OXYGEN REDUCTION REACTION ON PT ELECTRODE IN MIXTURE OF BRØNSTED ACID AND ROOM TEMPERATURE MOLTEN SALTS AT MEDIUM TEMPERATURE

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ABSTRACT

Oxygen reduction reaction (ORR) on Pt in mixtures of Brønsted acid and room temperature molten salts based on triflate anion has been investigated as a fundamental study for an application to medium temperature polymer electrolyte fuel cells. The ORR was determined by the slow scan voltammetry and the rotating ring disk electrode voltammetry under oxygen atmosphere on a Pt electrode. The oxygen reduction current in a mixture of trifluoromethanesulfonic acid (HTf) and 1-ethyl-3-methylimidazolium triflate (EMITf) was larger than that in a mixture of HTf and 2-ethylimidazolium triflate (2EtHImTf) and 85 wt.% aqueous phosphoric acid at 140 °C. The 63.5 kJ mol⁻¹ of the activation energy of the ORR at Pt/HTf-EMITf was larger than that of HTf in water at reversible potential. Hydrogen peroxide was not detected as a by-product in the range from 0.1 to 1.1 V vs. RHE by RRDE measurement. Consequently, HTf-EMITf would be a good electrolyte for the medium temperature fuel cells.

INTRODUCTION

Polymer electrolyte fuel cells (PEFCs) have been developed for applications to vehicles and residential co-generation systems (1-4), since PEFCs are expected to have high power density and low emission to environment. Conventional PEFCs have some problems for a practical use. For example, large overpotential of oxygen reduction reaction (ORR), CO poisoning for Pt electrocatalysts, difficulties of water management, low temperature for exhaust co-generation systems, and difficulties of temperature control of the cells by using a radiator in vehicles. One method to improve their problems would be medium temperature operation of PEFCs, which are operated in the temperature range from 100 to 200 °C, since the rates of the ORR and the CO oxidation reaction increase with temperature. In addition, the medium temperature exhaust heat will be useful for the residential co-generation systems, and the radiator will be compact because of the larger temperature differences between the cells and ambient temperature.

The conventional PEFCs can’t be operated at the medium temperature under atmospheric pressure because a conventional proton exchange membrane such as
Nafion® shows poor conductivity in low relative humidity (5). Therefore the proton conductor that works above 100 °C under low humidity is needed for the medium temperature fuel cell.

Room temperature molten salts (RTMSs), in other words room temperature ionic liquids, would have a potential to apply the electrolyte of the medium temperature PEFCs because RTMSs show good chemical and physicochemical properties, such as high thermal stability, very low vapor pressure, high ionic conductivity and electrochemical stability. The RTMSs could form ionic gel that might lead to a self-standing membrane with high ionic conductivity (6-8). Ionic conductivity of the RTMSs and the composites with RTMSs have been studied (9-11). The kinetics of the electrode reaction in RTMSs is also very important to develop efficient PEFCs.

In this study, properties of ORR on a Pt, which is the cathode reaction of PEFCs, in a mixture of Brønsted acid and RTMSs have been investigated as a fundamental study.

Trifluoromethanesulfonic acid (CF$_3$SO$_3$H, HTf) was selected as Brønsted acid because the ORR rate on Pt in aqueous HTf solution was faster than that in aqueous phosphoric acid solution (12). 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (EMITf) and 2-ethylimidazolium triflate (2EtHImTf) were chosen as RTMSs, because they have the same anion as HTf, EMI is one of the conventional cation among RTMSs, and imidazole that don’t have alkyl chains at nitrogen atoms has been developed as a proton conductive electrolyte itself (9,13).

**EXPERIMENTAL**

**Sample preparation**

The structures of the HTf, EMITf and 2EtHImTf are shown in Figure 1. The mixture of HTf and EMITf (HTf-EMITf) was prepared by the ion exchange reaction from 1-ethyl-3-methylimidazolium bromide (EMIBr) and HTf. Equivalent mole of 1-methylimidazole (99%, Aldrich) and ethylbromide (98%, Junsei chemicals) was refluxed with stirring in cyclohexane (reagent grade, Junsei chemicals) at 60 °C for 12h. The EMIBr was obtained after that cyclohexane was evaporated and purified by recrystallization in the mixture of ethyl acetate (reagent grade, Junsei chemicals) and 2-propanol (reagent grade, Junsei chemicals) several times (14). The EMIBr and 1.2 times

![Chemical structures of trifluoromethanesulfonic acid and room temperature molten salts.](image)
excess molar ratio of the HTf were mixed slowly. The mixture was pre-dried at 150 °C with stirring to remove HBr, and dried at 180 °C under vacuum for 24 hours. After the drying process, the concentration of the HTf was 11 mol % which was determined by the titration of sodium hydroxide.

2-ethylimidazoliumtriflate was prepared by neutralization. 2-ethylimidazole (98%, Tokyo Kasei Kogyo) purified by sublimation. Equivalent mole of 2-ethylimidazole and the HTf was dissolved to water and stirring at room temperature for 12 hours. The mixture was pre-dried at 100 °C under air for 12 hours, and dried at 80 °C under vacuum for 24 hours. HTf was added to the 2EtHImTf in the concentration of 11 mol% (HTf-2EtHImTf).

Measurements

Thermal stability was measured by thermogravimetry (TG) (Shinku Riko TGD 9600) with 5 °C min⁻¹ of the scan rate from room temperature to 450 °C in air.

The ORR was determined by slow scan voltammetry (SSV) in a three-electrode cell made of Pyrex Glass. The cell scheme is shown in Figure 2. The cell consisted of five compartments that were connected with 0.5 mm diameter capillary, and had gas input and output. Glass sealed electrodes and Teflon⁸ tube were connected to the cell by the Swagelok⁸ fittings. Volume of samples was approximately 1 cm³. Counter and reference electrodes were 0.3 mm diameter Pt wire sealed in a glass tube under hydrogen atmosphere and placed in both end compartments of the cell. The reference electrode should work as a reversible hydrogen electrode (RHE). The working electrode, which placed in the center compartment of the cell under oxygen atmosphere, was a 0.3 mm diameter Pt disk electrode sealed in a glass tube that was polished by #2000 emery paper and #6000 lapping tape (Fuji Film Co. Ltd). Nitrogen was flowed in the second and fourth compartments to prevent contamination of hydrogen and oxygen. The condition of SSV was the potential range from 0.05 to 1.2 V vs. RHE at 140 °C, and 0.5 V to 1.1 V.
vs. RHE in the temperature range from 40 to 180 °C at 1 mV s\(^{-1}\) scan rate under oxygen atmosphere by using HOKUTO DENKO model HSV-100 potentiostat. The current densities were normalized by roughness factor of Pt disk electrode, which was obtained by the hydrogen desorption peak in 1 mol dm\(^{-3}\) aqueous sulfuric acid solution. The temperatures were monitored temperatures by thermocouples (K) and controlled by a convection oven.

By-products of ORR were investigated by rotating ring disk electrode (RRDE) measurement with a Pt disk electrode (6mm diameter) and a Pt ring electrode (9 mm outer diameter and 7 mm inner diameter) in another three-electrode cell made of Pyrex Glass. The cell scheme is shown in Figure 3. A reference electrode was Pt under hydrogen atmosphere (RHE). A counter electrode was Pt placed on bottom of the cell.

The potential of the disk electrode was scanned from 0.05 to 1.2V vs. RHE with 10 mV s\(^{-1}\) scan rate under oxygen atmosphere. Potential of ring electrode was kept at 1.1 V vs. RHE. The RRDE was rotated 500, 1000 and 2000 rpm by using a rotating speed controller (NIKKO KEISOKU). The potential control was carried out with HOKUTO DENKO model HA1020mM2B bipotentiostat. The temperatures were monitored by thermocouples (K) and controlled by ribbon heater with insulation material at 140 °C.

RESULTS AND DISCUSSION

Thermal stability

Figure 4 shows weight loss ratio of 11 mol% HTf-EMITf by the TG from room temperature to 450 °C with the heating rate of 5 °C min\(^{-1}\). The weight losses were observed from 280 °C to 340 °C and above 410 °C. The former weight loss would indicate evaporation of HTf, because the weight loss was almost the same as concentration of HTf, which were about 7 wt. %. HTF-EMITf showed higher thermal stability than HTF itself, which boiling point is ca. 160 °C. The later would be decomposition of EMITf.
Fig. 4 Thermogravimetry curve at a heating rate of 5 °C min\(^{-1}\) for 11 mol% HTf-EMITf.

**Oxygen reduction reaction on Pt**

Figure 5 shows the voltammograms of the Pt in 11 mol% HTf-2EtHImTf and 11 mol% HTf-EMITf under oxygen atmosphere at 140 °C. Oxygen reduction current was observed in lower potential than 1.06 V vs. RHE in HTf-2EtHImTf, and than 1.09 V vs. RHE in HTf-EMITf. The values were near to theoretical oxygen reduction potential, which was 1.16 V vs. RHE at 140 °C. The ORR rate on the Pt in HTf-EMITf was faster than that in HTf-2EtHImTf. Since differences between the two materials were the existence of the nitrogen site without alkyl groups which should give high reactivity, therefore the nitrogen sites of 2-ethylimidazolium might absorb on Pt surface, and prevent ORR compared to EMI cation.

![Graph](image)

Fig. 5 Slow scan voltammograms of Pt for 11 mol% HTf-EMITf and 11 mol% HTf-2EtHImTf under oxygen atmosphere at 140 °C. (scan rate = 1 mV sec\(^{-1}\))

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The reduction currents had an inflection point around 0.5 V vs. RHE, and the increase of the reduction currents below 0.5 V vs. RHE was significantly larger than over 0.5 V, especially HTf-2EtHImTf. It would be hard that this behavior was explained by only one mechanism that should follow to Tafel equation. The large increase of the reduction currents would indicate another reaction or mechanism. The cause of the behavior was not clear.

Figure 6 shows the Tafel plots of the high potential region of Figure 5 with oxide-free Pt in 85 wt. % aqueous phosphoric acid solution at 136 °C (15). The theoretical Tafel slopes, assuming $\alpha n = 1$ and 0.5, are -82 and -164 mV dec.$^{-1}$, respectively at 140 °C. $\alpha$ is symmetry factor and $n$ is the number of electrons at the rate-determining step per molecule of reaction. Supposing $\alpha = 0.5$, $n$ was 2 at high potential region, and decreased to 1 gradually at lower potential. Since the behaviors of the three Tafel plots were similar, the mechanisms of oxygen reduction on Pt in HTf-EMITf and HTf-2EtHImTf would be almost the same as that on oxide-free Pt in phosphoric acid. The current density at 0.9V vs. RHE in HTf-EMITf was one order of magnitude larger than that in 85 wt.% phosphoric acid.

Figure 7 shows the temperature dependence of current densities for ORR on the Pt in the HTf-EMITf at the overpotential of 0.2 V by theoretical oxygen reduction potential of each temperature. The current densities significantly increased with temperature. The HTf-EMITf would be able to use up to medium temperature, and the reaction mechanism would not changed from 40 to 180 °C. Activation energy of exchange current density, which was extrapolated assuming $\alpha n = 0.5$, was 63.5 kJ mol$^{-1}$, according to following equation [1].

$$E_a = \alpha n F \eta - 2.303 \times R \times \text{slope}$$

[1]
Fig. 7 Temperature dependence of current densities for ORR on Pt in HTf-EMITf at the overpotential of 0.2 V.

\( E_a, F, \eta, R \) are activation energy of exchange current density, Faraday constant, overpotential and gas constant, respectively. The activation energies of 85 wt. % phosphoric acid aq. (15) and 1.1 mol dm\(^{-3}\) HTf aq. (12) are 62.4 and 52.7 kJ mol\(^{-1}\) at the reversible potential, respectively. Since the activation energy of HTf-EMITf was similar to that of 85 wt. % phosphoric acid aq., the current densities in HTf-EMITf would be 10 times higher than that in 85 wt. % phosphoric acid aq. at any temperature. On the other hand, the activation energy of HTf-EMITf was larger than that of 1.1 mol dm\(^{-3}\) HTf aq., so the HTf in EMITf would be more suitable at medium temperature than HTf in water.

**Rotating ring disk electrode measurement**

The ORR mechanism is proposed as the following reactions [1]-[4] in an acidic aqueous solution (16). The ORR produces water according to following reaction,

\[ \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O} \quad 1.23 \text{ V (vs. SHE)} \quad [2] \]

On the other hands, hydrogen peroxide is generated by 2-electron reduction reaction depending on electrodes materials, electrolytes and impurities (17), according to following reaction.

\[ \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2 \quad 0.67 \text{ V (vs. SHE)} \quad [3] \]

The hydrogen peroxide reduces to water,

\[ \text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O} \quad 1.77 \text{ V (vs. SHE)} \quad [4] \]

Or the hydrogen peroxide decomposes to oxygen and proton by the reverse reaction of [2]. The direct 4-electron pathway, the reaction [1], may involve an adsorbed hydrogen peroxide as intermediate (16), but the adsorbed peroxide are not emitted into the solution. On the other hand, the hydrogen peroxide pathway that is the chain of the reaction [3]
and [4] emits hydrogen peroxide into the solution. The diffusing hydrogen peroxide would lead to degradation of electrolytes of the cells, so combinations of electrode and electrolyte that don’t generate hydrogen peroxide should be better for fuel cells.

Figure 8 shows RRDE voltammograms on the Pt disk and the Pt ring electrode in the HTf-EMITf at 140 °C. The disk electrode showed oxygen reduction current as a similar behavior to Figure 5. The reduction currents increased with rotating rate by the enhancement of diffusion.

![Graph](image_url)

**Fig. 8** Disk (I disk) and Ring (I ring) currents during oxygen reduction on Pt in 11 mol% HTf-EMITf at 140 °C, and sweep rate of 500, 1000 and 2000 rpm at a sweep rate of 10 mV s⁻¹ (ring potential = 1.1 V vs. RHE).

Hydrogen peroxide should be detected as oxidation current on ring electrode at 1.1 V vs. RHE due to the reverse reaction of [2]. However, oxidation currents were not detected at the ring electrode in the wide potential range from 0.1 to 1.1 V vs. RHE of the disk electrode, so hydrogen peroxide would not be generated in the potential range. This behavior might make an advantage for a lifetime of the fuel cells. Oxidation current was only observed from 0.05 to 0.1 V vs. RHE. This oxidation current would indicate generations of hydrogen peroxide or hydrogen. Small reduction current was observed at the ring electrode in the potential range from 0.1 to 0.8 V vs. RHE. This current increased with rotating rate. This current might be affected with some productions at counter electrode, or involved an unknown intermediate of the ORR that could reduce at 1.1 V vs. RHE.

**CONCLUSIONS**

Thermal stability and oxygen reduction reaction on Pt in the mixture of Brønsted acid and room temperature molten salts based on triflate anion have been investigated as a fundamental study for application to medium temperature PEFCs. 11 mol% HTf-
EMITf was thermally stable up to 280 °C, which was higher than HTf itself. Oxygen reduction current on Pt at 140 °C in HTf-EMITf was larger than that in HTf-2EtHImTf and 85 wt. % aqueous phosphoric acid solution. The 63.5 kJ mol⁻¹ of the activation energy of the ORR at Pt/HTf-EMITf was larger than that of HTf in water at reversible potential. Hydrogen peroxide was not detected as a by-product in the range from 0.1 to 1.1 V vs. RHE. Consequently, HTf-EMITf would be a good electrolyte for medium temperature fuel cells.

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