether. The recovered [bmim][BF$_4$]-NaOH mixture (1mL) was weighted to obtain the density so as to retrieve the optimized volume ratio of [bmim][BF$_4$] to NaOH (v/v 8:2) according to the calibration curve which is plotted by the density of [bmim][BF$_4$]-NaOH *versus* different volume ratio of [bmim][BF$_4$] to NaOH.

After the suitable amount of water was compensated in the reused [bmim][BF_4]-NaOH mixture to the optimal ratio of v/v 8:2., the electrogeneration of hydrogen peroxide was performed again for the second cycle.

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List of Selected Publications during Master of Philosophy Study

1. Tang, Michael Chi-Yung; Wong, Kwok-Yin; Chan, Tak Hang. **Electrosynthesis of hydrogen peroxide in room temperature ionic liquids and in situ epoxidation of alkenes.** Chemical Communications (Cambridge, United Kingdom) (2005), (10), 1345-1347.
2. Tang, Michael Chi-Yung; Wong, Kwok-Yin; Chan, Tak Hang. **Epoxidation of alkenes with electrogenerated hydrogen peroxide in room temperature ionic liquid.** Abstracts of Papers, 12th Symposim on Chemistry Postgraduate Research in Hong Kong, Hong Kong, April 23, 2005 (2005),
3. Tang, Michael Chi-Yung; Wong, Kwok-Yin; Chan, Tak Hang. **Epoxidation of alkenes with electrogenerated hydrogen peroxide in room temperature ionic liquid.** Abstracts of Papers, 6th Green Chemistry Conference, Barcelona, Spain, November 8-November 10, 2004 (2004),
4. Tang, Michael Chi-Yung; Wong, Kwok-Yin; Chan, Tak Hang. **Electrochemical generation of hydrogen peroxide in room temperature ionic liquid.** Abstracts of Papers, 11th Symposim on Chemistry Postgraduate Research in Hong Kong, Hong Kong, April 17, 2004 (2004),