

Temperature Effect on Methanol and Ethanol Electrooxidation at Pt/C and Pt-Ru/C Microporous Electrodes

C.-G. Lee,^a M. Umeda,^b and I. Uchida^c

^aKorea Electric Power Research Institute,
103-16 Munji-dong, Yuseong-gu, Daejeon 305-380 Korea

^bDept. of Chemistry, Nagaoka Univ. of Technology,
Kamitomioka, Nagaoka 940-2188, Japan

^cDept. of Applied Chemistry, Tohoku Univ.,
Aramaki-aoba, Aoba-ku, Sendai 980-8579, Japan

Owing to the several merits of liquid alcohol fuels over gaseous fuels, i.e., high energy density, availability of the gasoline infrastructure and unnecessary of the reforming, direct alcohol fuel cell (DAFC) has been focused as a new power source. Methanol and ethanol have been considered as fuels for the DAFC and their electrochemical oxidation behaviors have been investigated intensively at various electrocatalysts. In practice, DAFC is fabricated by carbon supported porous catalysts. Recently, Uchida's group has succeeded in evaluating carbon supported catalyst powders without using binders with microporous electrode.¹⁾ In this work, the temperature effect on methanol and ethanol electrooxidation was investigated at carbon supported Pt and Pt-Ru. Cyclic voltammetry with microporous electrodes, which enabled evaluation of these catalysts, was employed at different temperatures up to 80°C.

Electrocatalysts used in this work were Pt/C and Pt-Ru/C supplied by Tanaka Kikinokoku Co. Platinum content of Pt/C was 45.9 wt%, while Pt-Ru/C was composed of 29.8 wt% Pt and 23.1 wt% Ru (atomic ratio of Pt/Ru=1/1.5). In order to evaluate the Pt/C and Pt-Ru/C as received, microporous electrode was employed. It had a cylindrical cavity with 50 μm dia. and ca. 10 μm depth filled with the electrocatalysts, which was served as a working electrode. Reference electrode was Ag|AgCl, and platinum black was served as a counter electrode. Methanol and ethanol solutions were prepared by adding 0.5 M methanol and ethanol to 1 N H_2SO_4 , respectively. The cell temperature was controlled between 25 °C to 80 °C with a forced convection type oven.

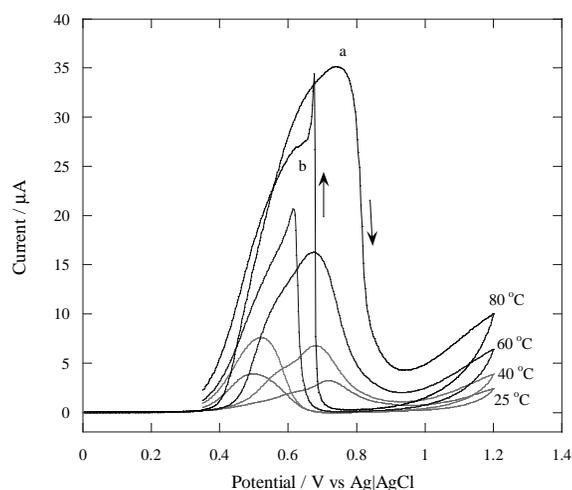


Fig. 1 Cyclic voltammograms with Pt/C at different temperatures in 0.5 M MeOH+1N H_2SO_4 , scan rate=0.1 V/s

Figure 1 shows CVs obtained by Pt/C at different temperatures in methanol solution. With increasing temperature from 25 °C to 80 °C, oxidation current ('a'

peak) rises by a factor of 10. Presumably CO coverage on the Pt/C is reduced with temperature increasing. Contrary to the CO coverage decreasing, methanol adsorption would increase, resulting in a higher methanol oxidation rate at higher temperature. Another temperature effect of Pt/C in methanol oxidation is almost vertical increase of reoxidation peak ('b' peak) with needle like peak top at higher temperature. Since the reoxidation peak is related to the reduction of adsorbed OH, the vertical increase indicates that reduction of the adsorbed OH occurs very fast at high temperature on Pt/C. Lower H_2O binding energy of Pt could be a reason for this behavior. Peak potential shift with temperature change should be noted as another temperature effect. With temperature increasing, the potential differences between 'a' and 'b' peaks are reduced. Potential of 'a' peak moves negatively with temperature, whereas the 'b' peak potential goes positively. Since those peaks are significantly related to OH production by H_2O dissociation, the reduced potential difference suggests that OH production on Pt/C is activated at higher temperature. In addition, the onset potential of methanol oxidation shows temperature dependence. At higher temperature, lower onset potential is observed probably due to the activated H_2O decomposition reaction on the surface of Pt/C.

From the CV results at Pt-Ru/C in the same temperature range, the current increase at 80 °C was a factor of 20. Comparing with Pt/C which showed a factor of 10 for the same temperature range, Pt-Ru/C appears to have much larger temperature dependence of methanol oxidation. Another different feature from Pt/C was the shape of reoxidation peak at 80 °C. Compared with the vertical increase of 'b' peak at Pt/C in Fig. 1, Pt-Ru/C showed milder slope at negative potential scanning probably due to the stronger adsorption of OH at Pt-Ru/C. This ruthenium effect in Pt-Ru/C was also represented at the onset potential. Larger onset potential decrease was observed with temperature at Pt-Ru/C than Pt/C.

In the ethanol oxidation, the CV results showed that Pt/C increased currents only by a factor of 4 whereas Pt-Ru/C raised it about 8 times for the same temperature range. Lower temperature dependence of currents in the ethanol solution is probably caused by weaker OH adsorption in the ethanol solution than in the methanol solution. The ruthenium addition remarkably enhanced ethanol oxidation performance probably due to the strong adsorption of OH.

In both alcohols, Pt-Ru/C showed larger apparent activation energies of oxidation than Pt/C, representing higher temperature dependence of OH adsorption on ruthenium. More complex oxidation path of ethanol seemed to provide less temperature effect than methanol.

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Reference

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