Electrochemical Characterization of TEMPO Radical in Ionic Liquids

Yuki MARUYAMA,a Kuniaki NAGAMINE,a,b,* Ayako NOMURA,a Shigeyuki IWASA,b,c and Shizuo TOKITOa,*

a Department of Organic Materials Science, Yamagata University, 4-3-16 Jonan, Yonezawa, Yamagata 992-8510, Japan
b Research Center for Organic Electronics, Yamagata University, 4-3-16 Jonan, Yonezawa, Yamagata 992-8510, Japan
c System Platform Research Laboratories, NEC Corporation, 34, Miyukigaoka, Tsukuba, Ibaraki 305-8501, Japan
* Corresponding authors: nagamine@yz.yamagata-u.ac.jp, tokito@yz.yamagata-u.ac.jp

ABSTRACT

Both p- and n-type redox reactions for 2,2,6,6-tetramethylpiperidin-4-yl methacrylate) (PTMA) swollen with a carbonate solvent into the p-(radicals can be reversibly oxidized into the oxoammonium cations from the nitroxyl radicals) are observed in the ionic liquid-based electrolyte systems. The electron-transfer constants estimated from the cyclic voltammograms were in the range of the quasi-reversible reactions, although only p-type redox proceeds reversibly in conventional organic electrolytes. The heterogeneous electron-transfer processes estimated from the cyclic voltammograms were in the range of the quasi-reversible system for both p- and n-type TEMPO reactions in ionic liquids. The rate constant for a p-type reaction in ionic liquids were lower by three orders of magnitude than that in the acetonitrile-based electrolyte due to the high viscosity of the electrolyte solutions. Quasi-reversible p- and n-type redox TEMPO reactions in the ionic liquid-based electrolyte systems suggest the potential realization totally-organic, flexible, safe, and symmetric organic radical batteries (ORBs) which are composed of TEMPO-based polymers for both positive and negative electrodes. The difference between p- and n-type redox electrode potential was 1.7 V in the tested ionic liquids, a value that suggests the electromotive force of symmetric ORB.

Keywords: Organic Radical Battery, Ionic Liquids, Cyclic Voltammetry, TEMPO

1. Introduction

Organic radical batteries (ORBs) are promising for use as a secondary battery due to their high power density, flexibility, and fast charge/discharge properties. In particular, flexibility is an excellent characteristic of the ORB because the various types of recently developed wearable devices have required the flexible battery which is conformable to the human body. Representative ORBs have utilized an organic radical compound-linked polymer as either positive or negative active materials. This polymer with organic radical compounds is swollen with the organic solvent-based electrolyte solution to form soft gel-based electrolyte, endowing the battery with flexibility. The nitroxyl radicals such as 2,2,6,6-tetramethylpiperidin-4-yl (TEMPO) is one of the typical radical compounds because of their high electrochemical stability and fast electrochemical reaction in an organic solvent-based electrolyte. The nitroxyl radicals can be reversibly oxidized into the oxoammonium cations (p-type reaction) both chemically and electrochemically, and reduced into the N-oxyl anions (n-type reaction) as shown in Scheme 1.

The first ORB developed by Nakahara et al. in 2002 is composed of a positive active material of poly(2,2,6,6-tetramethylpiperidin-4-yl methacrylate) (PTMA) swollen with a carbonate solvent containing lithium bis(trifluoromethanesulfonyl)imide liquid electrolyte. The ORB composed of the polynorbornene derivative radical polymer-based positive electrode and a lithium metal negative electrode. Y. Dai et al. applied 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide liquid containing lithium bis(trifluoromethanesulfonyl)imide to an electrolyte of the ORB composed of the polybororne derivative radical polymer-based positive electrode and a lithium metal negative electrode. However, to the best of our knowledge, fundamental electrochemical studies on issues such as the diffusion coefficient and the reaction rate constant of organic radical compounds in ionic liquids have not been reported yet.

In this study, the electrochemical properties of TEMPO radicals were studied in ionic liquids by means of cyclic voltammetry. The examined ionic liquids were composed of imidazolium, ammonium, or pyrrolidinium as cations, and BF4- or TFSI- as anions because these electrolytes have much wider electrochemical potential windows enough to be applied to ORBs. The heterogeneous electron-transfer rate constant and the diffusion coefficient of TEMPO in ionic liquids and conventional organic solvent-based electrolytes were calculated using the Nicholson method to compare the electrochemical behavior of TEMPO in these electrolytes.

Scheme 1. p- and n-type redox reactions of TEMPO.
2. Experimental

2.1 Chemicals

TEMPO was purchased from Kanto Chemical Co., Inc. Capacitor grade of tetraethylammonium tetrafluoroborate (TEA-BF₄) and propylene carbonate (PC) were purchased from Kishida Chemical Co. and used without further purification. The chemical structures of the ionic liquids used in this study are shown in Fig. 1. 1-ethyl-3-methylimidazolium tetrafluoroborate (EMI-BF₄) and 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMI-TFSI) were purchased from Tokyo Chemical Industry Co., Ltd. \( \text{N}^\text{N} \)-diethyl-\( \text{N}^\text{N} \)-methylpyrrolidinium tetrafluoroborate (MEMP-BF₄), \( \text{N}^\text{N} \)-diethyl-\( \text{N}^\text{N} \)-methyl-N-(2-methoxyethyl)ammonium bis(trifluoromethanesulfonyl)imide (MEMP-TFSI), \( \text{N}^\text{N} \)-diethyl-N-methyl-N-(2-methoxyethyl)ammonium bis(trifluoromethanesulfonyl)imide (DEME-TFSI), and dehydrated dichloromethane were purchased from Kanto Chemical Co., Inc. All the ionic liquids were dried in vacuum for 24 h at 100°C just before use.¹⁹ Dichloromethane was used without further purification.

2.2 Cyclic voltammetry of TEMPO in the ionic liquids

A three-electrode system was employed to make the cyclic voltammetry (CV) measurements for TEMPO dissolved in an ionic liquid or 1 M TEA-BF₄ in PC. A glassy carbon (GC) electrode, Fc\(^+\)/Fc\(^-\) (0.01 M AgNO₃, 0.1 M tetrabutylammonium perchlorate in acetonitrile) as a reference electrode, and Ag/Ag\(^+\) (0.1 M AgNO₃, 0.1 M tetrabutylammonium perchlorate in acetonitrile) as a counter electrode, and Ag/Ag\(^+\) were used as working electrodes, a coiled platinum wire as a counter electrode, and Ag/Ag\(^+\) (0.1 M AgNO₃, 0.1 M tetrabutylammonium perchlorate in acetonitrile) as a reference electrode, respectively. These electrodes were set in a VC-4 Voltammetry cell (BAS Inc.) with 0.1 M TEMPO solution previously degassed by bubbling in pure Ar gas for 30 minutes. Then, two cycles of CV measurements were performed under an Ar gas flow. All the electrochemical measurements were carried out using an ALS electrochemical analyzer (model 660E, BAS Inc.).

3. Results and Discussion

Figure 2 shows the cyclic voltammograms (CVs) of TEMPO in an ionic liquid and a conventional organic solvent-based electrolyte (TEA-BF₄ in PC) as a comparison. A glassy carbon (GC) electrode was used as the working electrode. CV measurements for each ionic liquid were performed for two cycles under an Ar gas flow and the second cycle of CVs were shown in Fig. 2. A clear current peak was observed at around 0.25 V vs. Ag/Ag\(^+\) for TEA-BF₄ in PC, suggesting that the generation of a reversible p-type redox TEMPO reaction as described in a previous study.²² Similar current peaks were observed when using each type of ionic liquid, suggesting a p-type reversible redox reaction of TEMPO even in ionic liquids. The detected peak current values and peak potential separation were different depending on the type of ionic liquids used. As discussed below, the viscosity of the ionic liquids could be responsible for the peak current values and peak separation in the CV measurements for a heterogeneous redox TEMPO reaction.

However, another peak current was observed at a negative potential of around −1.4 V vs. Ag/Ag\(^+\) in some ionic liquids that was not observed in the TEA-BF₄ in PC. Supporting Fig. S1 indicates the linear sweep voltammograms and the electrochemical windows of TEA-BF₄ in PC solution and six kinds of ionic liquid on GC electrode. Electrochemical windows were determined from the oxidation/reduction current values under 1 mA cm\(^{-2}\) on the voltammograms scanned at 50 mV s\(^{-1}\). These ionic liquids were not decomposed within the potential range of Fig. 2, suggesting that the peak current in Fig. 2 could be attributed from a redox reaction between nitroxyl radicals and aminoxy anions, or n-type reaction. Since aminoxy anions have potential to react with nucleophilic PC molecules, we also studied the electrochemical behavior the n-type reaction of TEMPO in dichloromethane solvent referring to previous report.²¹ The oxidation current peak of aminoxy anion was not observed in dichloromethane system as shown in Supporting Fig. S2. Therefore, n-type reaction of nitroxy radical was considered to be an irreversible process in organic solvent-based electrolyte systems.

Both p- and n-type TEMPO redox potentials of six kinds of ionic liquids calculated from oxidation/reduction current peaks in Fig. 2 were summarized in Supporting Fig. S3. The TFSI-based systems gained higher redox potential (0.26–0.28 V vs. Ag/Ag\(^+\)) for p-type reaction than that of the BF₄-based systems (0.20–0.21 V vs. Ag/Ag\(^+\)). X. H. Xu et al. reported that the redox potential in ionic liquids positively increased as the donor number of anionic cations.²³ Therefore, TFSI-based ionic liquids with higher donor number than BF₄-base done could exhibit more positive redox potential. On the other hands, clear relationship between the n-type redox reaction and counter ion species was not found in the present experimental condition. We need the other theory to discuss this phenomenon more detail. Now we are planning to carry out additional experiments in near the future.

The difference between p- and n-type redox reactions is a value that suggests the electromotive force of a symmetric battery composed of a TEMPO-based polymer for both positive and
and n-TEMPO reactions increased with increases in scan rate from 1 to an oxidized carbon electrode, which was not detected using the reversible type of working electrode. J. B. Gerken et al. detected a quasi-type TEMPO reactions in aqueous solutions were a was reduced to forming insoluble solid salt with EMI-TFSI. The disappearance in second cycle (Supporting Fig. S4) probably because first report current peak detected in the study. Changing a scan rate. The current peak for both n-type and p-type reaction of TEMPO in (a) and (c), respectively, depending on the square root of scan rate.

Figure 3. (a, c) Cyclic voltammograms of TEMPO in EMI-BF4 measured with changing scan rate. The potential ranges were −0.4 to 0.9 V vs. Ag/Ag⁺ for p-type (a) and −2.0 to −0.6 V for n-type (c), respectively. (b, d) Change of anodic peak current for p-type and n-type reaction of TEMPO in (a) and (c), respectively, depending on the square root of scan rate.

Negative electrodes. For example, the DEME-BF₄ system will exhibit about 1.79 V of electromotive force.

It was noted that in the case of EMI-TFSI, an n-type reaction-based peak current detected in the first CV measurement cycle disappeared in second cycle (Supporting Fig. S4) probably because the TEMPO absorbed onto the surface of glassy carbon electrode was reduced to forming insoluble solid salt with EMI-TFSI. The effect of working electrode materials was also studied. When platinum (Pt) was used as the working electrode, the peak currents for n-type TEMPO reaction decreased with increases in the peak separation width as shown in Supporting Fig. SS. Several additional current peaks also appeared in DEME- and MEMP-based ionic liquids. Supporting Fig. S6 shows the linear sweep voltammograms (a) and the electrochemical windows (b) of the ionic liquid samples detected using a Pt working electrode. All of the ionic liquid samples were decomposed when the potential was swept more negatively than −2 V vs. Ag/Ag⁺. Therefore, in DEME- and MEMP-based ionic liquid systems, the n-type reactions would competitively occur along with the cation decomposition.

Previous studies suggest that the electrochemical behavior of n-type TEMPO reactions in aqueous solutions were affected by the type of working electrode. J. B. Gerken et al. detected a quasi-reversible n-type TEMPO reaction in basic aqueous solution using an oxidized carbon electrode, which was not detected using the glassy carbon electrode. To our knowledge, this is the first report to show the detection of a n-type TEMPO reaction in ionic liquids using a glassy carbon electrode, while the detailed effects of ionic liquid chemical structures and the electrode materials on the stability of n-type TEMPO reactions will be further assessed in a future study.

Figure 3a and b shows the CV measurements for p-type (Fig. 3a) and n-type TEMPO reactions (Fig. 3b) measured in EMI-BF₄ with changing a scan rate. The current peak for both p-type and n-type TEMPO reactions increased with increases in scan rate from 1 to 500 mV s⁻¹. The peak potential separation widths for both types of reaction were more than 59 mV and increased with increases in scan rate. Figure 3c and d show the change of anodic current peaks depending on the square root of the scan rate (ν¹/₂). The peak current linearly increased with lower values of ν¹/₂ as shown in the figure inserts, followed by changes in slope in the region of higher ν¹/₂ values. These are typical electrochemical characteristics for quasi-reversible heterogeneous redox reactions. The diffusion coefficient D can be calculated from the slope in the linear regions based on the following equation:

\[ i_p = (2.69 \times 10^6)n^{1/2}D^{1/2}ν^{1/2}C \]  \( (1) \)

where \( i_p \) is a peak anodic current density, \( n \) is number of electrons involved in the redox process, \( D \) is a diffusion coefficient, \( ν \) is a scan rate, and \( C \) is the redox species concentration. The heterogeneous electron-transfer rate constant \( (k^0) \) was calculated using the Nicholson method according to the following equation:

\[ k^0 = 11.0ψD^{1/2}ν^{1/2} \]  \( (2) \)

where \( ψ \) is the dimensionless number corresponding to the peak separation. Table 1 summarizes the \( k^0 \) and \( D \) values for p-type and n-type TEMPO reactions in the tested ionic liquids. The magnitude of \( k^0 \) for a p-type reaction \( (k^0_p) \) was on the order of less than several 10⁻¹⁰ cm² s⁻¹ which is lower by three-orders vs. previous studies of acetonitrile-based electrolyte. The magnitude of \( D \) for a p-type TEMPO reaction \( (D_p) \) was on the order of less than several 10⁻⁰⁹ cm² s⁻¹ in the tested ionic liquids, whose value was lower by two-orders than the reported \( D_p \) values.

A previous study discussed that lower \( k^0 \) and \( D_p \) values in ionic liquids are attributed their viscosities. Therefore, the relation between the viscosity of each ionic liquid and \( k^0_p \) or \( D_p \) were plotted in Fig. 4a and b, respectively. The viscosities of EMI-BF₄ and EMI-TFSI were referred to previous report, and those of the other ionic liquids were referred to technical document from Kanto Chemical Co., Inc. The viscosities of ionic liquids are one order of magnitude higher than 1 M-TEA-BF₄ in PC solution (2.6 mPa s). Higher
values of \( k_0 \) and \( D \) for \( p \)-type reactions were obtained in ionic liquids with lower viscosities. These Marcus theory and Stokes-Einstein relationship-like behaviors were similar to the previously observed behaviors for ferrocene and other redox mediators in ionic liquids.25 On the other hand, the magnitude of \( k_0 \) and \( D \) for \( n \)-type reactions (\( k_{0n} \) and \( D_n \), respectively) were on the order of less than several \( 10^{-5} \) cm s\(^{-1} \) and \( 10^{-8} \) cm\(^2\) s\(^{-1} \), respectively (Table 1). Higher values of \( k_{0n} \) were obtained in BF4 anion-based ionic liquids with lower viscosities, while no apparent relationship was observed in the TFSI anion-based ionic liquids (Supporting Fig. S7). Unfortunately, we could not discuss these phenomena anymore from the present primitive experimental data. For more detail discussion in near the future, we have to carry out additional experiments, for example, AC-impedance measurement to discuss activation energy and solvation energy, or in some case, discussion using the Marcus-theory.26

4. Conclusions

We found for the first time that quasi-reversible \( p \)- and \( n \)-type redox TEMPO reactions successfully proceeded in ionic liquids when using a glassy carbon electrode, while only a \( p \)-type redox TEMPO reaction was observed in conventional organic electrolytes. The heterogeneous electron-transfer rate constant and diffusion coefficient for \( p \) - and \( n \)-type reactions were calculated by the Nicholson method. \( k_{0p} \) or \( D_p \) in the ionic liquids were smaller by three-orders than those previously studied in the acetonitrile-based electrolytes. These characteristics could be attributed the viscosities of ionic liquids based on Marcus theory and Stokes-Einstein relationship. However, a clear relationship between \( k_0, D \) and the viscosity of the ionic liquids was not observed for the \( n \)-type reaction. Quasi-reversible \( p \)- and \( n \)-type TEMPO reactions lead to the realization totally-organic,29,30 flexible, and furthermore, symmetric ORBs which have a TEMPO polymer as the active material for both positive and negative electrodes. In addition, the radical polymer changed its form into a gel containing the electrolyte solution and exhibited good cyclical performance even when the battery was flexed.31 Therefore, symmetric ORBs look to be a promising candidate for power sources in wearable devices owing to the possibility of simplified manufacturing, a high degree of safety and exceptional flexibility. In near the future, we will carry out further experimental and theoretical discussions, and apply this redox system to ionic liquid-based symmetric organic radical batteries.

Supporting Information

The Supporting Information is available on the website at DOI: https://doi.org/10.5796/electrochemistry.19-00054.

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Conflict of interest

The authors declare no competing financial interest.

Table 1. Rate constants and diffusion coefficients for \( p \)-type and \( n \)-type TEMPO reactions in ionic liquids calculated by Nicholson method and reported viscosity.

<table>
<thead>
<tr>
<th></th>
<th>( 10^{-4} k_0 / \text{cm s}^{-1} )</th>
<th>( 10^{-7} D / \text{cm}^2 \text{s}^{-1} )</th>
<th>( 10^{-4} k_{0n} / \text{cm s}^{-1} )</th>
<th>( 10^{-7} D_n / \text{cm}^2 \text{s}^{-1} )</th>
<th>( \eta / \text{mPa s} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>EMI-BF4</td>
<td>4.8</td>
<td>3.2</td>
<td>0.44</td>
<td>0.78</td>
<td>43</td>
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<tr>
<td>EMI-TFSI</td>
<td>3.0</td>
<td>3.8</td>
<td>N/A</td>
<td>N/A</td>
<td>28</td>
</tr>
<tr>
<td>DEME-BF4</td>
<td>0.61</td>
<td>0.50</td>
<td>0.18</td>
<td>0.35</td>
<td>272</td>
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<tr>
<td>DEME-TFSI</td>
<td>0.91</td>
<td>1.9</td>
<td>0.13</td>
<td>0.88</td>
<td>67</td>
</tr>
<tr>
<td>MEMP-BF4</td>
<td>1.2</td>
<td>0.93</td>
<td>0.28</td>
<td>0.55</td>
<td>154</td>
</tr>
<tr>
<td>MEMP-TFSI</td>
<td>1.2</td>
<td>2.2</td>
<td>0.095</td>
<td>0.70</td>
<td>50</td>
</tr>
</tbody>
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Figure 4. Relationship between the \( k_{0p} \) (a) and \( D_p \) (b) for \( p \)-type reaction of TEMPO in the ionic liquids with different value of viscosity. (○ and △ means ionic liquids having BF4 and TFSI anion, respectively.)
Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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