

RRDE Study on Oxygen Reduction Reaction in Phosphonium Ionic Liquids

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Abstract

For an application of ionic liquids (ILs) to fuel cells, it is important to understand mechanism of oxygen reduction reaction (ORR) in ILs. Recently, we found that the onset potential of ORR changes to the high potential side in protic ILs. Based on this, in this study, we investigated ORR in (i) aprotic ILs mixed with protons and (ii) pure protic ILs using the Rotating Ring Disk Electrode (RRDE) method. By combining pulsed-field gradient NMR, We demonstrated that proton transport properties of aprotic ILs mixed with protons and pure protic ILs differed with that of aprotic ILs mixed with protons and pure protic ILs.

1. Introduction

Ionic liquids (ILs) are liquid salts at room temperature composed of organic cation and anion. Because of their many excellent electrical properties, such as a wide potential window, ILs have many potential applications, especially, in electrochemical devices. For an application of ILs to fuel cells, it is important to understand mechanism of oxygen reduction reaction (ORR) in ILs. Among ILs, we have focused on quaternary phosphonium cation-based ILs. In addition, we recently found that the onset potential of ORR changes to the high potential side in protic ILs. Based on this finding, in this study, we investigated ORR in aprotic ILs mixed with protons using the Rotating Ring Disk Electrode (RRDE) method.

2. Experiment

For electrolytes, ILs (Fig 1) were dried at 120 °C in vacuum for 24 h. Cyclic voltammetry (CV) and hydrodynamic voltammetry were performed using a three electrode cell at 25 °C. RRDE constructed a glassy carbon (GC) or platinum (Pt) disk, and Pt ring electrodes were used as the working electrodes. The ring current was measured at a potential of 0.5 V vs. Ag/Ag⁺ reference electrode, where the intermediate oxidation reaction enough attached to diffusion limit.

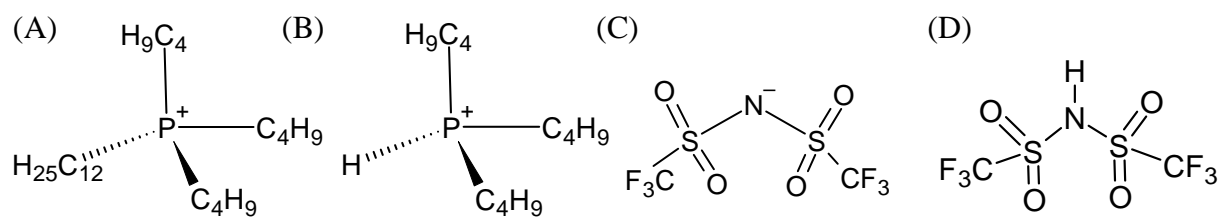


Fig.1. Chemical structure of (a) P444(12) cation, (b) P444H cation (C) TFSA anion (D) HTFSA

3. Results and discussion

Fig. 2 shows hydrodynamic voltammograms of the disk electrode in P444H-TFSA and P444(12)-TFSA mixed with HTFSA. The ORR onset potential of P444H-TFSA was about 0.4 V vs. Ag/Ag⁺, which was higher than that of P444(12)-TFSA. Based on the pulsed-field gradient NMR measurements, we evaluated the diffusion coefficient (D) of each ion specie. In P444H-TFSA, we observed close D values in phosphorus and hydrogen atoms. However, P444(12)-TFSA mixed with HTFSA showed different D values in fluorine and hydrogen atoms. This result indicates that diffusive proton was generated from HTFSA.

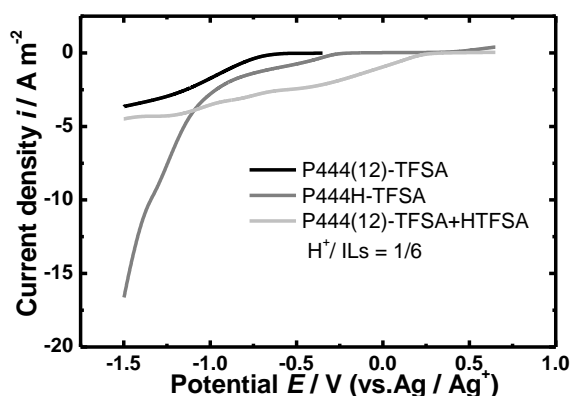


Fig.2. Hydrodynamic voltammograms on the platinum disk electrode during ORR in O₂-saturated prepared ILs.

4. Conclusions

In this study, we investigated ORR behaviors and proton transport properties in phosphonium ILs. Our results indicated that the proton in protic ILs diffused as phosphonium cation. On the other hand, we observed that the proton in HTFSA could diffuse independent on TFSA as proton. We concluded that such higher proton transport in aprotic ILs mixed with HTFSA should highly contribute multiple-electron ORR.

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