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Irreversible One-Electron Reduction of Dioxygen in Ionic Liquid Containing Olefinic Substituents

Md. Mominul Islam[1], Shimpei Kojima[2], Begum Nadira ferdousi[3] Ferdousi[3] and Takeo Ohsaka[4,]*

[1]Department of Chemistry, Faculty of Science, University of Dhaka, Dhaka 1000, Bangladesh
[2] Bio-medical Engineering Laboratories, Teijin Pharma Ltd, 4-3-2, Asahigaoka, Hino, Tokyo 191-8512, Japan
[3] Department of Arts and Sciences, Ahsanullah University of Sciences and Technology, 141-142 Love Road, Tejgaon Industrial Area ,Dhaka 1208, Bangladesh
[4] Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, Mail Box G1-5, 4259 Nagatsuta, Midori-ku, Yokohama 226-8502, Japan
[*]E-mail: ohsaka@echem.titech.ac.jp

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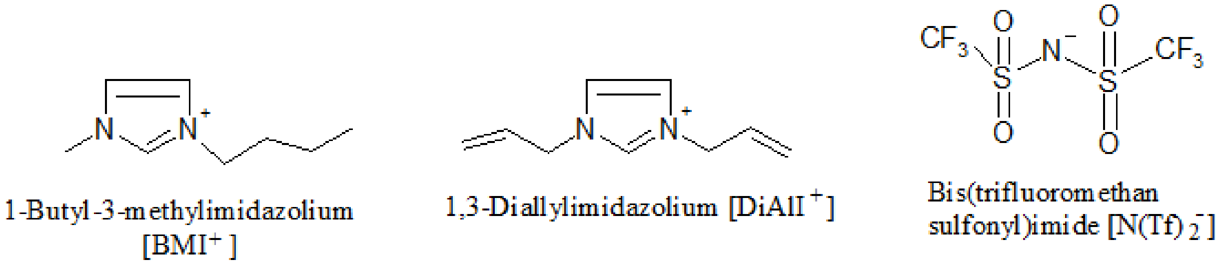
We observed for the first time an irreversible one-electron oxygen (O_2) reduction reaction (ORR) in an ionic liquid (IL) containing olefinic substituents, 1,3-diallylimidazolium bis(trifluoromethansulfonyl)imide ($[DiAlI^+][N(Tf)_2^-]$). Cyclic voltammograms measured for the ORR at glassy carbon, gold and platinum electrodes in the potential range of 0 → –1.3 → 0 V in $[DiAlI^+][N(Tf)_2^-]$ were observed with an irreversible cathodic peak at –0.95 V vs. Ag wire, while a quasi-reversible redox response for the O_2/superoxide ion ($O_2^{\bullet-}$) couple at a formal potential of –0.87 V was obtained in an analogous IL, $[BMI^+][N(Tf)_2^-]$ ($[BMI^+]$: 1-butyl-3-methylimidazolium). The plot of current density (*j*) of the cathodic peak vs. square root of potential scan rate in $[DiAlI^+][N(Tf)_2^-]$ was found to be a straight line passing through the origin, suggesting that the ORR in $[DiAlI^+][N(Tf)_2^-]$ is diffusion-controlled. By examining the effect of water on the ORR, its irreversibility was justified not to result from the protonic impurity in $[DiAlI^+][N(Tf)_2^-]$. The number of electrons involved in the ORR was confirmed to be one by comparing the experimental chronoamperometric current-time *(j-t)* curve with that derived theoretically. The saturated concentration and diffusion coefficient of O_2 were simultaneously determined to be 1.6 mM and 1.3×10^{-4} cm^2 s^{-1}, respectively, via a computer simulation of the *j-t* curve. The one-electron reduction product of O_2 (i.e., $O_2^{\bullet-}$ species) was proposed to undergo a follow-up reaction with the allyl group of $[DiAlI^+]$ to form an "intermediate". Using a double-potential step chronoamperometric technique, the rate constant of this reaction was estimated to be 0.1 M^{-1} s^{-1}.

Keywords: Irreversible oxygen reduction; Ionic liquids; Reaction of superoxide ion with olefin; Cyclic voltametry; Double-potential step chronoamperometry

1. INTRODUCTION

Dioxygen (O_2) reduction reaction (ORR), which has a great importance in many practical applications including industrial, environmental, fuel cells and biological purposes, has been extensively studied in different media (e.g., aqueous, non-aqueous and aprotic solutions and ionic liquids (ILs) (Scheme 1)) [1-20].



Scheme 1. Structures of cations and anion of ILs used in this study.

In aprotic solutions, the first step of ORR is a redox reaction of the $O_2/O_2^{\bullet-}$ (superoxide ion) couple (Eq. (1)), while the second step is an irreversible, one-electron reduction of $O_2^{\bullet-}$ to form peroxide species (Eq. (2)) [1-3,15,18]. So far, similar mechanism has been reported to prevail in various ILs [7-18], except for ion-paring phenomenon [18], two-electron ORR in phosphonium cation-based ILs [13,14] and two-electron ORR only at mercury electrode in imidazolium cation-based ILs (ImILs) [7]. AlNashef et al. have first observed the cyclic voltammetric redox peaks of the $O_2/O_2^{\bullet-}$ couple at platinum (Pt), gold (Au) and glassy carbon (GC) electrodes in ImILs [9,10]. Recently, ILs have been employed as the alternative of to volatile organic solvents (e.g., dimethylsulfoxide and acetonitrile) for in situ synthesis of $O_2^{\bullet-}$ used in different applications [10,14,15,21-25].

$$O_2 + e^- \rightleftharpoons O_2^{\bullet-} \qquad (1)$$

$$O_2^{\bullet-} + e^- \rightarrow O_2^{2-} \qquad (2)$$

$$2\,O_2^{\bullet-} + H_2O \rightarrow O_2 + HO_2^- + OH^- \qquad (3)$$

Several research groups have studied the ORR in different ILs to determine the solubility and diffusibility of O_2 and the stability of $O_2^{\bullet-}$ in such highly viscous and ionic media [8,11-17]. The stability of $O_2^{\bullet-}$ species practically depends on the type and the degree of purity of media, since the $O_2^{\bullet-}$ species undergoes various chemical reactions (e.g., Eq. (3)) [1,2,4,10,14,15,18,19,21-30]. In fact, the $O_2^{\bullet-}$ species is not “super” as an oxidant [1,2] but offers numerous reactions, e.g., a one-electron transfer, de-protonation, nucleophilic substitution, disproportionation (Eq. (3)) etc. The de-protonation reaction of the $O_2^{\bullet-}$ species that leads to an irreversible two- or four-electron ORR in aqueous solution is familiar [5,6,20,26,30]. Also, by the addition of a protonic additive (e.g., H_2O and alcohol) in aprotic solutions including ILs [4,7,8,20,26-30], the reversible, one-electron ORR becomes an irreversible, two-electron reaction. Besides, the $O_2^{\bullet-}$ species is generally inert towards simple olefins, but it can react with the activated olefins, e.g., the $O_2^{\bullet-}$ species is inert towards cyclohexene but can react with styrene and perfluorooctene [22]. Clennan et al. [25] have synthesized a stable adamantylideneadamantane-1,2-dioxetane by the reaction of the adamantylideneadamantane and the electrogenerated $O_2^{\bullet-}$ species in methylene chloride solution. We have recently previously reported that the $O_2^{\bullet-}$ species undergoes ion-pairing [18] in ILs and often can react with the acidic proton of imidazolium cation of ImILs [19]. At present, the quasi-reversible redox reaction of the $O_2/O_2^{\bullet-}$ couple that occurs especially in *N,N*-dialkylimidazolium cation-based ILs (i.e., ImILs) [7-12] is found for the first time to become irreversible in ImIL containing *N,N*-diallyl groups (Scheme 1).

In this study, the ORR was studied in 1,3-diallylimidazolium bis(trifluoromethansulfonyl)imide ($[DiAlI^+][N(Tf)_2^-]$) and 1-butyl-3-methylimidazolium bis(trifluoromethansulfonyl)imide ($[BMI^+][N(Tf)_2^-]$) (Scheme 1) at Pt, Au and GC electrodes using cyclic voltammetric and double-potential step chronoamperometric (DPSCA) techniques and the obtained results were compared. The effect of H_2O on the ORR in both ILs was also examined. The ORR in $[DiAlI^+][N(Tf)_2^-]$ was proposed to be a one-electron process in which the electrogenerated $O_2^{\bullet-}$ species was thought to undergo a follow-up chemical reaction with $[DiAlI^+]$ cation to form an “intermediate” [24,25]. Using a DPSCA method [31,32], the rate constant of this reaction was also determined.

2. EXPERIMENTAL

2.1. Chemicals

$[DiAlI^+][N(Tf)_2^-]$ and $[BMI^+][N(Tf)_2^-]$ (Scheme 1) were obtained from Kanto Chemical Co. Inc., Japan with a purity of more than 99% and contains less than 0.005 % H_2O and halides. All the ILs were used as received. The H_2O used was deionized H_2O purified with a Millipore Milli-Q system.

2.2. Apparatus and procedures

Cyclic voltammetric and potential step chronoamperometric measurements were carried out with a computer-controlled electrochemical system (Model: ALS/CHI 832A). The electrochemical cell was a conventional two-compartment Pyrex glass container with a working electrode (Au; $\phi = 1.6$ mm, Pt; $\phi = 1.6$ mm, GC; $\phi = 1.0$ mm), a spiral Pt-wire counter electrode and a silver (Ag) wire (quasi-)reference electrode. The working electrodes were carefully polished with alumina powder (down to 0.6 μm) with the help of a micro-cloth and then washed with Milli-Q water by sonication for 15 min. After that, the Au and Pt electrodes were electrochemically pretreated in Ar-saturated 0.05 M H_2SO_4 solution by repeating the potential scan in the range of –0.2 to 1.5 V until the voltammograms characteristic of the individual clean electrodes were obtained. Prior to use, the electrode was washed well with deionized water and dried by blowing air. Before measurements, N_2 or O_2 gas was bubbled directly into the cell to obtain their saturated solutions and during the measurements, N_2 or O_2 gas was flushed over the cell solution. All the measurements were carried out at room temperature (25 ± 2 ºC).

2.3. Determination of diffusion coefficient (D_{O2}) and saturated concentration (C_{O2}) of O_2

The measured *j*-*t* curves were analyzed by considering the modified Cottrell equation [31,33]:

$$I = 4\,n\,F\,r\,D_{O2}\,C_{O2}\;f(\tau) \qquad (4)$$

when $\tau < 1.44$

$$f(\tau) = 0.88623\,\tau^{-1/2} + 0.78540 + 0.094\;\tau^{5/2} \quad \text{where } \tau = 4\,D_{O2}\,t\,/\,r^2 \qquad (5)$$

D_{O2} and C_{O2} represent the diffusion coefficient and concentration of O_2, respectively, and *n*, *r* and *F* stand for the number of electron, electrode radius and Faraday constant, respectively. The data for the theoretical *j*-*t* curves (Fig. 5) were generated using Eqs. (4) and (5) where the *r* is the radius (0.05 cm) of the GC electrode used for the measurement of the *j*-*t* curves. The simultaneous determination of D_{O2} and C_{O2} was performed by a nonlinear curve fitting program available in Origin 6.1 (Microcal Software, Inc.).

3. RESULTS AND DISCUSSION

3.1. Redox reaction of the $O_2/O_2^{\bullet-}$ couple in $[BMI^+][N(Tf)_2^-]$

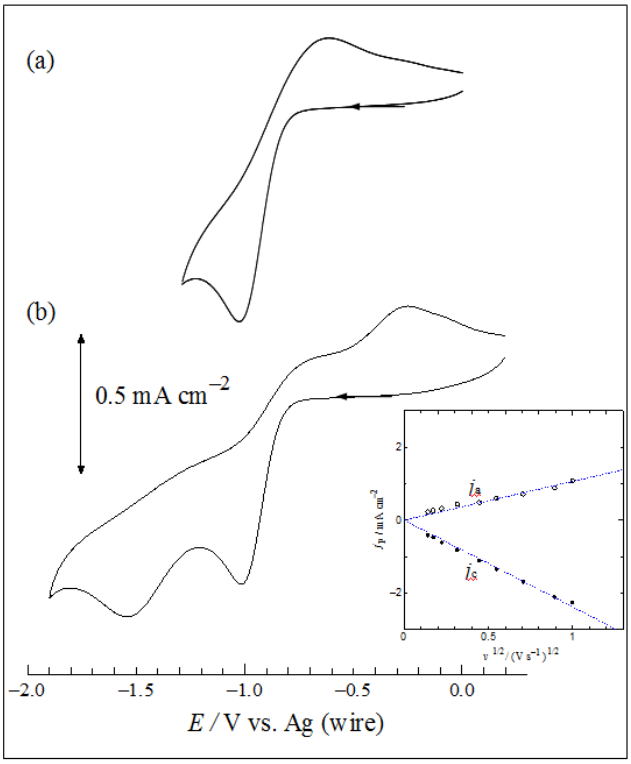


Figure 1. CVs obtained at GC electrode in O_2-saturated $[BMI^+][N(Tf)_2^-]$ in the potential range of (a) 0 → −1.3 → 0 V and (b) 0.2 → −1.9 → 0.2 V at υ of 0.1 V s^{-1}. Inset shows the plot of j_c (and j_a) vs. $\upsilon^{1/2}$, where the data were obtained from the CVs measured at various υ in the potential range of 0 → −1.3 → 0 V (not shown).

Fig. 1 shows the typical CVs obtained at GC electrode in O_2-saturated $[BMI^+][N(Tf)_2^-]$. When the CV was measured in the potential range of 0 → –1.3 → 0 V, a couple of well-defined cathodic and anodic peaks were observed at –0.95 and –0.8 V vs. Ag wire, respectively. In analogy with aprotic solutions [1-4] and other ILs [7-14,16-20], the cathodic and anodic peaks may be ascribed to a one-electron reduction of O_2 to $O_2^{\bullet-}$ (Eq. (1)) and the reoxidation of $O_2^{\bullet-}$ to O_2, respectively. The plots of current density (j) (anodic (j_a) and cathodic (j_c)) vs. the square root of potential scan rate ($\upsilon^{1/2}$) were found to be straight lines, indicating that the redox reaction of the $O_2/O_2^{\bullet-}$ couple is a diffusion-controlled process [31]. Remarkably, at a given υ, the value of j_c is significantly greater than j_a (i.e., $j_c > j_a$). In ILs, the diffusion coefficient of $O_2^{\bullet-}$ ($D_{O2\bullet-}$) has been reported to be generally smaller by two orders of magnitude than that of O_2 (D_{O2}) [12-17,20]). Thus, the observed fact that $j_c > j_a$ may be rational [17]. When the CV was measured in the potential range of 0.2 → –1.9 → 0.2 V, a new cathodic peak (–1.5 V) and anodic peak (–0.4 V) with a concurrent decrease in j_a at –0.8 V were obtained (Fig. 1(b)). The cathodic peak at –1.5 V may be regarded as a further one-electron reduction of $O_2^{\bullet-}$ to peroxide species (Eq. (2)) following by the ion-pairing phenomenon [18] and the anodic peak at –0.4 V for the re-oxidation of the formed peroxides species to O_2 [7,11,18]. Therefore, we observed a quasi-reversible behavior of the $O_2/O_2^{\bullet-}$ redox couple in $[BMI^+][N(Tf)_2^-]$.

3.2. Irreversible ORR in $[DiAlI^+][N(Tf)_2^-]$

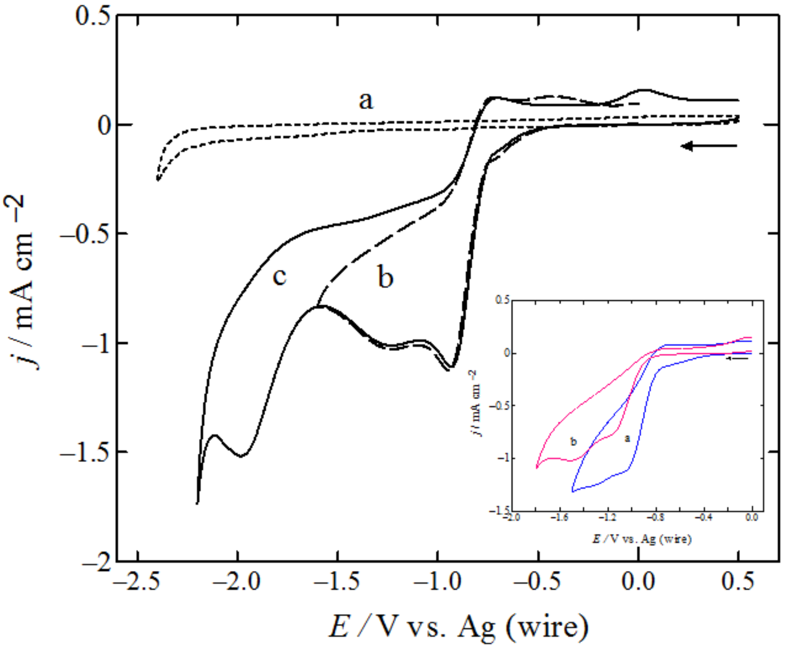


Figure 2. CVs measured at GC electrode in (a) N_2- and (b and c) O_2-saturated $[DiAlI^+][N(Tf)_2^-]$ at υ of 0.1 V s^{-1}. Inset represents the CVs obtained at (a) Au and (b) Pt electrodes in O_2-saturated $[DiAlI^+][N(Tf)_2^-]$ at υ of 0.1 V s^{-1}.

Fig. 2 represents typical CVs measured at GC, Au and Pt electrodes (inset) in $[DiAlI^+][N(Tf)_2^-]$. In N_2-saturated solution, no peak was observed except for the background current below ca. –2.4 V (Fig. 2(a)), indicating that the IL used is electrochemically stable within the measured potential range. On the contrary, during the cathodic potential scan in O_2-saturated $[DiAlI^+][N(Tf)_2^-]$, well-defined cathodic peaks at –0.95 and –1.95 V (discussed later) with a small shoulder at –1.25 V (unknown) were observed (Fig. 2(b)).

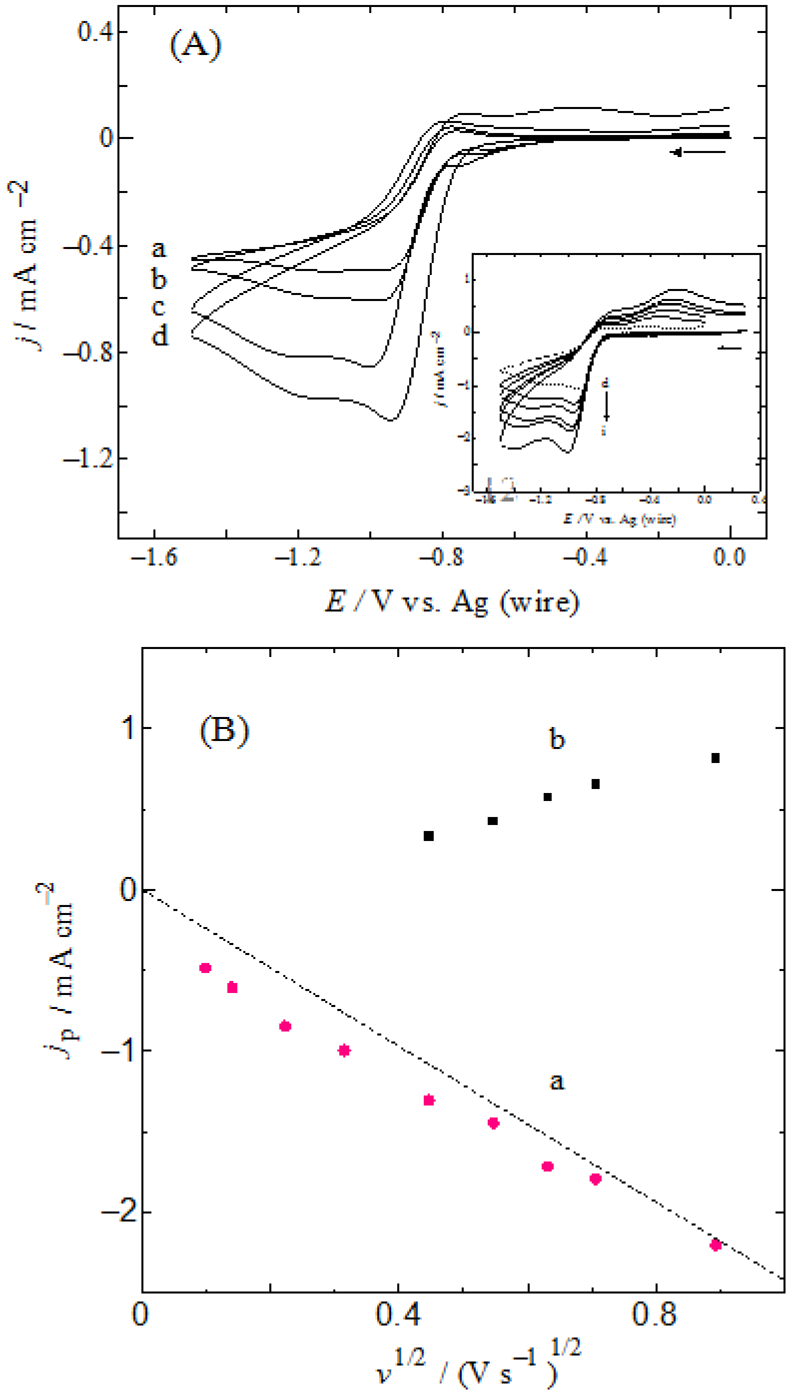
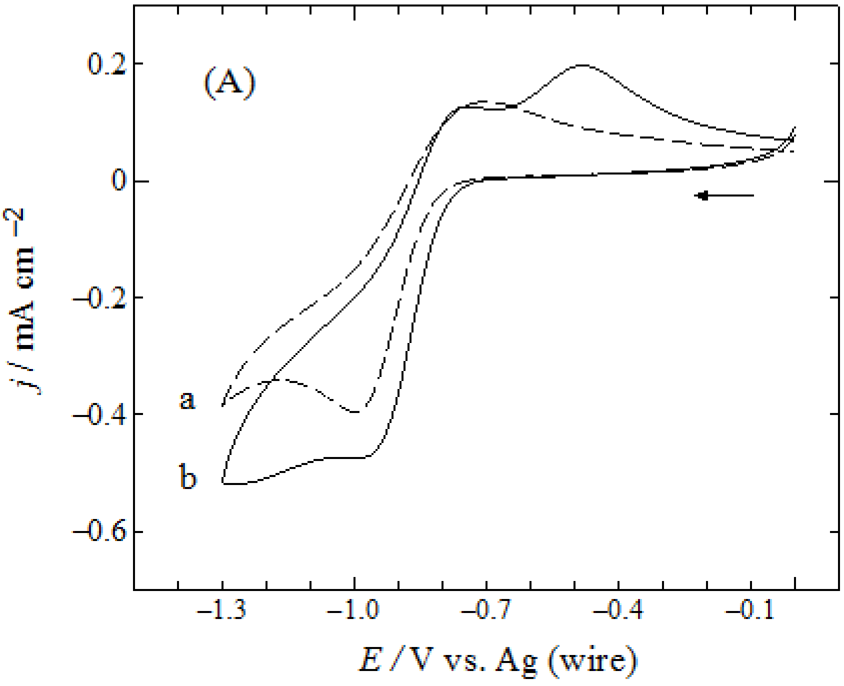


Figure 3. (A) CVs obtained at GC electrode in O_2-saturated $[DiAlI^+][N(Tf)_2^-]$ at potential scan rates of (a) 0.01, (b) 0.02, (c) 0.5, (d) 0.1, (e) 0.2, (f) 0.3, (g) 0.4, (h) 0.5 and (i) 0.8 V s^{-1}. (B) Plots of current density (j_p) vs. $\upsilon^{1/2}$ obtained for the cathodic peak at –0.95 V (a) and anodic peak at > –0.4 V (b).

No anodic peak except for the small shoulders at –0.4 and 0 V was were observed during the anodic potential scan at a slow υ, i.e., the ORR was irreversible regardless of the switching potential and the electrode used. When υ was increased, the j_c at –0.95 V and the anodic shoulder at –0.4 V increased (inset in Fig. 3A). The plot of j_c vs. $\upsilon^{1/2}$ was found to be a straight line passing through the origin (Fig. 3B), being comparable with that observed in $[BMI^+][N(Tf)_2^-]$ (inset in Fig. 1). In fact, the ratio of j_c obtained in $[DiAlI^+][N(Tf)_2^-]$ to that in $[BMI^+][N(Tf)_2^-]$ is almost unity (i.e., 1.2). Based on the above-mentioned results, the ORR in $[DiAlI^+][N(Tf)_2^-]$ may be regarded as a diffusion-controlled, irreversible one-electron process.

3.3. Effect of H_2O on the ORR in ILs

The ILs supplied commercially often contain a trace amount of H_2O and instantaneously absorb moisture from the ambient environment, and consequently H_2O is known to result in an irreversible two-electron ORR (Eq. (3)) (described above). Osteryoung group has observed the irreversible redox responses of the $O_2/O_2^{\bullet-}$ couple due to the presence of protonic impurities (e.g., H_2O, H^+) in imidazolium chloride-aluminum chloride molten salts [34]. Here, the effect of H_2O on the ORR was studied in both ILs used and the obtained results are shown in Fig. 4. When H_2O was added into $[BMI^+][N(Tf)_2^-]$, the shape of the obtained CV was found to deform (Fig. 4A): The midpoint potential shifted to more positive potential with a concurrent increase in j_c and a new anodic peak occurred at –0.5 V with a decrease of j_a (at a glance, the decrease in j_a at –0.75 V may not be recognized, but can be really seen by considering the baseline used for measuring the peak current). Note that unlikely the results in $[BF_4^-]$-based ILs [8], the j_c did not increase largely, for example, twice that observed in the absence of H_2O. However, the observed increase and decrease in j_c and j_a, respectively, obviously result from an overall two-electron ORR via the reactions shown in Eqs. (1) and (3).



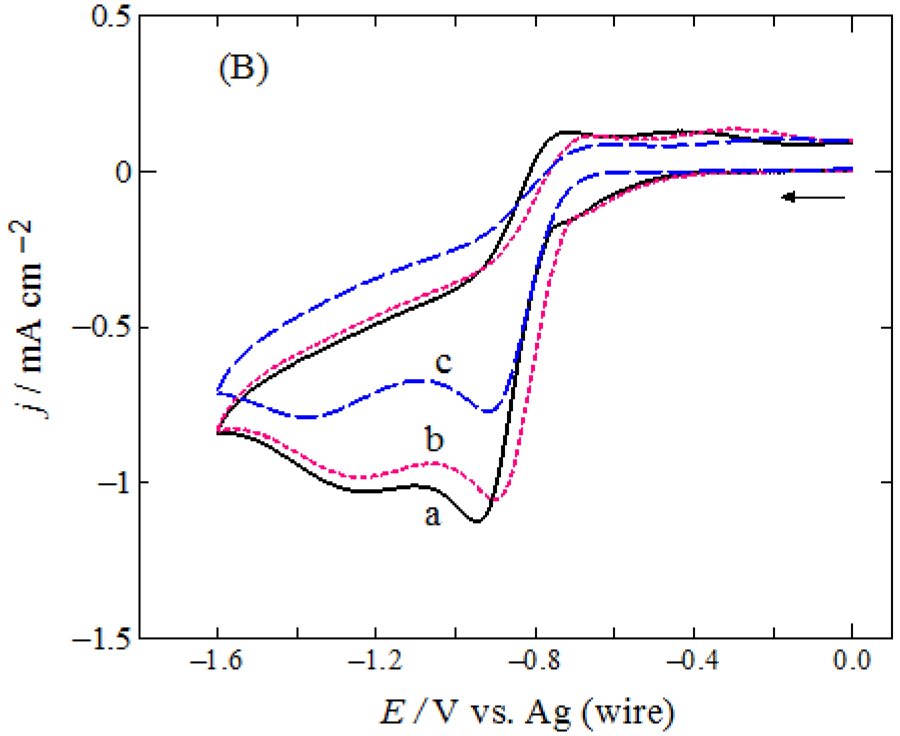


Figure 4. (A) CVs measured at GC electrode in O_2-saturated $[BMI^+][N(Tf)_2^-]$ in the absence (a) and presence (b) 2.0 M H_2O at υ of 0.02 V s^{-1}. (B) CVs obtained at GC electrode in O_2-saturated $[DiAlI^+][N(Tf)_2^-]$ containing (a) 0, (b) 0.4 and (c) 1.0 M H_2O.

In contrast, in the presence of H_2O in $[DiAlI^+][N(Tf)_2^-]$, almost no change in the peak potential took place and j_c decreased (Fig. 4B). In fact, the j_c decreased regularly with increasing the concentration of H_2O. These observations may be due to the smaller C_{O2} and/or D_{O2} in the presence of H_2O in $[DiAlI^+][N(Tf)_2^-]$ compared to those in pure $[DiAlI^+][N(Tf)_2^-]$. Thus, the claim of the inherent H_2O in $[DiAlI^+][N(Tf)_2^-]$ resulting in the irreversible CV response would be evidently negligible. Thus, the irreversibility in ORR in $[DiAlI^+][N(Tf)_2^-]$ may result from the consumption of the $O_2^{\bullet-}$ species via a follow-up chemical reaction. As described in the Introduction Section, the $O_2^{\bullet-}$ species can react with the activated double bond [22,24,25]. Therefore, the electrogenerated $O_2^{\bullet-}$ species may favorably react with the allyl group of $[DiAlI^+]$ to form a “dioxetane intermediate” (Eq. (6)) as in the case of since the allyl groups of $[DiAlI^+]$ are attached to the imidazolium ring (i.e., the positive center)

$$O_2^{\bullet-} + \mathrm{IL} \xrightarrow{k_{IL}} [\mathrm{IL\text{-}O_2}] \qquad (6)$$

3.3. DPSCA measurements and the mechanism of ORR in $[DiAlI^+][N(Tf)_2^-]$

To confirm further the number of electrons involved in such an irreversible ORR in $[DiAlI^+][N(Tf)_2^-]$ and determine the values of C_{O2}, D_{O2} and k_{IL} (rate constant (Eq. (6)), the DPSCA measurements were carried out (Fig. 5). Since the stepping potential (–1.2 V) is chosen to be more negative than cathodic peak potential of ORR (Fig. 2(a)), the cathodic *j*-*t* curve (curve a in Fig. 5A) corresponds to the reduction of O_2 to form $O_2^{\bullet-}$ species that reacts with $[DiAlI^+]$ (Eq. (6)).

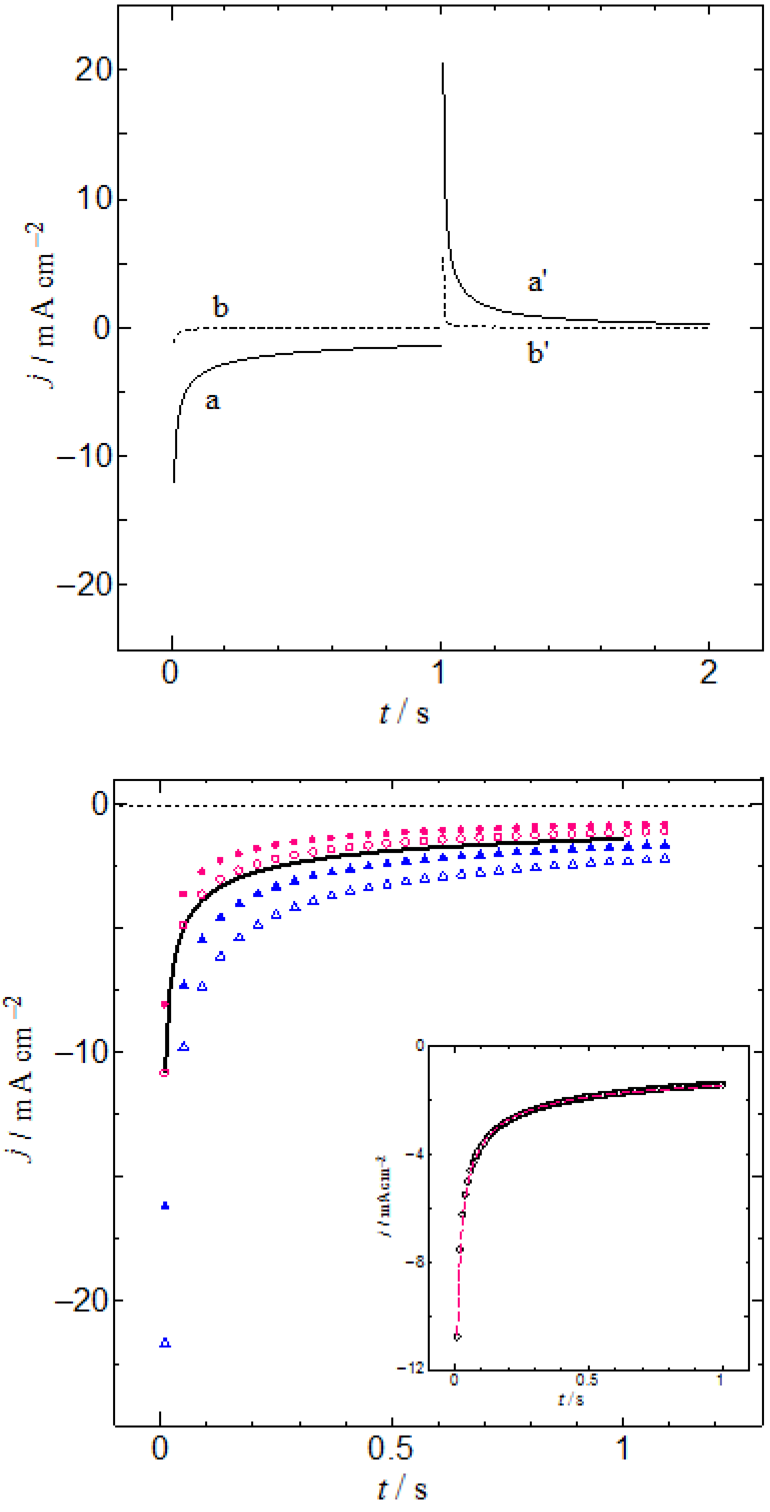


Figure 5. (A) Double-potential step *j*-*t* responses measured at GC electrode in (a,a′) O_2- and (b, b′) N_2-saturated $[DiAlI^+][N(Tf)_2^-]$. The initial, stepping and final potentials were 0, –1.2 and 0 V, respectively. (B) The background-corrected *j*-*t* curve (solid line) obtained from panel (A) overlaid with those derived theoretically (symbols) according to the modified Cottrell equation [33]. The plots with circles and triangles represent one- and two-electron ORR, respectively. The data of the plots shown by filled and open symbols were calculated by considering C_{O2} of 6.7 and 10.0 mM, respectively, while the D_{O2} was assumed to be the same as 4.8×10^{-6} cm^2 s^{-1}. Inset in panel (B) shows the experimental (open circle) and fitted (dashed line) *j*-*t* curves.

Thus, the anodic *j-t* curve (curve a′ in Fig. 5A) represents the re-oxidation of the un-reacted $O_2^{\bullet-}$. Based on Eqs. (4) and (5) [33], the several theoretical *j-t* curves were derived and the obtained curves were overlaid with the experimental *j-t* curve (Fig. 5B). It can be clearly seen that the experimental *j-t* curve nearly fits with that derived theoretically for a one-electron ORR (curve shown by open circles), indicating that the ORR in $[\text{DiAlI}^+][\text{N(Tf)}_2^-]$ is a one-electron process (Eq. (1)). Here, the obtained *j-t* curve was simulated for the determination of the actual C_{O2} and D_{O2} in $[\text{DiAlI}^+][\text{N(Tf)}_2^-]$ (inset in Fig. 5B) and the values of C_{O2} and D_{O2} were found to be 1.6 mM and 1.3×10^{-4} $cm^2\ s^{-1}$, respectively. These values are different from those (C_{O2} = 6.7 mM and $D_{O2} = 4.8 \times 10^{-6}$ $cm^2\ s^{-1}$) reported in $[\text{BMI}^+][\text{N(Tf)}_2^-]$, while the viscosities of $[\text{BMI}^+][\text{N(Tf)}_2^-]$ (0.52 g $cm^{-1}s^{-1}$) and $[\text{DiAlI}^+][\text{N(Tf)}_2^-]$ (0.31 g $cm^{-1}s^{-1}$) are almost comparable [20]. The ratio of ($C_{O2} \times (D_{O2})^{1/2}$) obtained in $[\text{DiAlI}^+][\text{N(Tf)}_2^-]$ to that in $[\text{BMI}^+][\text{N(Tf)}_2^-]$ is about 1.2 that is comparable with the ratio of the values of j_c obtained in the CVs measurements in the same ILs (described above). This harmony worthily verifies that the ORR in $[\text{DiAlI}^+][\text{N(Tf)}_2^-]$ is a one-electron process and that the obtained values of C_{O2} and D_{O2} are reasonable [20]. By analyzing the obtained DPSCA responses by Schwarz and Shain's method [32], the values of the pseudo-first order rate constant and k_{IL} were estimated to be 0.42 s^{-1} and 0.1 $M^{-1}\ s^{-1}$, respectively. The obtained k_{IL} is significantly larger than those of the reactions of $O_2^{\bullet-}$ species with styrene in acetonitrile solution (5.5×10^{-7} $M^{-1}\ s^{-1}$ [22]) or with H_2O in DMSO solution (2.8×10^{-4} $M^{-1}\ s^{-1}$ [23]). Although the product of the reaction expressed by Eq. (6) is not known, the second cathodic peak at −1.95 V (Fig. 2 (b)) may be ascribed to the reduction of the formed product. Moreover, the anodic peak at −0.4 V observed at faster υ (Inset in Fig. 3A) may be due to the re-oxidation of the unknown "initial product" formed by the reaction of the $O_2^{\bullet-}$ species and $[\text{DiAlI}^+]$ cation.

4. CONCLUSIONS

Cyclic voltammetric ORR measured at GC, Au and Pt electrodes in $[\text{DiAlI}^+][\text{N(Tf)}_2^-]$ was found to be a diffusion-controlled, irreversible one-electron process, whereas a quasi-reversible redox reaction of the $O_2/O_2^{\bullet-}$ couple has been essentially found in $[\text{BMI}^+][\text{N(Tf)}_2^-]$ [8-12]. The observed irreversibility in the ORR was justified not to be associated with the protonic impurities in $[\text{DiAlI}^+][\text{N(Tf)}_2^-]$. The number of electrons involved in the ORR was confirmed to be one by considering the CVs results obtained in both ILs as well as by comparing the experimental *j-t* curve with that derived theoretically based on the modified Cottrell equation [33]. The C_{O2} and D_{O2} were obtained to be 1.6 mM and 1.3×10^{-4} $cm^2\ s^{-1}$, respectively. In the mechanism, the electrogenerated $O_2^{\bullet-}$ species was proposed to undergo a follow-up reaction with allyl group of $[\text{DiAlI}^+]$ to form an "intermediate". With a DPSCA method, the rate constant of this reaction was estimated to be 0.1 $M^{-1}\ s^{-1}$ that is much larger than that (5.5×10^{-7} $M^{-1}\ s^{-1}$) reported for the reaction of the $O_2^{\bullet-}$ species with the olefinic group of styrene in acetonitrile solution [22]. A further study concerning the analysis of the product is in progress.

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