

## Electrochemical Oxidation of Dimethyl Ether and Reaction Products

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### Introduction

Dimethyl ether (DME) can be easily made by the reaction of CO and H<sub>2</sub>, and it has been considered as a fuel for a direct feeding fuel cell. The theoretical electromotive force and theoretical efficiency of the direct DME fuel cell (DDFC) are almost equal to those of a direct methanol fuel cell (DMFC). However, considering the practical applications of the DDFC, there are several problems to be solved. One of them is the high overpotential for anodic reaction of DME on currently available catalysts. In order to develop a DDFC, the overpotential should be reduced and the detailed understanding of the electrochemical oxidation of DME is needed. In this paper, anodic reaction characteristics and reaction products of DME have been studied in sulfuric acid by the electrochemical methods, combined with gas-chromatograph(GC), and the Attenuated Total Reflection-Fourier transform infrared (ATR-FTIR) analyses.

### Experimental

The electrochemical experiments are conducted using a conventional three-electrode glass cell. The electrolyte is 1M (M= mol dm<sup>-3</sup>) H<sub>2</sub>SO<sub>4</sub> solution saturated with DME. The solubilities of DME (P=1atm) in the 1M H<sub>2</sub>SO<sub>4</sub> are 0.65, 0.45, 0.29 and 0.12M at the temperature of 30, 40, 50 and 60°C, respectively, by a volumetric method<sup>[1]</sup>. The working electrodes are smooth Pt rods, Pt/C and Pt-Me/C (N.E. CHEMCAT Co, JAP, Me=Ru, Sn). The reference electrode was the reversible hydrogen electrode (RHE) in the same solution. The cell temperature was from 30~70°C.

The CO<sub>2</sub> current efficiency ( $\epsilon_{CO_2}$ ) is defined as:

$$\epsilon_{CO_2} = \frac{R_{CO_2} \times F \times n}{i \times t}$$

R<sub>CO<sub>2</sub></sub>: yield rate of CO<sub>2</sub> (molmin<sup>-1</sup>), F: Faraday constant, n: number of electrons per reaction (=12), i: current density, t: time.

### Results and Discussion

The GC analysis of product gas showed that CO<sub>2</sub> was the main product of DME oxidation reaction (DOR), the remaining products were methyl formate and small amount of methanol, formic acid and formaldehyde.

The CO<sub>2</sub> current efficiency ( $\epsilon_{CO_2}$ , at 0.6V) of DME oxidation was shown in Fig.1.  $\epsilon_{CO_2}$  increases with temperature and varies in the range of ca. 80~100%. In contrast to the results of methanol oxidation reaction (MOR)<sup>[2]</sup>, the  $\epsilon_{CO_2}$  of DOR on Pt/C is higher than that on PtRu/C at 0.6V (30~70°C). As shown in Fig. 2, at E<0.55V, the activities of PtRu/C and Pt<sub>3</sub>Sn/C are higher than Pt/C. This might be due to the alloying effects which weaken or even overcome poisoning by the DOR intermediates; especially the adsorbed CO-like species. At E>0.55V, Pt<sub>3</sub>Sn/C and Pt/C are better than PtRu/C. The poisoning species might be easily oxidized to CO<sub>2</sub> at high overpotentials. The current density of DOR (at 0.4V) was

shown in Fig. 3. It increased in the order: Pt/C < Pt<sub>3</sub>Sn/C < PtRu/C. PtRu/C is the best catalyst among them.

The activation energies for DOR were shown in Fig. 3, too. They decreased in the order: Pt<sub>3</sub>Sn/C (64.8) > PtRu/C (57.9) > Pt/C (46.5 kJmol<sup>-1</sup>). It is evident that the activation energy increases by alloying Pt with the second metals. This is different from MOR, the activation energy for MOR decreased in the order: Pt/C (43.4) > Pt<sub>3</sub>Sn/C (35.2) > PtRu/C (33.6 kJmol<sup>-1</sup>). The addition of Ru, or Sn enhanced the oxidation of pre-oxidation species such as CO<sub>ad</sub>, hence, the activation energies for MOR decreased. But for DOR, there are two C atoms in one DME molecular, the oxidation of DME (e.g., DME → pre-oxidation species) would be more complicated than that

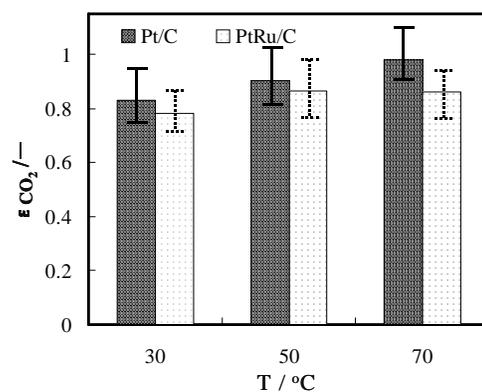


Fig.1 CO<sub>2</sub> current efficiency of DOR on Pt/C and PtRu/C electrodes at 0.6V.

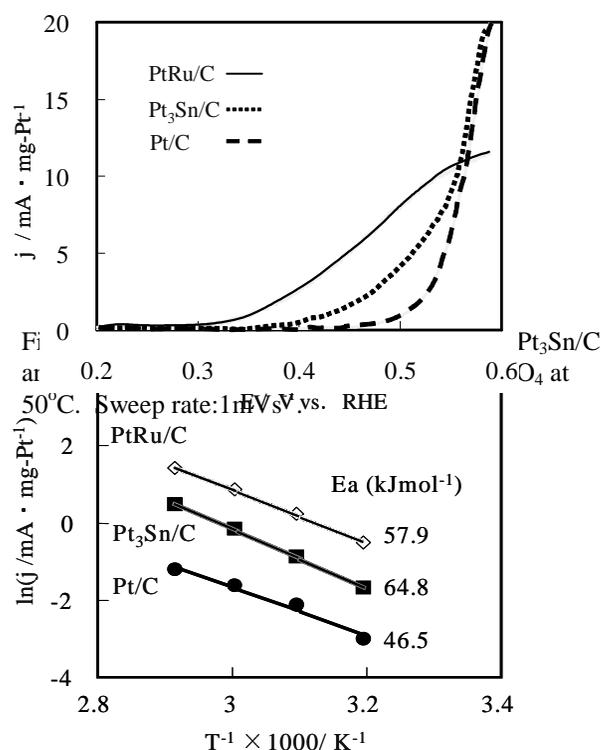


Fig.3 Arrhenius plots for DOR current densities on PtRu/C, Pt<sub>3</sub>Sn/C, Pt/C electrodes at 0.4V in 1M H<sub>2</sub>SO<sub>4</sub>.

### References

- [1] S. Okuma, Graduation thesis of Dept. Energy & Safety Eng., Yokohama Nat.Univ., p.20 (2000).
- [2] L. Gao et al., *Electrochim. Acta.*, 49, 1285 (2004).