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Electrochemical Generation of Superoxide in Room-Temperature Ionic Liquids

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We have demonstrated that superoxide ion can be generated electrochemically in room-temperature ionic-liquid solvents. In the absence of impurities, cyclic voltammetry showed that the super oxide ion is stable in these solvents. Similar superoxide ion chemistry has previously been demonstrated in volatile and environmentally suspect aprotic solvents such as dimethyl formamide and acetonitrile. However, ionic liquids are nonvolatile and should minimize the problems of secondary solvent waste. It is proposed that the resultant superoxide ion can be used to perform low-temperature oxidation of wastes. Low-temperature oxidation of waste solvents can provide a much needed alternative to high-temperature waste incinerators, whose use is greatly complicated by regulatory requirements and locating suitable sites.

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Sawyer and co-workers¹⁻³ pioneered work on superoxide ion ($O_2^{\bullet-}$), particularly the direct electrochemical reduction of dissolved oxygen gas in aprotic solvents to form $O_2^{\bullet-}$ according to the following reaction



A comprehensive review of superoxide ion chemistry is given by Sawyer *et al.*⁴ Superoxide ion can be formed directly from solvation of K_2O in aprotic solvents, or electrochemically via direct cathodic reduction of dioxygen (typically $E = -1.0$ V vs. SCE).⁵ $O_2^{\bullet-}$ is a strong nucleophile and disproportionates in water to O_2 and hydroperoxide



For this reason, generation and utilization of $O_2^{\bullet-}$ must be done in aprotic solvents. Acetonitrile (MeCN), dimethyl formamide (DMF), and dimethyl sulfoxide (DMSO) are commonly used. The superoxide ion can degrade polychlorinated aromatics and polychlorinated biphenyls (PCBs) to bicarbonates and chlorides.^{2,3,6}

Room-temperature ionic liquids (RTILs) are stable mixtures of an organic cation/anion salt with an inorganic salt.⁷ They are directly related to more familiar high-temperature molten salts that are used, for example, as heat transfer media. Early work on RTILs in electrochemistry focused on their use as an electrolyte for advanced battery systems. Certain RTILs are electrically stable over a range of 2-4 V and higher, are thermally stable, and are resistant to oxidation. Various electrochemical syntheses have been attempted, including polymerization of arenes to form conducting polymers,⁸ polymerization of benzene to poly(*p*-phenylenes),⁹⁻¹¹ oligomerization of anthracene,¹² and preparation of silane polymer films.¹³ More fundamental studies on redox reaction kinetics and behavior in RTILs have been done for anthracene,¹⁴ methylanthracene,¹⁵ and other aromatics.¹⁶⁻¹⁸ It is clear that some RTILs can be used to support electrochemistry. Osteryoung *et al.*¹⁹ showed that superoxide ion could be generated by the reduction of dioxygen in imidazolium chloride-aluminum chloride molten salt. However, the resulting superoxide ion was unstable and thus cannot be used as a reagent in subsequent reactions.

In this paper, we also show that superoxide ion can be generated via Reaction 1 in RTIL solvents. In addition, we show, using cyclic voltammetry (CV), that in the absence of impurities, the superoxide ion is stable in these solvents. As far as we are aware, this is the first

time the generation of stable superoxide ions in ionic liquids is reported. Blanchard and Brennecke²⁰ showed that halogen-carbon compounds are soluble in RTILs. These findings offer promise that electrochemical oxidation of chlorinated compounds in ionic liquid media may be an environmentally acceptable route for destruction of these pollutants.

Experimental

CV tests were performed on the aprotic solvent system tetraethylammonium perchlorate (TEAP, 0.1 M) in acetonitrile (MeCN) and in the ionic liquids 1-*n*-butyl-3-methylimidazolium hexafluorophosphate, [bmim][HFP], and 1,2-dimethyl-3-*n*-butylimidazolium hexafluorophosphate, [dmbim][HFP]. TEAP (GFS Chemicals) was dried overnight in a vacuum oven at 40°C, HPLC grade MeCN (Fisher Scientific) was used as provided, and [bmim][HFP], [dmbim][HFP] (SACHEM), both with a stated purity of 97%, were dried overnight in a vacuum oven at 50°C. The electrochemistry was performed using an EG&G 263A potentiostat/galvanostat controlled by computer and data acquisition software. The electrode configuration was a glassy carbon working (BAS, 3 mm diam) and a platinum mesh counter (Aldrich) using SCE and Ag/AgCl references (both Fisher Scientific) for the experiments in MeCN and [bmim][HFP], [dmbim][HFP], respectively. The MeCN sample was sealed or handled under nitrogen sparge to prevent water contamination. All [bmim][HFP] and [dmbim][HFP] experiments were performed in a dry glove box under an argon atmosphere. The systems were sparged prior to electrochemical experiments with ultrahigh purity (UHP) nitrogen or oxygen fitted through a Drierite gas purification column (W. A. Hammond).

Prior to superoxide ion generation, a nitrogen sparge was used while obtaining a background voltammogram. Oxygen was then bubbled through the system for 30 min to allow sufficient solubilization. Between consecutive CV runs, oxygen was bubbled briefly to refresh the system with oxygen and to remove any concentration gradients. Nitrogen or oxygen sparging was discontinued during the CV data acquisition.

Results and Discussion

Figure 1 shows CVs in (a) 0.1 M TEAP/MeCN and (b) [bmim][HFP]. Reduction currents are positive throughout this paper. The CVs were run with nitrogen and oxygen sparging. In MeCN, the presence of oxygen results in a faradic reduction and oxidation peaks at -1.00 and -0.72 V vs. SCE, respectively. This CV is consistent with that obtained by Sawyer *et al.*⁴ They concluded that the reduction peak is due to the generation of superoxide ion according to Reaction 1 and the oxidation peak due to the reverse of Reaction 1. The negligible background current in the presence of nitrogen indicates that the solvent is stable under these conditions.

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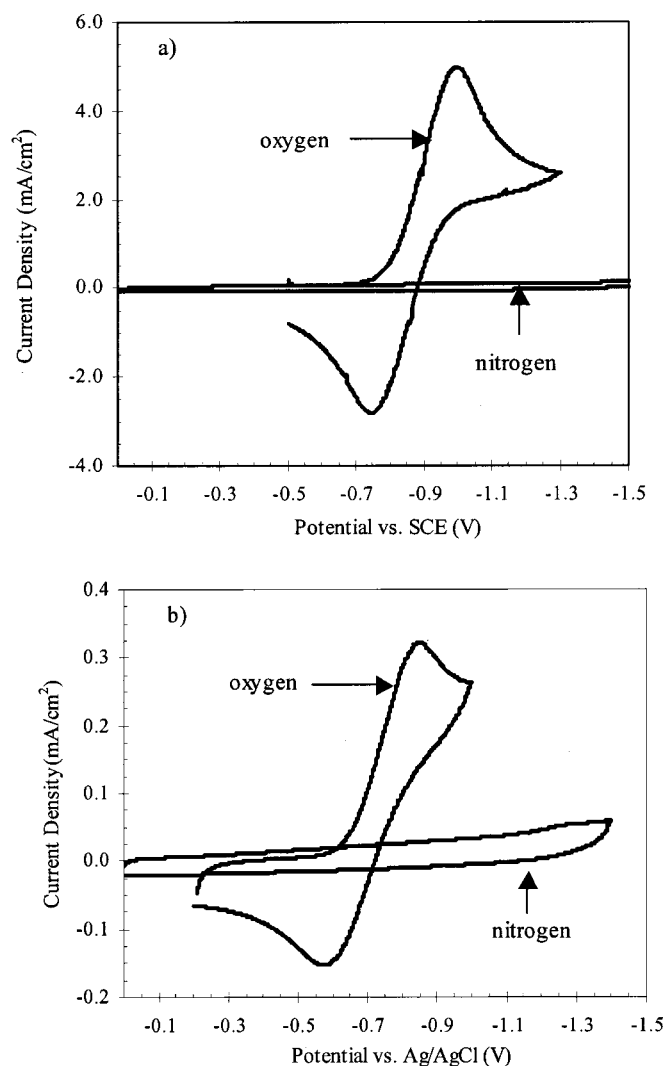


Figure 1. CVs with nitrogen and oxygen sparging in (a) 0.1 M TEAP in MeCN and (b) [bmim][HFP]. All scans used a glassy carbon working electrode at a scan rate of 100 mV/s.

In [bmim][HFP], Fig. 1b, the presence of oxygen showed a reduction peak at approximately -0.86 V and an oxidation peak at -0.54 V vs. Ag/AgCl. Sawyer *et al.*⁴ showed that the solvent and electrode materials can effect the reversibility and peak separation of the CVs. The reduction potential for $O_2/O_2^{\cdot-}$ couple shifts to more negative values as the solvating properties of the solvent decrease. The variation in the peak potential for $O_2/O_2^{\cdot-}$ in MeCN and [bmim][HFP] is small enough that the peaks seen in the two solvents are consistent with Reaction 1. The current density for the O_2 /MeCN system, however, is more than an order of magnitude larger than that in the O_2 /[bmim][HFP] system. The background currents in the two reaction medium are comparable, which indicates that the ionic liquid is also electrochemically stable.

To further quantify the difference in magnitude of the currents in Fig. 1, CVs were run in 0.1 M TEAP/MeCN and [bmim][HFP] for several scan rates, 9, 16, 25, 36, 49, 64, 81, and 100 mV/s. Four of the scans in [bmim][HFP] are shown in Fig. 2. In both solvents, the peak currents and peak potentials are proportional to the square root and the log of the sweep rate, respectively. This is consistent with the electrochemistry of a kinetically irreversible soluble redox couple.²¹ Plotting the peak potential vs. the log of the sweep rate gives a cathodic transfer coefficient for Reaction 1 of $\alpha_c = 0.31$. This is then used, along with the solubility of oxygen in MeCN of

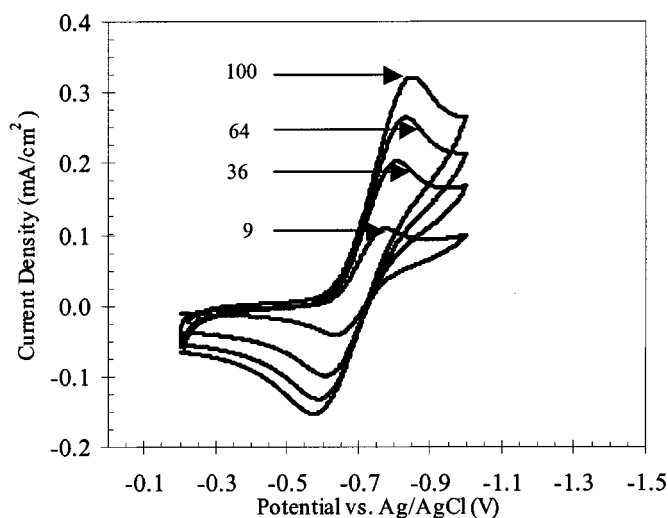


Figure 2. CVs for various scan rates (mV/s) in [bmim][HFP] with oxygen. The working electrode was glassy carbon and the reference electrode was Ag/AgCl.

8.1 mM^4 and the peak current data, to obtain an O_2 diffusion coefficient of $D_{O_2} = 2.1 \times 10^{-4} \text{ cm}^2/\text{s}$. A similar procedure in [bmim][HFP] gives $\alpha_c = 0.42$ and $D_{O_2} = 2.2 \times 10^{-6} \text{ cm}^2/\text{s}$ (the solubility of oxygen in [bmim][HFP] at room temperature is 3.6 mM^{22}). The two orders of magnitude difference in diffusion coefficient is consistent with the fact that the viscosity of MeCN (0.345 cP^{23}) is an order of magnitude lower than that of [bmim][HFP] (312 cP^{24}).

The cathode scan in Fig. 1b shows that $O_2^{\cdot-}$ can be generated in RTILs, and the reverse scan shows that $O_2^{\cdot-}$ is stable. Figure 3 shows CVs at 37°C in [bmim][HFP] and [dmbim][HFP]. An elevated temperature was chosen for these CVs because [dmbim][HFP] has a melting point of 30°C . The nitrogen background shows comparable currents, indicating both RTILs are electrochemically stable. For oxygen in [bmim][HFP], the elevated temperature caused a slight shift in the reduction and oxidation peaks toward more positive potentials, but the qualitative features of the CV are not affected by temperature. That is, Reaction 1 produces a

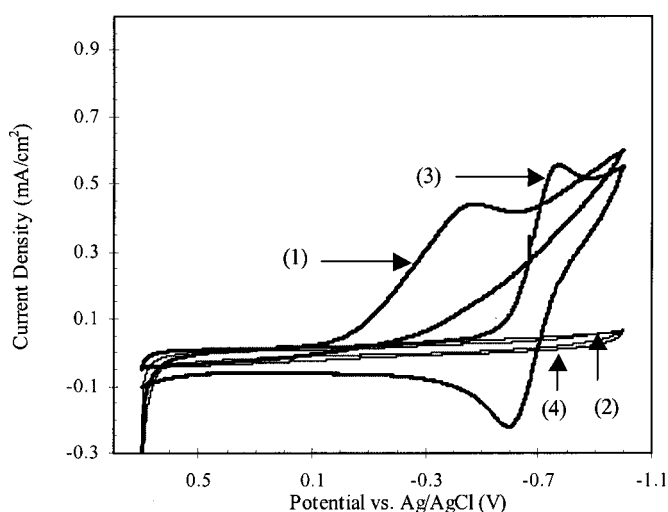


Figure 3. CVs at 37°C in (1) [dmbim][HFP] with oxygen, (2) [dmbim][HFP] with nitrogen, (3) [bmim][HFP] with oxygen, and (4) [bmim][HFP] with nitrogen, all at 100 mV/s scan rate. The working electrode was glassy carbon and the reference electrode was Ag/AgCl.

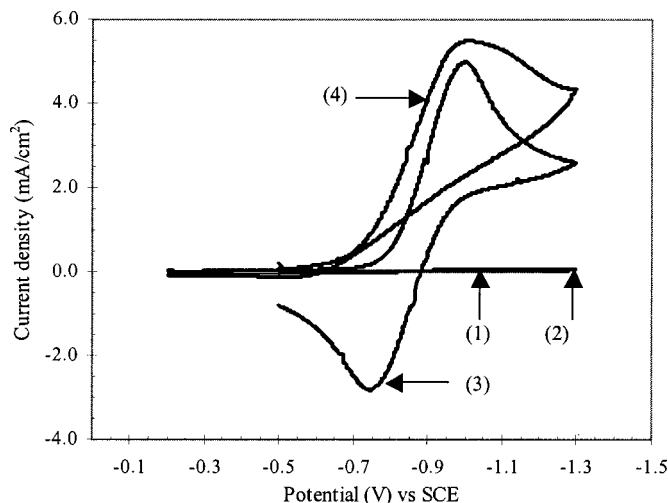


Figure 4. Effect of water on the stability of superoxide ion in MeCN (0.1 M TEAP). The working electrode was glassy carbon, the reference electrode was Ag/AgCl, and the scan rate was 100 mV/s. (1) Nitrogen, (2) nitrogen with 3.2% by weight water, (3) oxygen without water, and (4) oxygen with 3.2% by weight water.

symmetric CV. For [dmbim][HFP] in the presence of oxygen, an ill-defined reduction peak at approximately -0.46 V vs. Ag/AgCl is observed. In addition, the scans showed no reverse (oxidation) peak. This indicates that the superoxide ion generated in the forward scan is not stable in this ionic liquid as received. Carter *et al.*¹⁹ reported the absence of the reverse peak for the system 1-ethyl-3-methylimidazolium chloride mixed with AlCl_3 and attributed this to inadvertent introduction of protons while conducting their experiments.

To estimate the sensitivity of the oxidation peak resulting from Reaction 1 to an additive, a small quantity of deionized water was added to the 0.1 M TEAP/MeCN solution. The resulting CVs are shown in Fig. 4. The background currents run with and without the addition of water resulted in comparable currents. Therefore, the water was not electrochemically active on glassy carbon in this potential window. When O_2 was bubbled through the solvent, a slight increase in the current due to the production of the superoxide was observed. A more dramatic result was seen in the reverse scan. In the presence of 3.2% water, no oxidation current was observed even at a positive potential of 0.5 V. Reaction 2 consumed the superoxide, thus preventing the reverse of Reaction 1 to occur. The CVs in the presence of water and O_2 is qualitatively similar to that seen for O_2 in [dmbim][HFP] (see curve 1, Fig. 3). The only difference between these two ionic liquids, Fig. 5, is the additional methyl group in position 2 for [dmbim][HFP]. Both ionic liquids should have comparable proton acidity; therefore, it is doubtful that the protons on [dmbim][HFP] are reacting with the superoxide ion. Rather, the instability of the superoxide ion is believed to be due to the presence of impurities in the RTIL, even though the stated impurities of the two RTILs were 3%.

Conclusions

Preliminary experiments with the RTIL, 1-butyl-3-methylimidazolium hexafluorophosphate [bmim][HFP], showed promise that this solvent was capable of supporting the electrochemical generation of a stable superoxide ion. This finding may lead to new

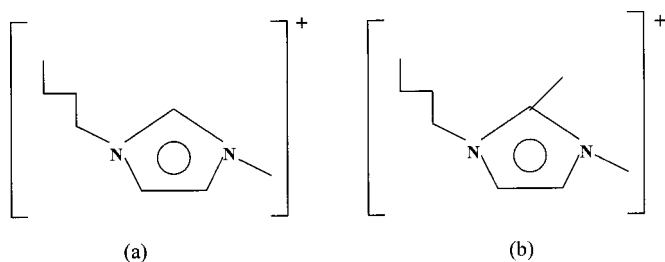


Figure 5. Structure of (a) 1-*n*-butyl-3-methylimidazolium and (b) 1,2-dimethyl-3-*n*-butylimidazolium cations.

routes for electrochemical oxidation of chlorinated compounds in ionic liquid media. The presence of impurities can have a dramatic effect on the stability of the superoxide ion in the ionic liquid. Therefore, work is continuing on controlling the levels of impurities in the RTILs.

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