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Electro-oxidation of dimethyl ether on Pt/C and PtMe/C catalysts in sulfuric acid

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Abstract

The electro-oxidation of dimethyl ether (DME) on PtMe/Cs (Me = Ru, Sn, Mo, Cr, Ni, Co, and W) and Pt/C electro-catalysts were investigated in an aqueous half-cell, and compared to the methanol oxidation. The addition of a second metal enhanced the tolerance of Pt to the poisonous species during the DME oxidation reaction (DOR). The PtRu/C electro-catalyst showed the best electro-catalytic activity and the highest tolerance to the poisonous species in the low over-potential range (<0.55 V, 50 °C) among the binary electro-catalysts and the Pt/C, but at the higher potential (>ca. 0.55 V, 50 °C), the Pt/C behaved better than PtRu/C. The apparent activation energy for the DOR decreased in the order: PtRu/C (57 kJ mol^{-1}) > Pt_3Sn/C (48 kJ mol^{-1}) ≈ Pt/C (46 kJ mol^{-1}). On the other hand, the activation energy for the MOR showed a different turn, decreased in the following order: Pt/C (43 kJ mol^{-1}) > Pt_3Sn/C (35 kJ mol^{-1}) ≈ PtRu/C (34 kJ mol^{-1}). The temperature dependence of the DOR was greater than that of the oxidation of methanol (MOR) on the PtRu/C.

Keywords: Dimethyl ether; Methanol; Electro-oxidation; PtMe/C; Pt/C catalysts; A direct DME fuel cell

1. Introduction

In recent years, much attention has been paid to a direct methanol fuel cell (DMFC), because a direct-fed liquid fuel cell is ideal for mobile applications due to its compact system and high energy density fuel storage. However, the real commercialization of DMFCs is still hindered by significant energy losses and the safety issues of methanol. The major losses are caused by the poor activity of the methanol oxidation and methanol crossover from the anode to the cathode that leads a decreased cathode potential [1–4]. In order to develop a suitable fuel for a direct-fed fuel cell, some organic fuels have been studied. For example, the electro-oxidation of ethanol [5–7], dimethoxymethane (DMM) [8], trimethoxymethane (TMM) [9], formic acid [10], propane [11], ethyleneglycol [12], cyclohexane and methylcyclohexane [13] have been investigated. However, these fuels still have some problems regarding their electrochemical activity, crossover problem, or energy density.

Dimethyl ether (DME) is one of the alternative fuels that have been investigated for use in direct fuel cells [14–16]. DME is less toxic than methanol. It is a clean and alternative fuel which can be economically produced from a variety of hydrocarbon materials. DME can also be stored in the high-density liquid phase at modest pressures of around 5 atm, and delivered as a gas-phase fuel in a pumpless operation. Therefore, the use of DME can combine the advantages of the easy fuel delivery of pressurized hydrogen, and the high energy density storage of liquid fuel. Moreover, DME can be almost completely oxidized to CO_2 [14]. DME is expected to have less effect on fuel crossover when compared to methanol. The permeability of DME through a polymer electrolyte membrane was about one-tenth as small as that of methanol [15]. Since DME is not [16] or less oxidized [14] at the cathode than methanol, the energy loss at the cathode might be low even though it crosses over to the cathode. A direct DME fuel cell (DDMEFC) was demonstrated to yield a comparable power density and higher total efficiency than DMFC at 130 °C [16].

DME could been considered a new alternative fuel for direct fuel cells, however, for practical applications of the DDMEFC, the high over-potential for the anodic reaction of DME on Pt catalysts should be reduced, and the electrochemical oxidation

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reaction mechanism of DME needs to be clarified. Platinum, one of the typical catalysts for the oxidation of organic molecules, is quite active for the dehydrogenation step, but suffers from the CO oxidation step. Therefore, more active catalysts must be developed for the DME oxidation reaction (DOR). The addition of a second metal to Pt [17–20] has been widely investigated for the methanol oxidation reaction (MOR) and CO oxidation. W [21], Sn [22], and Mo [23] have been reported to improve the catalytic activity for the MOR. PtRu, PtFe, PtNi, PtCo, and PtMo alloys showed good CO tolerances [24]. The Pt–Ru binary metallic catalyst is commonly accepted as the best electro-catalyst for the MOR.

The understanding of the electro-catalytic activities of the DOR on the Pt binary metallic catalyst, and the electro-oxidation mechanism of the DOR on the Pt/C and Pt binary metallic catalysts are very important for developing more active catalysts for the direct DME fuel cell. In this study, an understanding of the DME oxidation on the carbon supported PtMe (Me = Ru, Sn, Mo, Cr, Ni, Co, and W) and Pt electrodes have been investigated by the electrochemical measurements in an aqueous half-cell. The catalytic activities have been discussed in comparison to the MOR.

2. Experimental

The electrochemical experiments were conducted using a conventional three-electrode glass cell. The electrolyte was a 1 M (M = mol dm^{-3}) sulfuric acid solution. A spiral Pt-plated Pt wire was used as the counter electrode. The reference electrode was a reversible hydrogen electrode (RHE). All the potentials reported in this paper were expressed with respect to a RHE. In order to remove oxygen from the electrolyte, nitrogen gas was bubbled into the electrolyte for more than 1 h. DME was then saturated in the electrolyte. The cell temperature was from 30 to 70 °C. The solubility of DME (P = 1 atm) in the 1 M sulfuric acid from 30 to 70 °C are shown in Table 1 [25].

Table 2 shows the characteristics of the PtMe/C and Pt/C electro-catalyst powders (N.E. CHEMCAT Co., Japan). The atomic ratio of Pt:metal in the PtRu/C, PtW/C, PtNi/C, and PtCo/C catalysts is 1:1, it is 2:1 in the Pt_2Cr/C, and 3:1 in the Pt_3Sn/C and Pt_3Mo/C catalysts. The average particle size of Pt was calculated from the Pt(1 1 1) peak measured by X-ray diffraction using the Scherrer equation [26]. CO-MSA (CO metal surface area) was measured by the BET method with the adsorption of CO gas.

The working electrodes were made by the following steps: the mixture of the electro-catalyst powder, 5 wt.% Nafion® solution (Aldrich), and ethylene glycol dimethyl ether (EGDE) were used as the catalyst ink. The weight ratio of Pt:Nafion®:EGDE was 2:1:30. The catalyst ink was uniformly painted onto a gold mesh (1 cm × 1 cm, 100 mesh) to get a 1 mg cm^{-2} Pt loading. The painted gold mesh was dried for 30 min at 80 °C in air, and then heated for 1 h at 120 °C under a nitrogen atmosphere. Additionally, 50 μl of a 1 wt.% Nafion® solution (Aldrich) was painted onto the catalyst layer to protect the catalyst layer from mechanical damage.

Table 1
Solubility of DME (P = 1 atm) in 1 M sulfuric acid [25]

Temperature (°C)	Solubility (M)
30	0.67
40	0.45
50	0.29
60	0.20
70	0.12

Table 2
Characteristics of electro-catalysts

Catalysts	Atomic ratio Pt:Me	Pt (wt.%)	Me (wt.%)	Pt(1 1 1) (nm)	CO-MSA (m^2/g)
PtRu/C	1:1	26.7	13.4	5.6	107
Pt_3Sn/C	3:1	46.2	8.6	4.1	41.5
PtW/C	1:1	32.2	31.1	3.9	79
Pt_3Mo/C	3:1	47.0	6.3	3.4	55.5
PtCo/C	1:1	43.2	13.6	3.0	85.5
PtNi/C	1:1	44.7	13.5	3.7	85.5
Pt_2Cr/C	2:1	46.8	6.0	3.7	76
Pt/C	–	50.3	–	2.38	61

The electrode was electrochemically cleaned under a nitrogen atmosphere in the electrolyte. After maintaining at the rest potential for 60 s, it was cycled between 0.05 and 1.2 V at a scan rate of 500 mV s^{-1} until a steady-state voltammogram was obtained. The following electrochemical measurements were carried out after these pretreatments: (i) cyclic voltammetry: the potential was scanned between 0.05 and 0.5 V at a scan rate of 50 mV s^{-1}. (ii) Slow scanning voltammetry: the potential was scanned from 0.2 to 0.6 V with a scan rate of 1 mV s^{-1}. The slow scan rate is to minimize the contribution of the double-layer charging to the total current and to obtain a quasi-steady-state. (iii) Chronoamperometry: the potential of the Pt/C was held at 1.0 V (at 0.7 V for the PtMe/C catalysts) for 10 s, then the potential was set for the working potential of 0.4 V versus RHE. The HZ3000 electrochemical measurement system (Hokuto Denko, Japan) was used in these measurements.

3. Results and discussion

3.1. Activity of the DOR for Pt/C and PtMe/Cs

Fig. 1 shows the steady-state cyclic voltammograms (CVs) of the Pt/C in 1 M sulfuric acid saturated with DME, which is 0.29 M and without DME under a nitrogen atmosphere at 50 °C in the potential range from 0.05 to 1.2 V. The scan rate was 50 mV s^{-1}. The CV without DME during the anodic and cathodic scans in the potential region from 0.05 to 0.4 V correspond to the adsorption and desorption of the hydrogen, however, the peaks in the hydrogen region of the CV with DME were significantly suppressed because the Pt sites were poisoned by the DME oxidation intermediates. During the anodic potential scan, no clear oxidation current was observed up to 0.5 V. A sharp peak and a shoulder oxidation current were formed at E_p = 0.74 V (Peak I) and ca. 0.8 V (Peak II), which were correlated to the oxidation current of the intermediate adsorbed