Full Paper

Electrochemical Generation of Superoxide Ions in five different Fluorine rich Room Temperature Ionic Liquids

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Abstract-Stable superoxide ion $O_2^{\bullet-}$ is electrochemically generated in five room temperature ionic liquids namely 1-hexyl-3-methylimidazolium hexafluorophosphate [hmim][PF_6], 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [bmim] [btfmsi], 1-butyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide [bdmim] [btfmsi], N-butyl-N-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide [N-Bu-N-MePyrr] [btfmsi], 1-butyl-2,3-dimethylimidazolium tetrafluoroborate [bdmim] [BF_4]. Cyclic voltammetry studies were used to check for the short-term stability of $O_2^{\bullet-}$ in these RTIL's. In the absence of impurities, especially water, the $O_2^{\bullet-}$ is stable in these three RTIL's in the timescale of the cyclic voltammetry. The formal potential for the $O_2/ O_2^{\bullet-}$ couple is found to be -0.86 V *vs*. Ag/AgCl reference electrode. Hydrophobicity, Viscosity, Oxygen Solubility and Electrical Conductivity were found to be key parameters in the generation of stable superoxide ions in RTILs.

Keywords- Superoxide, Ionic liquids, Cyclic voltammetry, Oxygen reduction

1-INTRODUCTION

Showed that superoxide can be generated by the reduction of dioxygen in imidazolium chloride – ammonium chloride molten salt. However [1], the superoxide was not stable and could not be used as a reagent for subsequent reactions [2]. Studied the electrochemical reduction of oxygen in two different room temperature ionic liquids, 1-ethyl-3-methylimidazolium bis((trifluoromethyl)-sulfonyl)imide, [emim][N(Tf)$_2$], and hexyltriethylammonium bis((trifluoromethyl)-sulfonyl)imide. They used chronoamperometric measurements to determine the diffusion coefficient and concentration of electroactive oxygen dissolved in the ionic liquid by fitting the experimental transients to the Aoki model. They also determined the diffusion coefficient of the electrogenerated superoxide species. In the ionic liquid hexyltriethylammonium bis(trifluoromethylsulfonyl)imide, both steady state and transient behaviour were observed in the same voltammogram [3]. Investigated the electrochemical reduction of O$_2$ in RTILs consisting of bis(trifluoromethanesulfone)imide anion with trimethyl-n-hexylammonium, 1-butyl-1-methylpyrrolidinium,1-ethyl-3-methylimidazolium or 1,2-dimethyl-3-propylimidazolium cation. They found that the superoxide ion was stable in aliphatic and alicyclic organic cations but reacted with aromatic cations, suggesting that the superoxide ion might be reactive with imidazolium cations [4]. Studied the electroreduction of oxygen to superoxide in a series of room temperature ionic liquids composed of N and P centered cations and anions. They reported electrochemical reduction of oxygen in four RTIL's based on quarternary alkyl –onium cations and heavily fluorinated anions in which the central atom is either nitrogen or phosphorus. Data were collected using cyclic voltammetry and potential step chronoamperometry at gold, platinum and glassy-carbon disk electrodes of micrometer dimensions under water-free conditions at controlled temperatures [5]. studied the quantitativel electrode reaction of the molecular oxygen/superoxide couple at the same three electrodes in three 1-n-alkyl-3-methylimidazolium tetrafluoroborate ionic liquids, specifically, 1-ethyl-3-methylimidazolium tetrafluoroborate, 1-n-propyl-3-methylimidazolium tetrafluoroborate and 1-n-butyl-3-methylimidazolium tetrafluoroborate using cyclic voltammetry, normal pulse voltammetry and hydrodyanamic chronocoulometry (HCC). In another paper [6], studied the electrochemical behavior of oxygen/superoxide couple with the aid of ultramicroelectrode techniques in 1-butyl-1-methylpyrrolidinium bistrifluoromethylsulfonylimide (BMPTFSI). They estimated the diffusion coefficient of oxygen and superoxide and also the formal potential of oxygen/superoxide couple *vs*. ferrocene/ferrocenium couple. They also determined the solubility and the effect of temperature on solubility of O$_2$ in this ionic liquid [7]. studied the superoxide electrochemistry in the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate [bmim][PF$_6$] and in the aprotic solvent acetonitrile (ACN). They also studied the effect of increasing the partial pressure of oxygen on the rate of generation of superoxide. Further,

they showed that the addition of carbon dioxide results in the formation of a carboxylating agent. In another paper [8], demonstrated that superoxide ion is stable in the absence of H_2O in RTILs such as 1-butyl-3-methylimidazolium hexafluorophosphate and 1-butyl-2,3-dimethylimidazolium hexafluorophosphate. They also proposed that this superoxide ion can be used in the low temperature oxidation of wastes [9] demonstrated that stable superoxide ion can be generated in the RTIL N-butyl-N-trimethylammonium bis(trifluoromethylsulfonyl)imide ionic liquid and has effectively been employed in the synthesis of functional siloxanes.

In aprotic media electrochemical measurement is the most simple and precise method for determining the one-electron reduction potential of dioxygen. Therefore, all known values were determined by this method. The most important works were made after the introduction in experimental practice of tetra alkylammonium salts as electrolytes that also made possible the use of electrochemical reduction of dioxygen for the preparation of stable superoxide solutions. The one electron reduction potential of dioxygen in aprotic media is -0.86 V *vs* SCE [10]. Sawyer and co-workers pioneered the work on superoxide, particularly the electrochemical generation of superoxide. A comprehensive review of superoxide chemistry is given in his text [11]. Since $O_2^{\bullet-}$ is a strong nucleophile and it rapidly disproportionates in water to form dioxygen and hydroperoxide ($^{\bullet}OOH$), aprotic solvents were used. The electrochemical behaviour of oxygen and the superoxide ion in non-aqueous solutions has been studied extensively [1-5,15] and it has been shown that stable solutions of $O_2^{\bullet-}$ can be generated in a variety of aprotic media containing tetraalkylammonium salts, in addition, $O_2^{\bullet-}$ undergoes several reactions as a base, nucleophile and a one-electron donor. In these works several techniques including cyclic voltammetry, chronopotentiometry, chronoamperometry and polarography were used to study the one electron reduction of oxygen.

2. EXPERIMENTAL

Cyclic voltammetry (CV) tests were performed using the ionic liquids. The electrochemistry was performed using EG & G 273 A potentiostat/galvanostat controlled by computer and data acquisition software. The electrode configuration consisted of a glassy carbon working electrode (BAS, 3 mm dia) and a platinum mesh counter electrode, both using Ag/AgCl as the reference electrodes. The systems were sparged prior to electrochemical experiments with UHP argon or Nitrogen passed through a drierite gas purification column (W.A. Hammond). The glassy carbon electrode was first polished with 0.1 μ alumina and then rinsed with water, followed by diamond polish. Texmet pads were used for the alumina polish and nylon pads were used for the diamond polish.

Prior to superoxide generation, a nitrogen sparge was used to obtain a background voltammogram. Oxygen was then bubbled through the system for 30 minutes to allow

sufficient solubilization. Between consecutive runs, oxygen gas was bubbled briefly to refresh the system with oxygen and to remove any concentration gradients. The sparging was discontinued during data acquisition. CV tests were run at different scan rates.

3. RESULTS AND DISCUSSION

A select few of the RTILs that have been tested for short-term stability using cyclic voltammetry studies are described below.

1: hexyl-3-methylimidazolium hexafluorophosphate

Fig. 1 below shows the CV of superoxide generation in the RTIL [hmim][PF6] at 60 mV/s. Here, well shaped forward and reverse peaks are obtained, corresponding to the superoxide formation and its corresponding oxidation to molecular oxygen.
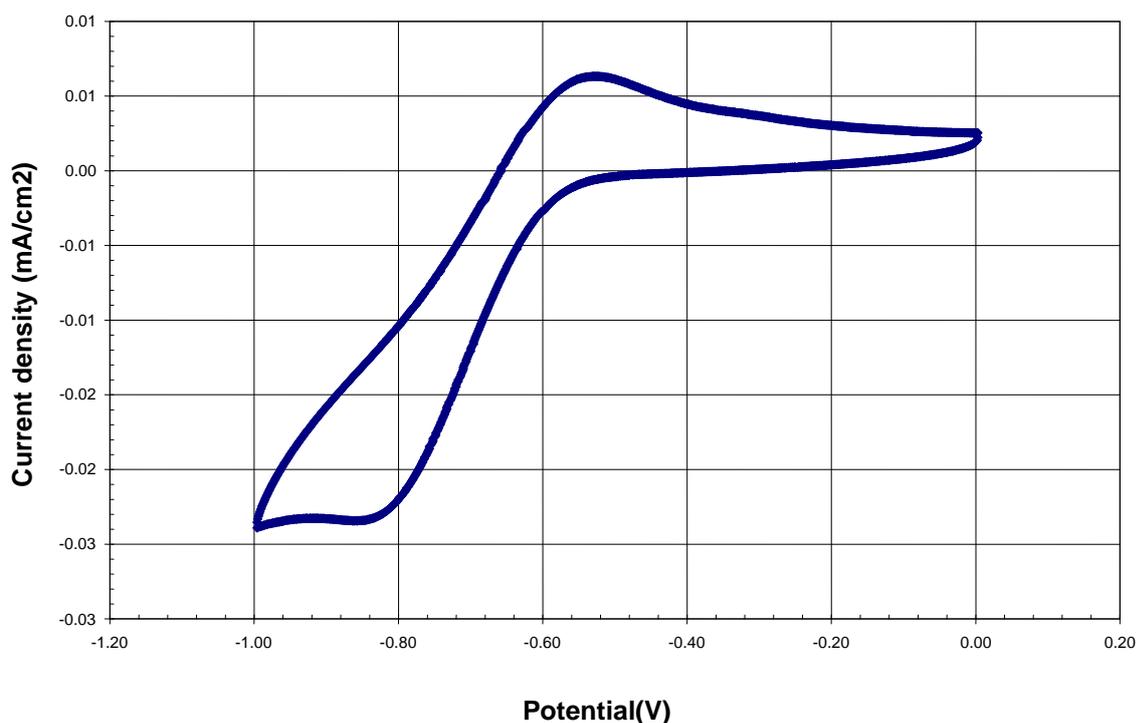

Fig. 1. CV of superoxide generation in the RTIL [hmim][PF$_6$] on a 3 mm glassy carbon(GC) disc electrode at a scan rate of 60 mV/s

2: 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide

Fig. 2 shows CV of superoxide generation in bmim [btfmsi] at different scan rates, specifically 10, 20 30, 40, 50, 60, 70, 80, and 100 mV/s. This ionic liquid demonstrates short-term stability of the superoxide ion.
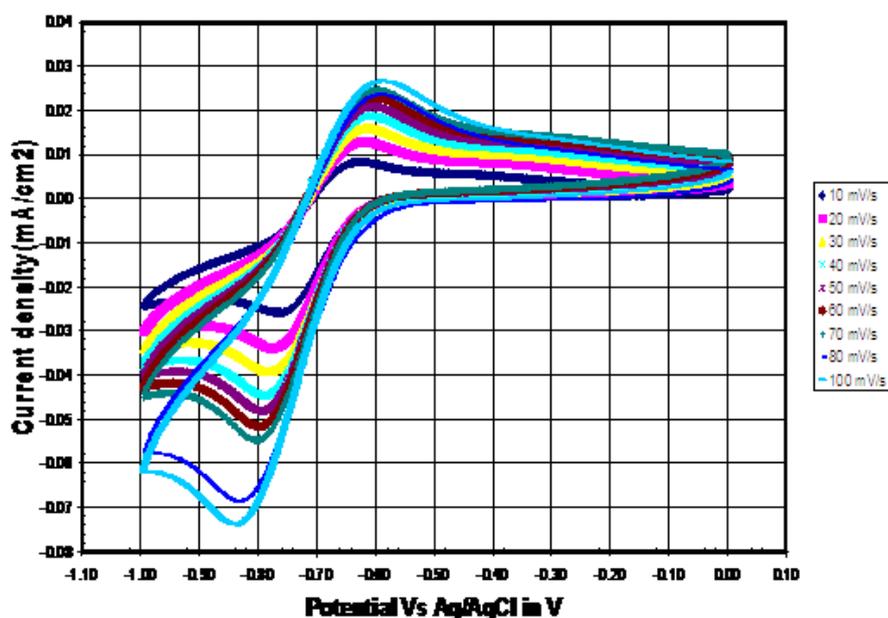
Fig. 2. CV of superoxide generation at 25 °C in the RTIL [bmim][btfmsi] on a 3 mm glassy carbon(GC) disc electrode at different scan rates

    3: 1-butyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide

The CV curves of superoxide generation in the RTIL bmim [btfmsi] at different scan rates namely 20, 40, 60, 80, 100 mV/s are shown below in Fig. 3. This ionic liquid demonstrates short-term stability of superoxide ion.
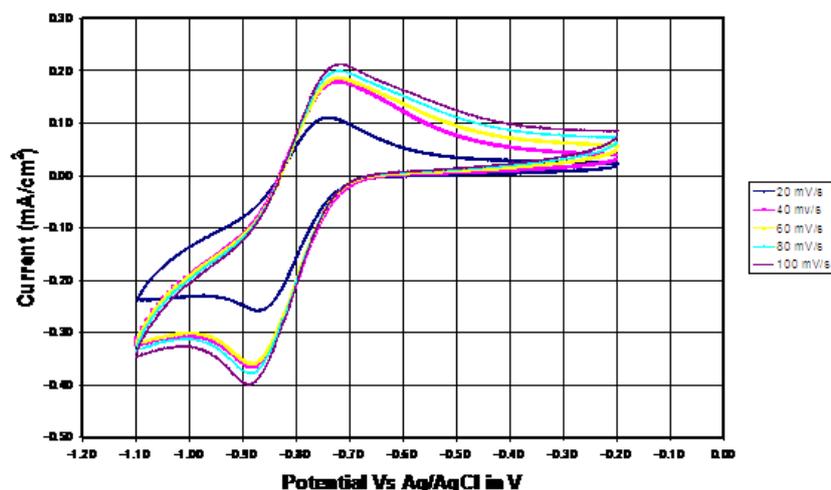

Fig. 3. CV of superoxide generation in the RTIL [bdmim][btfmsi] on a 3 mm glassy carbon(GC) disc electrode at different scan rates at 25 °C

4: N-butyl-N-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide

Fig. 4 below shows the CV curves of superoxide generation in the RTIL bmim [btfmsi] at scan rates namely 20, 40, 60, 80, and 100 mV/s. This ionic liquid demonstrates short-term stability of superoxide ion.
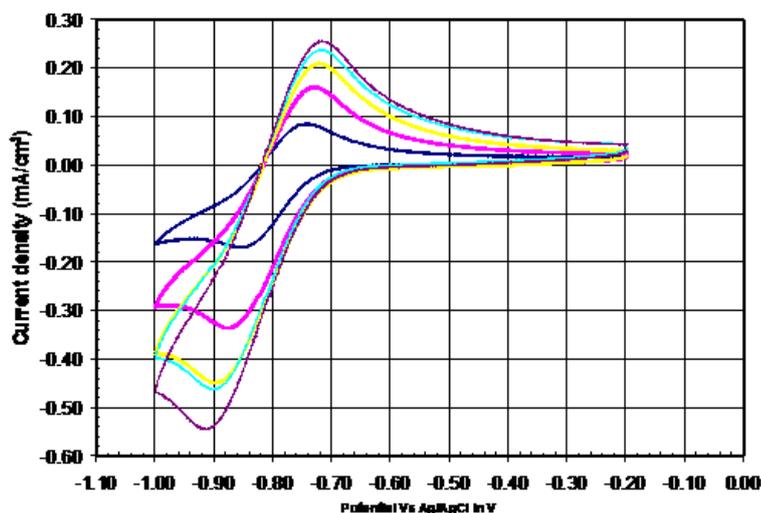

Fig. 4. CV curves of superoxide generation at 25 $^\circ$C in the RTIL [bmpyrr][btfmsi] on a 3 mm glassy carbon(GC) disc electrode at different scan rates

5: 1-butyl-3-methylimidazolium tetrafluoroborate

Fig. 5 below shows the CV of superoxide ion generation in the IL [bmim][BF$_4$] at scan rates of 20, 40, 60, 80 and 100 mV/s.
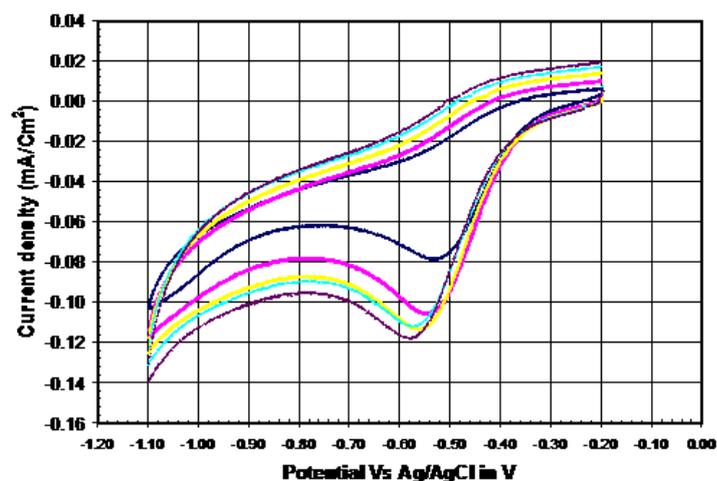

Fig. 5. CV curves of superoxide generation at 25 $^\circ$C in the RTIL [Bmim][BF$_4$] on a 3 mm glassy carbon(GC) disc electrode at different scan rates

6: 1-butyl-2,3-dimethylimidazolium tetrafluoroborate

In Figure 6 below we show the CV of superoxide ion generation in the IL [bmim][BF$_4$] at scan rates of 20, 40, 60, 80 and 100 mV/s.
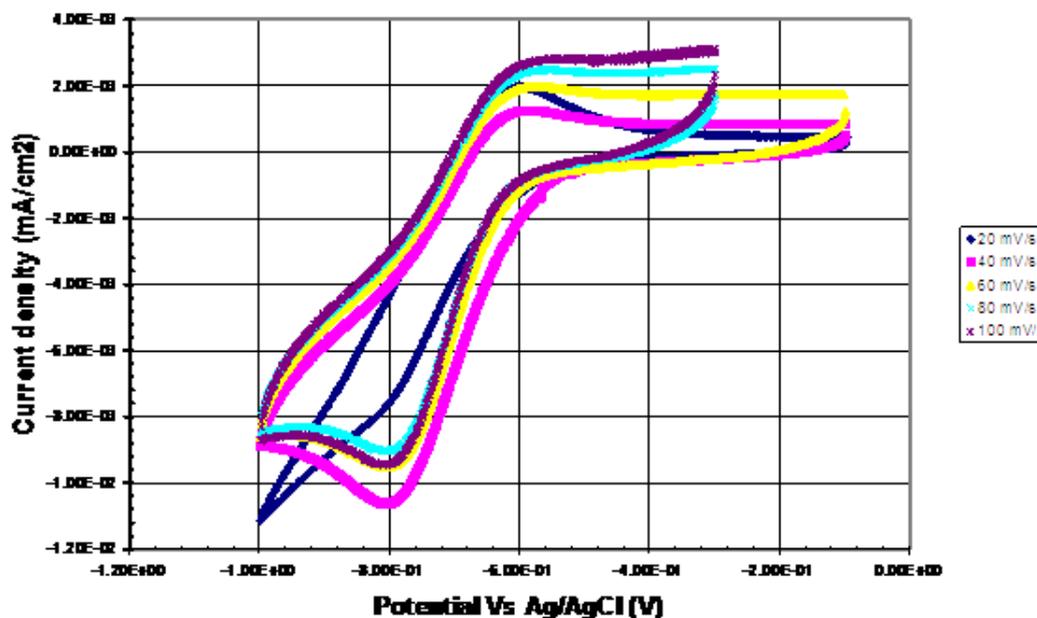

Fig. 6. CV curves of superoxide generation at 40 $^{\circ}$C in the RTIL [Bdmim][BF$_4$] on a 3 mm glassy carbon(GC) disc electrode at different scan rates

4. CONCLUSIONS

Several RTIL's that show short-term stability in the presence of electrochemically generated superoxide ions were identified. For the RTILs [bmim][PF$_6$], [hmim][PF$_6$], [bmim][BTFMSI], [bdmim][BTFMSI], [N-Bu-N-Me Pyrr][BTFMSI] and [bdmim][BF$_4$], the superoxide ion generated in the forward scan was stable in the reverse scan. For [bdmim][PF$_6$], water removal was required to obtain a well shaped peak. For [bmim][BF$_4$], the superoxide ion generated in the forward scan was not stable in the reverse scan, which may be due to its miscibility with water, as reported by others. The RTILs having [PF$_6$] and [BTFMSI] anions have greater hydrophobicity, favoring formation of stable superoxide ions. Other factors which affect the generation of stable superoxide are the solubility of oxygen, viscosity and electrical conductivity.

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