Anodic Oxidation of Methanol at a Pt Electrode in a Hydrophobic Room Temperature Ionic Liquid

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Anodic oxidation of methanol was investigated at a Pt electrode in 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide (BMPTFSA) room temperature ionic liquid. It was found that methanol can be oxidized electrochemically in the ionic liquid without water. The oxidation products were identified as dimethoxymethane and proton by gas chromatography and electrochemical measurements. The further oxidation of dimethoxymethane was also suggested by cyclic voltammetry.

Key Words : Ionic Liquid, Methanol Oxidation,

1 Introduction

Room-temperature ionic liquids are attracting much attention due to their unique properties, such as negligible vapor pressure, high thermal and chemical stability, low melting point and acceptable ionic conductivity. They are expected to be applied to various electrochemical processes. The electrochemical behavior of methanol is important for such electrochemical devices as fuel cells and gas sensors. The electrochemical oxidation of methanol on a Pt electrode has been studied extensively in aqueous solutions.¹⁻⁵⁾ However, the electrochemical oxidation of methanol has not been investigated in ionic liquids. In general, the oxidation mechanism of methanol in aqueous solutions is complicated due to the interaction with oxides on electrode surface and adsorption phenomena.⁶⁻⁸⁾ For methanol oxidation reaction in aqueous solutions, research interest is mostly devoted to adsorbed species on the electrodes. Adsorbed CO has been identified as a reaction intermediate and catalyst poison.⁹⁻¹¹⁾ In order to clarify the reaction mechanism, however, the analysis of the reaction products should be made since there are several reports that the reaction products of the electrochemical oxidation of methanol were not only CO₂ but also small amounts of HCOOCH₃, HCOOH and HCHO.^{12,13)} This means that there would be the reaction pathways of the electrochemical oxidation of methanol to CO₂ via non-CO intermediates. For oxidation of methanol in non-aqueous media, on the other hand, G. Sundholm et al. found that dimethoxymethane (DMM) was produced by the electrochemical oxidation of methanol using sodium perchlorate as a supporting electrolyte.¹⁴⁾

In this study, the analysis of the electrochemical oxidation products of methanol was investigated primarily at a platinum electrode in a hydrophobic room-temperature ionic liquid, 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide (BMPTFSA) in order to elucidate the reaction mechanism of methanol oxidation.

2 Experimental

The ionic liquid used in this study was BMPTFSA, which was prepared by the method described elsewhere.^{15,16)} Anhydrous methanol (Kanto chemical, 99.8%) and DMM (Junsei, 98.0%) were used as supplied. An air-tight electrochemical cell was used for all the electrochemical experiments. A platinum disk electrode (3 mm ϕ) was used as a working electrode. A platinum wire was used as a counter electrode. The reference electrode consisted of a silver wire immersed in 0.1 M AgCF₃SO₃/BMPTFSA separated from the bulk liquid with porous glass (Vycor).

The bulk electrolysis was carried out by the galvanostatic and potentiostatic methods using a Pt working electrode with a geometric area of 12.4 cm², which was calculated from the amount of electricity for hydrogen adsorption. In the potentiostatic method, the electric charge was measured by a coulometer.

The qualitative analysis of reaction products was performed by gas chromatography (Shimadzu, GC-2014) with a packed column (Shimadzu, TSG-1). The water content of BMPTFSA was below 20 ppm, which was determined by Karl-Fisher titration (Metrohm, 831). All the measurements were carried out at room temperature (25 °C).

3 Results and Discussion

Figure 1 shows the cyclic voltammogram of a Pt electrode in BMPTFSA containing 0.1 M methanol. The open-circuit potential was chosen as the initial potential for cyclic voltammetry. No current was observed in BMPTFSA in the absence of the methanol. However, several anodic and cathodic currents were observed with addition of methanol. The anodic current peak was observed at the potentials more positive than 0.8 V in the anodic potential sweep from -0.3 to 1.5 V. In the cathodic potential sweep from 1.5 to -2.0 V, an anodic current peak and a cathodic current peak were observed at 0.1 and -0.6 V, respectively. In addition, an anodic cur-

Fig. 1 Cyclic voltammograms of a Pt electrode in BMPTFSA with and without 0.1 M methanol. Scan rate : 50 mV s⁻¹.

Fig. 2 Cyclic voltammograms of a Pt electrode in BMPTFSA with and without 0.1 M DMM. Scan rate : 50 mV s⁻¹.

rent peak was observed at -0.5 V in the anodic potential sweep from -2.0 to 0 V. The anodic peak at -0.5 V can be assigned to the reverse reaction of the cathodic reaction observed at -0.6 V in the preceding cathodic potential sweep. The anodic current peak observed at the potentials more positive than 0.8 V could be attributed to the oxidation of methanol. The cathodic and anodic current peak around -0.6 V were attributable to the reduction of proton and oxidation of hydrogen (H₂) on a Pt electrode in BMPTFSA.^{15,16} These results indicate that the proton was produced by the methanol oxidation in BMPTFSA.

In order to identify the reaction products, the bulk electrolysis was performed at 1.3 V in 3 ml of BMPTFSA containing 0.1 M methanol. The charge passed during the electrolysis was 5 C. The gas sampled from the gaseous phase over the ionic liquid was found to contain DMM by gas chromatography. Thus, the anodic reaction above 0.8 V can be attributed to the oxidation of methanol to DMM, as known in methanol-based electrolytes.¹⁴

This reaction shows formation of protons, of which the reduction was observed at -0.6 V in Fig. 1.

Figure 2 shows the cyclic voltammogram of a Pt electrode in BMPTFSA containing 0.1 M DMM. When the

potential was swept from -0.8 V toward positive direction, no significant current was observed below 1.3 V. However, an anodic current was observed in the preceding cathodic potential sweep below 0.6 V in addition to the cathodic current peak at -0.6 V, which can be attributed to the reduction of proton, as described above. These results suggest that the anodic current observed at 0.1 V during the cathodic potential sweep in Fig. 1 can be ascribed to the oxidation of DMM. It is interesting that DMM oxidation is possible only after keeping the electrode potential higher than 0.8 V. This unusual response may be caused by the hindrance of DMM oxidation by adsorption of the ions of the ionic liquid. The similar phenomena for hydrogen oxidation have been known in organic electrolytes¹⁸ and ionic liquids.^{15,17}

In general, it is widely accepted that methanol can be oxidized to CO₂ via adsorbed CO at a platinum electrode in acidic aqueous solution. On the other hand, the anodic oxidation of methanol in BMPTFSA leads to the formation of dimethoxymethane in the absence of water.

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