

Oxygen Reduction Reaction on Pt Electrode in Mixture of Brønsted Acid and Room Temperature Molten Salts at Medium Temperature

K. Kudo, S. Mitsushima, N. Kamiya, and K-I. Ota

Department of Energy and Safety Engineering,
Yokohama National University
79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501,
Japan

Introduction

The proton conductor that works above 100 °C under low humidity is needed for medium temperature fuel cells in order to get the higher energy conversion efficiency than the conventional polymer electrolyte fuel cells (PEFCs). Room temperature molten salts (RTMSs) have high ionic conductivity, thermal stability, and electrochemical stability^{1,2}, and form ionic gel that might lead to a self-standing membrane with high ionic conductivity³. Most of the relating reports studied the ionic conduction of RTMSs^{4, 5}. The kinetics of the electrode reaction in RTMSs is also very important to develop an efficient PEFC.

In this study, the properties of oxygen reduction reaction (ORR), which is the cathode reaction of PEFCs, on Pt in a mixture of Brønsted acid and RTMSs have been investigated in a liquid state as a fundamental study of the reaction in RTMS electrolyte.

Trifluoromethanesulfonic acid (CF₃SO₃H, HTf) was chosen as Brønsted acid because the oxygen reduction rate on Pt in aqueous HTf solution was faster than that in phosphoric acid⁶. 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (EMITf) was chosen as RTMSs because it has the same anion as HTf and EMI cation is the most popular component among RTMSs.

Experimental

The mixture of EMITf and HTf was prepared by the ion exchange reaction from 1-ethyl-3-methylimidazolium bromide (EMIBr) and HTf. EMIBr was synthesized from 1-methylimidazole and ethylbromide⁷. EMIBr and HTf (1.2 times excess molar ratio) were mixed. The mixture was pre-dried on a hotplate stirrer at 150 °C to remove HBr, and dried at 180 °C under vacuum for 24h. After the drying process, the concentration of HTf was 6.7 wt. %, which was determined by the titration of sodium hydroxide.

Thermal stability was measured by thermogravimetry (TG) at the scan rate of 5 °C min⁻¹ from room temperature to 400 °C in air.

Slow scan voltammetry (SSV) was performed in a three-electrode cell made of Pyrex Glass. The counter and reference electrodes were 0.3 mm diameter Pt wire under hydrogen atmosphere. The reference electrode should be worked as a reversible hydrogen electrode (RHE). The working electrode was a 0.3 mm diameter Pt disk electrode sealed in a glass tube. The SSV was performed in the potential range of 0.5 to 1.1V vs. RHE at 1 mV s⁻¹ scan rate under oxygen atmosphere at 140 °C. The current of SSV was normalized by roughness factor of Pt electrode which was obtained by the hydrogen desorption peak in 1 mol dm⁻³ aqueous sulfuric solution.

Result and Discussion

The weight loss of 6.7 wt. % HTf-EMITf by TG from room temperature with the heating rate of 5 °C min⁻¹ was lower than 1 wt. % up to 200 °C. The boiling point of

HTf itself is ca. 160 °C, but HTf-EMITf was stable up to 200 °C.

Fig. 1 shows the Tafel plots for ORR on Pt in 6.7 wt. % HTf-EMITf at 140 °C observed in the cathodic and anodic sweep by SSV measurement. The theoretical Tafel slopes, assuming $\alpha n = 0.5$ and 1 were 82 and 164 mV dec.⁻¹, respectively at 140 °C. α is symmetry factor and n is the number of electrons at the rate-determining step per molecule of reaction. The Tafel slope changed gradually. The slope decreased at higher potential. Fig. 1 also shows the Tafel plots for ORR on oxide-free Pt in 85 wt. % aqueous phosphoric acid solution at 136 °C⁸. Since the behaviors of the two Tafel plots were similar, the mechanisms of oxygen reduction on Pt in HTf-EMITf would be almost the same as that on oxide-free Pt in phosphoric acid. The current density at 0.9 V vs. RHE in HTf-EMITf was one order of magnitude higher than that in 85 wt.% phosphoric acid.

Consequently HTf-EMITf would be a better electrolyte for medium temperature PEFCs.

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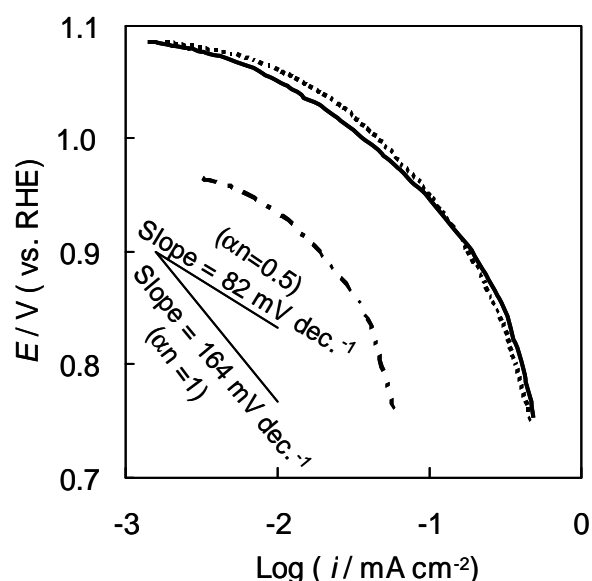


Fig. 1 Tafel plots for ORR on Pt electrode in 6.7wt. % HTf-EMITf at 140 °C. The solid line: cathodic sweep, the dotted line: anodic sweep, the dash-dotted line: oxide-free Pt in 85 wt. % phosphoric acid at 136 °C⁸.