



# Solubility and Diffusion Coefficient of Oxygen in Protic Ionic Liquids with Different Fluoroalkyl Chain Lengths



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## ABSTRACT

A series of protic ionic liquids (PILs) were synthesized from *N,N*-diethylmethylamine (dema) and three kinds of fluoroalkylsulfonic acids having different chain lengths ( $\text{H-SO}_3(\text{CF}_2)_n\text{F}$ ,  $n = 1\sim 3$ ) as electrolytes for fuel cells. Solubility and diffusion coefficient of oxygen in those PILs were determined from 30 °C to 120 °C by the combination measurement of linear-sweep voltammetry and hydrodynamic chronocoulometry with a rotating disk electrode (RDE). The solubility and diffusion coefficient of oxygen in *N,N*-diethylmethylammonium heptafluoropropanesulfonate ([dema][HfO]) was 10.5 mmol dm<sup>-3</sup> and  $1.48 \times 10^{-6}$  cm<sup>2</sup> s<sup>-1</sup> at 120 °C, respectively. With increasing the fluoroalkyl chain length of anion, the solubility increased. In contrast, the diffusion coefficient decreased. The activation energies of oxygen diffusion in *N,N*-diethylmethylammonium pentafluoroethanesulfonate ([dema][PFO]) and [dema][HfO] were estimated to be 35.5 kJ mol<sup>-1</sup> and 38.4 kJ mol<sup>-1</sup> from the Arrhenius plots, respectively. The permeabilities of oxygen in the synthesized PILs were also estimated and compared with Nafion® in water to discuss oxygen cross-over in fuel cell application.

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## 1. Introduction

Polymer electrolyte fuel cell (PEFC) is compact and has high energy density compared with other kinds of fuel cells. As the electrolytes for PEFC, fluoropolymer electrolytes such as Nafion® have been used because of high proton conductivity and good chemical stability. However, those electrolyte membranes have to be used under humidified conditions in order to maintain high proton conductivity. Therefore, the PEFC system becomes large to equip humidifying apparatus. As a result, PEFC operation is still limited up to 80 °C although the catalyst activity is strongly reduced by CO poisoning at low temperatures. Thus, new electrolyte materials, which can be used without humidification at higher temperatures than 100 °C, are needed [1–5].

Ionic liquids, which are molten salts at room temperature, have attracted considerable attention as PEFC electrolyte materials at intermediate temperatures (higher than 100 °C) under non-humidified conditions because of their special characteristics such as non-volatile, non-flammability, high thermal stability and electrochemical stability. The electrolyte used for PEFC needs proton conductivity. Thus, ionic liquids investigated for PEFC are generally

called as protic ionic liquids (PILs), which can be synthesized simply by neutralization of Brønsted acid and base. So far, various kinds of PILs have been synthesized. They are relatively stable against water and air [6]. However, the overvoltage of oxygen reduction reaction (ORR) on conventional platinum catalyst in those PILs is much larger than that in Nafion® [7].

In order to utilize PILs to fuel cells, the characteristics of PILs as electrolytes have been extensively studied. Watanabe et al. has studied PILs that were synthesized from various kinds of imidazolium-based or ammonium-based cations and various strong acid or super acid anions [8–13]. They have reported that *N,N*-diethylemethyleammonium trifluoromethanesulfonate ([dema][TfO]) is appropriate for ORR [12,13]. In addition, it has been reported that the PEFC applied with [dema][TfO] showed an output density of more than 100 mW cm<sup>-2</sup> [14]. Hagiwara et al. has developed fluorohydrogenate anion ([FHF<sup>-</sup>]) based PILs having layered crystal structures. Both cation and anion transports in those PILs are so fast and the proton transport is supported by [FHF<sup>-</sup>] anion rather than by cation. Therefore, [FHF<sup>-</sup>]-based PILs are preferable as fuel cell electrolytes. Actually, it has been reported that the single cell test using [FHF<sup>-</sup>]-based PILs shows the power density of 200 mW cm<sup>-2</sup> at 80 °C. It has been also reported that the cell operation at 130 °C under non-humidified condition [15–18]. In addition to those researches, studies on electrolyte membranes impregnated with PILs have been recently focused [19–23].

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So far, we have focused on the ORR in PILs which were synthesized by combination of anions having different fluoroalkyl chain lengths and [dema] cation. The ORR in those PILs on Pt electrode has been analyzed by *in-situ* infrared spectroscopy (*in-situ* FT-IR). From this measurement, it has been found that the adsorption and desorption behavior of the anion in PILs strongly affects the ORR activity. This result shows that the ionic liquid comprising an anion weakly absorbed on Pt surface, which can be easily released by applying a potential, is appropriate for the ORR [24]. In this study, we synthesized a series of PILs from [dema] and three kinds of fluoroalkylsulfonic acids having different chain lengths ( $\text{H-SO}_3(\text{CF}_2)_n\text{F}$ ,  $n = 1\sim 3$ ), and investigated the effect of fluoroalkyl chain length on the solubility and diffusion coefficient of oxygen in the [dema]-based PILs to discuss the appropriate design of PILs for intermediate temperature fuel cells.

## 2. Experimental

### 2.1. Preparation of protic ionic liquids with different fluoroalkyl chain lengths

As anion sources, trifluoromethanesulfonic acid ([TfO], Tokyo Kasei Ltd.), pentafluoroethanesulfonic acid ([PFO], Mitsubishi Materials Corp.) and heptafluoropropanesulfonic acid ([HFO], Mitsubishi Materials Corp.) were used. These were respectively mixed with an equimolar of *N,N*-diethylethylamine ([dema], Tokyo Kasei Ltd.) as a cation source in deionized water to prepare PILs with different fluoroalkyl chain lengths by neutralization method, in which the byproduct is only water. For example, [dema][TfO] was synthesized as follows. 14.12 g of [dema] was added into deionized water (100 ml) in a round-bottom flask equipped with a magnetic stirrer. Then, the round-bottom flask was cooled in ice bath. 25 g of [TfO] was added into the round-bottom flask by using a dropping funnel. This dropping was finished in 30 minutes. The water (solvent and byproduct) was removed with a rotary evaporator to obtain target PILs. The obtained PILs were then dried at 100 °C under vacuum at least for 48 h before use.

### 2.2. Characterizations

Thermogravimetry (TA-60WS, Shimadzu) was performed under nitrogen and oxygen atmospheres to investigate the thermal stability of PILs. A sample was weighed and placed in platinum pan and then heated from room temperature to 500 °C at a heating rate of 2 °C min<sup>-1</sup>. The viscosity was measured with a viscometer with (thermosel LVT, Brookfield Ltd.). The measurement temperature was controlled from 30 °C to 120 °C. For each sample, the measurement was carried out at least three times for accurate evaluation.

Electrochemical measurements for PILs were conducted using a glass cell equipped with a rotating disk electrode (RDE) system. A rotating Pt disk ( $\phi = 0.4$  mm) embedded in poly ether ether ketone was used as the working electrode. Pt mesh and reversible hydrogen electrode (RHE) were used as the counter and reference electrodes, respectively. Before electrochemical measurements, the Pt disk electrode was polished using 0.5  $\mu\text{m}$  alumina powder on a polishing felt pad and then was washed ultrasonically in deionized water for five minutes. The deoxygenation of PILs was conducted by nitrogen gas bubbling. The potential sweep measurements were conducted using an electrochemical analyzer (ALS-760B, BAS Inc.) in a potential range from 1.1 V to 0.2 V vs. RHE at a scan rate of 5 mV s<sup>-1</sup> by changing the rotation speed of Pt disk electrode from 100 rpm to 400 rpm. The chronocoulometry was also performed using the RDE. The electrode potential was changed from the open circuit potential (OCP) to 0.1 V, at which the ORR in PILs is governed by the diffusion of oxygen to the electrode surface. The rotation

speed of RDE was changed from 100 rpm to 900 rpm. The analysis of electrochemical parameters of ORR in PILs was carried out according to the following equations provided by chronocoulometry under the convection control of the solution [25,26],

$$Q = Q_{\text{intercept}} + I_L t \quad (1)$$

$$Q_{\text{intercept}} = Q_{\text{adsorption}} + Q_d \quad (2)$$

$$Q_\delta = 0.3764nFAC\delta \quad (3)$$

$$I_L = j_L A = nFADC/\delta \quad (4)$$

where  $Q$  is electric charge,  $Q_{\text{intercept}}$  is the intercept of the straight line of  $Q$ - $t$  plot (eq. (1)),  $I_L$  is the diffusion limited current,  $t$  is the time,  $Q_\delta$  is the charge passed by electrolysis of species present initially in the hydrodynamic boundary,  $Q_{\text{adsorption}}$  is the charge passed by electrolysis of adsorbed species,  $n$  is the reaction electron number,  $F$  is the Faraday constant,  $A$  is the electrode surface area,  $C$  is the solubility of oxygen,  $D$  is the diffusion coefficient of oxygen,  $\delta$  is the thickness of hydrodynamic boundary, and  $j_L$  is the diffusion limited current density. Furthermore, the thickness of hydrodynamic boundary, which is the diffusion layer thickness discussed by Newman et al., is given by the following equation [26–28].

$$\delta = 1.610D^{1/3} \nu^{1/6} \omega^{-1/2} (1 + 0.2980Sc^{-1/3} + 0.14514Sc^{-2/3}) \quad (5)$$

where  $\nu$  (cm<sup>2</sup> s<sup>-1</sup>) is kinetic viscosity of the solution,  $\omega$  (s<sup>-1</sup>) is electrode rotation speed and  $Sc$  ( $= \nu/D$ ) is Schmidt number. The reaction electron number  $n$  was estimated by linear sweep voltammetry using a rotating Pt ring-Pt disk electrode. The collection efficiency between the ring and disc electrodes was estimated using 0.1 mol dm<sup>-3</sup> KCl aqueous solution containing with 1 mmol dm<sup>-3</sup> ferricyanide, in which the potential of ring electrode was fixed at 1.4 V vs. RHE.

## 3. Results and discussion

The thermogravimetric traces of [dema][TfO], [dema][PFO] and [dema][HFO] under nitrogen and oxygen atmospheres are shown in Fig. 1. It was confirmed that the prepared PILs are stable at 150 °C, which is one of the target temperatures of non-humidified PEFC operation. Their weight losses at 150 °C were less than 2% in both nitrogen and oxygen atmospheres. We synthesized those PILs by equimolar mixing of [dema] and a different fluoroalkylsulfonic acid in deionized water. Therefore, it is considered that small amount of water was still included even after drying at 100 °C under vacuum for 48 h and appeared as the weight loss. After the gradual loss of water up to 250 °C, the PILs showed rapid weight losses at higher than 300 °C. From the thermogravimetric traces, the decomposition temperatures ( $T_d$ ) for [dema][TfO], [dema][PFO] and [dema][HFO] were estimated at 338 °C, 333 °C and 334 °C, respectively. Thus, the influence decomposition of PILs in the measurements at 120 °C could be eliminated.

The viscosity, density and kinetic viscosity of [dema][PFO] and [dema][HFO] are shown in Table 1. The kinetic viscosity is a necessary parameter to calculate the diffusion coefficient and solubility of oxygen in PILs. The kinetic viscosity is given by the following equation,

$$\nu = \eta/\rho \quad (6)$$

where  $\eta$  is viscosity,  $\rho$  is density and  $\nu$  is kinetic viscosity. It was difficult to measure viscosity, density and kinetic viscosity of [dema][PFO] at 30 °C due to its crystallization. Therefore, the measurement for [dema][PFO] was performed at 45 °C and higher temperatures. In contrast, [dema][HFO] having a longer fluoroalkyl chain than [dema][PFO], was not crystallized even at room temperature. Thus, those parameters were able to be measured. As listed in Table 1, the viscosities of [dema][PFO] and [dema][HFO]

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