

Electrochemical Behavior of Oxygen / Superoxide Ion Couple in 1-Butyl-1-Methylpyrrolidinium Bis(trifluoromethanesulfone)imide Room Temperature Molten Salt

Yasushi KATAYAMA, Kaori SEKIGUCHI,
Masaki Yamagata, and Takashi MIURA

Department of Applied Chemistry,
Faculty of Science and Technology, Keio University
3-14-1, Hiyoshi, Kohoku-ku, Yokohama 223-8522, Japan

Introduction

The electrochemical behavior of oxygen species in room temperature molten salt (ionic liquid) systems is important not only in the energy conversion and storage technology, such as fuel cells and metal-air batteries, but also in the organic syntheses. It has been reported that oxygen can be reduced to superoxide ion in some room temperature molten salt systems.¹⁻⁶ However, we have already found that both aliphatic and alicyclic ammonium cations are more stable against nucleophilic superoxide ion than imidazolium cations.⁵

In this study, the electrochemical behavior of oxygen and superoxide anion has been investigated by the ultra-micro electrode technique.

Experimental

1-butyl-1-methylpyrrolidinium bromide (BMPBr) was prepared by the reaction of 1-methylpyrrolidine and n-butyl bromide, purified by recrystallization and dried under vacuum. BMPTFSI molten salts were prepared by interacting BMPBr with LiTFSI in water at room temperature, followed by extraction into dichloromethane and vacuum drying.

All the hygroscopic reagents were handled in an argon-filled glove box. Platinum and gold disk electrodes were used as macro working electrodes (1 and 3 mm ϕ). Gold ultra-micro disk electrode were also used as working electrodes (10 and 25 μ m ϕ). Platinum was used as a counter electrode. The counter electrode was placed in a separated compartment with a glass filter in case of long-term electrolysis. The reference electrode consisted of a silver wire immersed in 0.1 M AgCF₃SO₃ / EMITFSI solution separated from the bulk solution with porous glass (Vycor). The potential of this reference electrode was +0.44 V vs. ferrocene (Fc) / ferrocenium (Fc⁺) couple.

Results and Discussion

The diffusion coefficient, D , and bulk concentration, C , of an electrochemical active species can be determined from the chronoamperometric measurements with a macro and an ultra-micro disk electrode. In case of the macro disk electrode, when a sufficient overpotential is applied, the current density is inversely proportional to the square root of time, as represented by the Cottrell's equation.

$$j(t) = \frac{nFD^{1/2}C}{\pi^{1/2}t^{1/2}} \quad [1]$$

where n and F are the number of electrons and Faraday's constant, respectively. On the other hand, the steady-state current, i_{ss} , for the ultra-micro disk electrode having the radius of r_0 is given by the following equation.

$$i_{ss} = 4nFDCr_0 \quad [2]$$

Thus, D and C can be calculated from the values of $D^{1/2}C$ and DC obtained for the macro and ultra-micro disk electrode, respectively.

The diffusion coefficient and concentration of O₂ were determined in BMPTFSI saturated with O₂. The

diffusion coefficient of O₂ was $1.8 \pm 0.2 \times 10^{-6}$ cm² s⁻¹ at 25°C while those of some metal species are of the order of 10^{-8} cm² s⁻¹. The fast diffusion of O₂ can be explained by the weak interaction between O₂ and the molten salt since there is no coulombic interaction between the organic ions and neutral O₂. In addition, the diffusion of O₂ seems not to be affected by the apparent viscosity of the molten salt probably because O₂ is small enough to move through the interstices between the bulky organic ions. The diffusion coefficient of O₂ in (C₂H₅)₃C₆H₁₃NTFSI at 25°C has been reported to be 1.48×10^{-6} cm² s⁻¹,⁴ which is close to that in BMPTFSI, while the viscosity of (C₂H₅)₃C₆H₁₃NTFSI is about twice higher than that of BMPTFSI. Figure 1 shows the temperature dependence of the diffusion coefficient of O₂ together with the viscosity of BMPTFSI. The activation energy for the diffusion coefficient of O₂ was 27 kJ mol⁻¹. The solubility of O₂ was 14 mmol dm⁻³ at 25°C and decreased with an increase in temperature.

The similar experiment for O₂⁻ was carried out in BMPTFSI containing O₂⁻ introduced by the potentiostatic cathodic reduction of O₂. The diffusion coefficient of O₂⁻ was 0.86×10^{-6} cm² s⁻¹, which is much smaller than that of O₂. The diffusion of O₂⁻ is expected to be affected by the coulombic interaction with the organic ions.

Acknowledgements

A part of this work was financially supported by Grant-in-Aid for Scientific Research on Priority Areas (B) of "New Technologies of DMFC" (No. 13134201) from MEXT. The authors are grateful for the financial support by Grant-in-Aid for the 21st Century COE program "KEIO Life Conjugate Chemistry" from MEXT.

References

- 1) M. T. Carter and C. L. Hussey, *Inorg. Chem.*, **30**, 1149 (1991).
- 2) I. M. AlNashef, M. L. Leonard, M. C. Kittle, M. A. Matthews and J. W. Weidner, *Electrochem. Solid-State Lett.*, **4**, D16 (2001).
- 3) I. M. AlNashef, M. L. Leonard, M. A. Matthews and J. W. Weidner, *Ind. Eng. Chem. Res.*, **41**, 4475 (2002).
- 4) M. C. Buzzeo, O. V. Klymenko, J. D. Wadhawan, C. Hardacre, K. R. Seddon and R. G. Compton, *J. Phys. Chem. A*, **107**, 8872 (2003).
- 5) Y. Katayama, H. Onodera, M. Yamagata and T. Miura, *J. Electrochem. Soc.*, **151**, A59 (2004).
- 6) D. Zhang, T. Okajima, F. Matsumoto and T. Ohsaka, *J. Electrochem. Soc.*, **151**, D31 (2004).

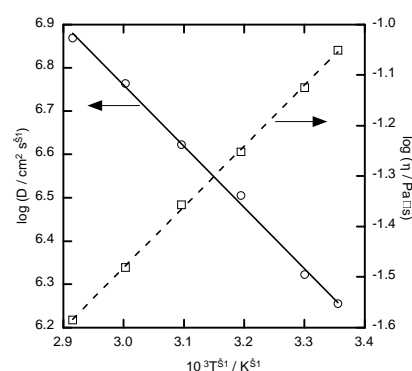


Fig. 1 Temperature dependence of the diffusion coefficient of O₂ and the viscosity of BMPTFSI.