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Electrochemical reduction of dioxygen in Bis (trifluoromethylsulfonyl) imide based ionic liquids

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ABSTRACT

Electrochemical generation of superoxide ion ($O_2^{\cdot-}$) has been investigated in three room temperature ionic liquids (ILs), based on bis (trifluoromethylsulfonyl) imide anion, $[N(Tf)_2]^-$, comprising the following cations N-(3-Hydroxypropyl)pyridinium, $[HPPy]^+$, 1-(3-methoxypropyl)-1-methylpiperidinium, $[MOPMPip]^+$, and 1-hexyl-1-methyl-pyrrolidinium, $[HMPyrr]^+$. Cyclic voltammetry (CV) and chronoamperometry (CA) techniques were used for the analysis of the the electrochemical process. It was found that the generated $O_2^{\cdot-}$ was not stable in the IL based on pyridinium cation, $[HPPy]^+$. While a stable $O_2^{\cdot-}$ was electrochemically generated in $[MOPMPip]^+$ and $[HMPyrr]^+$ based ILs. CV and CA techniques were used to determine the diffusion coefficients of O_2 and solubility of oxygen in the studied ILs as a function of temperature. The diffusional activation energies were then determined. It was found that $[HMPyrr]^+$ based IL, in general, has higher diffusion coefficient and solubility of O_2 and less diffusional activation energy than $[MOPMPip]^+$ based IL. For our best knowledge, this is the first time piperidinium based ILs has been used for the electrochemical generation of $O_2^{\cdot-}$.

1. Introduction

The electrochemical behavior of O_2 in ILs is important for various applications, including fuel cells, metal–air batteries, electrolytic synthesis of organic compounds, electro-synthesis of reactive oxygen species, such as the superoxide ($O_2^{\cdot-}$) and hydrogen peroxide (H_2O_2) [68,36].

Superoxide ion has been known since 1934, where Haber and Weiss have proposed that $O_2^{\cdot-}$ is formed in the decomposition of hydrogen peroxide and in the oxidation of ferrous ions by dioxygen in aqueous solutions [23].

Superoxide ion can be generated either chemically by solvation of potassium superoxide (KO_2) in aprotic solvents, or electrochemically via direct electrochemical reduction of dioxygen in aprotic organic solvents (typically $E = -1.0$ V vs. SCE) in the absence of water or protonic species [56,59]. Many aprotic solvents have been used as conventional media for the reduction of oxygen. These include dimethyl sulfoxide (DMSO) [50,66,30], dimethyl formamide (DMF) [50,33,66,67], acetonitrile [50,33,3,49,66], propylene carbonate [26], and acetone [50]. Superoxide is not super as an oxidant but it behaves as a strong nucleophile in aprotic media [58,62].

Many studies have been done on applications of $O_2^{\cdot-}$ such as destruction of polyhalogenated aromatic hydrocarbons (e.g., PCB's and HCB) [63,34,20], dichloroethene, trichloroethene, and tetrachloroethene in DMF or acetonitrile [11]; reduction of sulfur dioxide (SO_2) in DMF [42], reduction of elemental sulfur in DMSO [45]; nucleophilic oxygenation of carbon dioxide to form the peroxydicarbonate $C_2O_6^{2-}$ species [52,13]; reaction with vitamin K_1 and its related compounds in the presence of crown ether to produce the corresponding 2,3-oxide and phthalic acid [55]; reaction with 3,5-di-tert-butylcatechol ($DTBCH_2$), ascorbic acid, dihydrophenazine, and dihydrolumiflavin to produce their respective anion radicals [57]; reaction with 1,2-disubstituted hydrazines to produce the anion radical of the 1,2-disubstituted azo compound [10]; oxidation of primary and secondary alcohols to the corresponding carboxylic acids and ketones respectively [61,1].

However, due to the limitations of using aprotic solvents in terms of high volatility, low boiling points, and the negative ecological effects, no industrial implementation of the superoxide ion have been adopted.

Recently, ionic liquids (ILs) have become promising alternative solvents for conducting electrochemical investigations, and the reduction of oxygen [18]. Several book chapters and review articles dealing with the application of ILs in electrochemical sciences are

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available [60,22,24,65,38,40,64]. Ionic liquids have a negligible vapor pressure, and their non-volatility allows greener synthesis with reduced environmental impacts, in contrast to volatile organic solvents [16,41,25].

Carter et al. [12] were the first to show that superoxide ion could be generated by the reduction of dioxygen in ionic liquid imidizalium chloride–aluminum chloride. However, the resulting superoxide ion was unstable [12]. In a subsequent study, AlNashef and co-researchers reported the first evidence for a stable generation of $O_2^{\cdot -}$ in imidazolium based ionic liquid 1-methyl-3-*n*-butylimidazolium hexafluorophosphate [2].

Subsequently, many studies have been carried out on ILs based on imidazolium, quaternary ammonium, quaternary phosphonium, and pyrrolidinium cations [8,35,21,6,32,27,51,53]. It was found that the stability of the generated superoxide ion depends strongly on the type of the cation of the IL. For example, Evans et al. [18] and Hayyan et al. [25] reported that $O_2^{\cdot -}$ reacted with quaternary phosphonium cations [18,25]. Other research groups reported that $O_2^{\cdot -}$ is not stable in imidazolium based ILs [35,31,1]. AlNashef et al. [1] found that the superoxide ion reacted with the imidazolium cation of many ILs to give the corresponding 2-imidazolones [1]. So, although cyclic voltammetry may indicate short-term stability of $O_2^{\cdot -}$ in ILs, CVs may not be effective screening criteria for long-term stability. Rather, bulk electrolysis and appropriate analytical techniques are required.

The electrochemical reduction of oxygen was investigated in some ILs consisting of $[N(Tf)_2]^-$ anion [8,9,18,35,36,51,53].

Katayama et al. [35] investigated the electrochemical reduction of oxygen in some hydrophobic ILs 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 against the aliphatic and alicyclic organic cations but reacted with the aromatic ones. They suggested that nucleophilic reagents attack the imidazolium cations [35].

Huang et al. [27] studied the reduction of oxygen under different temperatures by cyclic voltammetry and potential-step chronoamperometry in six ILs consisting imidazolium, pyrrolidinium, and ammonium cations with bis (trifluoromethanesulfonyl) imide, tetrafluoroborate, and hexafluorophosphate anions. They reported diffusion coefficients and solubilities of oxygen in these media, and they observed an approximate relationship when analyzed in terms of Stokes–Einstein behavior for O_2 in all studied ILs [27].

Zigah et al. [69] used the one-electron reduction of oxygen as a probe system for studying the effects of the addition of a co-solvent such as DMF into a pure ionic liquid triethylbutylammonium bis (trifluoromethylsulfonyl) imide, they utilized scanning electrochemical microscopy (SECM) to obtain the diffusion coefficient ratios and the absolute values of the diffusion coefficients of the redox couple $O_2/O_2^{\cdot -}$, which are different because of their different interactions with the ions of the IL. The authors found that all of the values of diffusion coefficient ratio, diffusion coefficient of $O_2^{\cdot -}$, and diffusion coefficient of O_2 to vary exponentially with the increase of the co-solvent volume fractions. However, the diffusion coefficient $O_2^{\cdot -}$ was found to change on a much larger range than diffusion coefficient of O_2 (around 1000 times more), in line with the expected strong ionic interactions between $O_2^{\cdot -}$ and the IL cation [69].

Buzzeo et al. [8] reported interesting results for the *n*-hexyltriethylammonium bis (trifluoromethylsulfonyl) imide IL [N6222] $[N(Tf)_2]$, in which the diffusion coefficients of oxygen and superoxide ion were found to differ by more than a factor of 30, giving rise to a pronounced asymmetry in the forward and backward voltammetric waves; both transient and steady-state behavior was observed in a single voltammogram [8]. Evans et al. [18] reported that the superoxide diffusion coefficients in ammonium based ILs are over an order of magnitude lower than those of oxygen in the same media. They suggested that this because of the difference in the strength of the Coulombic forces between these highly ionic solvents and the neutral oxygen molecule and superoxide radical anion, respectively. In any case, the combination of this disparity in the diffusion rates of the reduced and oxidized species with a disk electrode of appropriate radius explains the observed asymmetry in the voltammetry of this system. Over the same experimental time scale, the faster diffusion rate of oxygen causes a spherical diffusion layer to develop at the electrode surface leading to steady-state behavior, whereas supply of the more slowly moving superoxide is always dominated by planar diffusion normal to the surface, resulting in a peak-shaped transient reverse wave [18].

In the present work we investigated the electrochemical generation of $O_2^{\cdot -}$ in new cations based ILs, namely; pyridinium, and piperidinium, as well as pyrrolidinium cations for comparison. The anion in all cases was bis (trifluoromethylsulfonyl) imide. This anion was selected because it gives wide electrochemical window (EW) for the ILs based on it [29,48,54]. Moreover, it is a hydrophobic anion [28,17,37,48], and hence its water content will be less than that of hydrophilic ILs. The presence of water is known to decrease the electrochemical window [48]. In addition, $O_2^{\cdot -}$ disproportionates in the presence of water to O_2 and hydroperoxide, Eq. (1) [14,59,2].

$$2O_2^{\cdot -} + H_2O \rightarrow O_2 + HOO^- + HO^- \qquad (1)$$

2. Experimental methodology

2.1. Materials used

The ILs used in this study are: N-(3-Hydroxypropyl)pyridinium bis (trifluoromethylsulfonyl) imide, $[HPPy][N(Tf)_2]$, 1-(3-methoxypropyl)-1-methylpiperidinium bis (trifluoromethylsulfonyl) imide, $[MOPMPip][N(Tf)_2]$, and 1-hexyl-1-methyl-pyrrolidinium bis (trifluoromethylsulfonyl) imide $[HMPyrr][N(Tf)_2]$. All ILs were of synthesis grade from MERCK. Scheme 1 shows the chemical structures of the used ILs, while their chemical formulas, molecular weights, and melting points are listed in Table 1.

2.2. Electrochemical reduction of dioxygen

Cyclic voltammetry (CV) experiments were conducted in a one compartment cell since the time of the experiment is relatively small to affect the ILs. All ILs were dried overnight in a vacuum oven at 50 °C before use. The electrochemistry was performed using EG&G 263A potentiostat/galvanostat controlled by computer and data acquisition software.

Glassy carbon macro-disk-electrode (BASi, 3 mm diam.) was used as working electrode for cyclic voltammetry while carbon fiber (CF) ultramicro-electrode (BASi, 11 μm diam) was used for chronoamperometry. Platinum electrode was used as a counter electrode, while Ag/AgCl electrode (BASi) was used as a reference electrode. All experiments were performed in a dry glove box under either an argon or helium atmosphere (both ultra-high pure). Prior to the superoxide ion generation, a nitrogen sparge was used before obtaining a background voltammogram. Oxygen was then bubbled through the system for at least 30 min before final measurements were taken to ensure that equilibration of the gas and the ionic liquid had been established [2,8,7,15], in order to confirm that saturation of O_2 was reached, CVs at different time intervals were conducted and the peak current of the CVs compared. Between consecutive CV runs, O_2 was bubbled briefly to refresh the system with oxygen and to remove any concentration gradients.