

**Temperature Dependence of the Electro-Oxidation of CO<sub>ad</sub> on Pt/C, PtRu/C, and Ru/C**

T. Kawaguchi, W. Sugimoto, Y. Murakami and Y. Takasu

Department of Fine Materials Engineering, Faculty of Textile Science and Technology, Shinshu University  
3-15-1 Tokida, Ueda 386-8567, JAPAN

- [1] Y. Takasu, T. Fujiwara, Y. Murakami, K. Sasaki, M. Oguri, T. Asaki, W. Sugimoto, *J. Electrochem. Soc.* **147**, 4421(2000).  
[2] T. Kawaguchi, W. Sugimoto, Y. Murakami, Y. Takasu, *Electrochem. Comm.* **6**, 480(2004).

Binary Pt<sub>50</sub>Ru<sub>50</sub>/C is a promising CO-tolerant anode catalyst for use in direct-methanol fuel cells (DMFCs). The CO<sub>ad</sub> oxidation process is postulated to be the rate determining step and Ru is widely accepted as a promoter for the CO<sub>ad</sub> oxidation. In order to prepare active CO-tolerant electrocatalysts, it is important that the fundamental catalysis of CO<sub>ad</sub> oxidation on catalyst metal particles is understood. In particular, the temperature dependence of the oxidation of CO<sub>ad</sub> should be characterized in view of the operation temperature of DMFCs. In this work, the CO<sub>ad</sub> oxidation on Pt/C, Pt<sub>50</sub>Ru<sub>50</sub>/C and Ru/C was studied by CO<sub>ad</sub> stripping voltammetry at temperatures ranging from 25 to 60°C.

Carbon supported Pt, Pt<sub>50</sub>Ru<sub>50</sub>, and Ru (30 mass% metal) electrocatalysts were prepared by an impregnation method reported previously [1]. The working electrode was a thin film electrode composed of a mirror polished Glassy Carbon rod (0.196 cm<sup>2</sup> exposed surface) modified with 40 µg of the active material (12 µg metal). A beaker-type electrochemical cell equipped with the working electrode, a platinum mesh counter electrode, and an Ag/AgCl reference electrode was used. Electrochemical measurements were conducted at 25, 30, 40, 50, and 60°C. All electrode potentials will be referred to the RHE scale corrected for the temperature effect. Oxidation of pre-adsorbed carbon monoxide (CO<sub>ad</sub>) was measured by CO<sub>ad</sub> stripping voltammetry in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution at a scan rate of 10 mV s<sup>-1</sup>.

For Pt/C, the CO<sub>ad</sub> oxidation potential decreased linearly with the increase in temperature and the amount of CO<sub>ad</sub> oxidation charge was independent of the temperature (Fig. 1 (top)).

The CO<sub>ad</sub> oxidation peak potential on Pt<sub>50</sub>Ru<sub>50</sub>/C decreased with the increase in temperature up to 40°C and became constant above this temperature, and the anodic charge due to CO<sub>ad</sub> oxidation on Pt<sub>50</sub>Ru<sub>50</sub> decreased with the increase in the temperature (Fig. 1 (middle)). The peak potential of the CO<sub>ad</sub> oxidation on Pt<sub>50</sub>Ru<sub>50</sub>/C is about 180 to 280 mV lower compared than on Pt/C depending on the operating temperature.

Similar to the behavior of Pt<sub>50</sub>Ru<sub>50</sub>/C, a non-linear decrease in the CO<sub>ad</sub> oxidation potential was observed for Ru/C with increasing temperature (Fig. 1 (bottom)). Besides the difference in the electrode potential, one can clearly see that the apparent amount of charge due to the CO<sub>ad</sub> oxidation on Pt<sub>50</sub>Ru<sub>50</sub>/C and Ru/C decreases with increasing temperature, even though the exposed metal area should not change as a function of the temperature. The CO<sub>ad</sub> oxidation charge was very sensitive to the CO adsorption potential [2]. For Ru/C, the CO<sub>ad</sub> oxidation charge exhibited a maximum when the CO adsorption potential was set to 280 mV vs. RHE. Hence, the decrease in the anodic charge with increasing temperature (Fig. 1 bottom graph) can be attributed to the lower CO<sub>ad</sub> coverage.

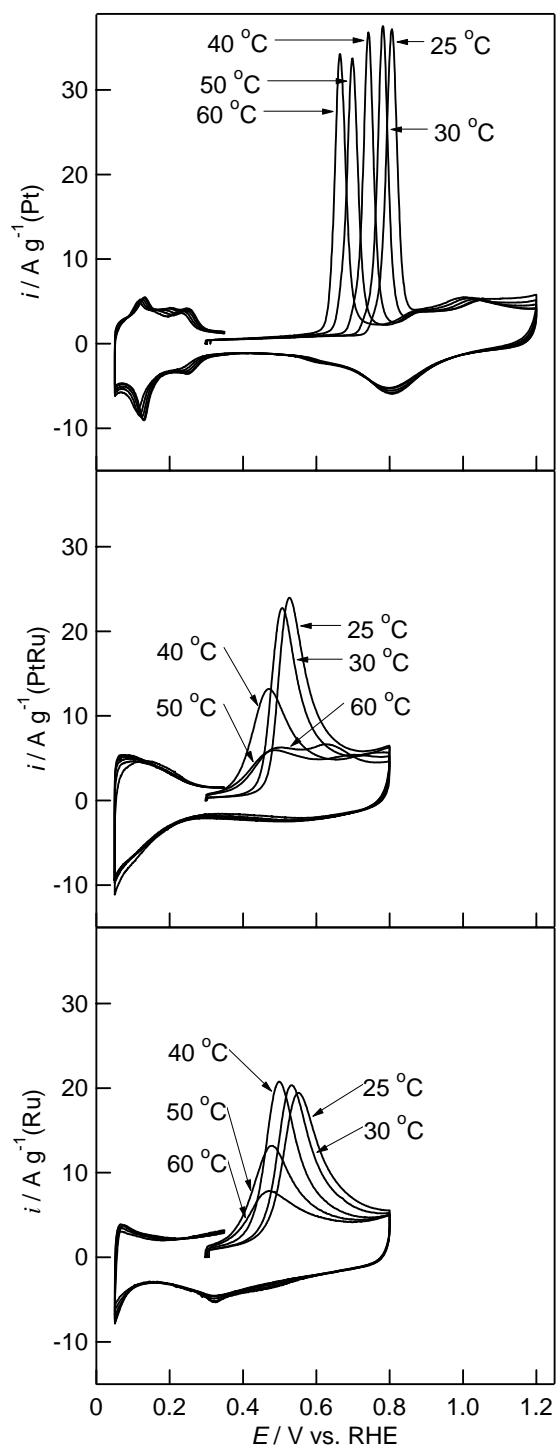


Fig. 1. CO<sub>ad</sub> stripping voltammograms of Pt/C (top graph), Pt<sub>50</sub>Ru<sub>50</sub>/C (middle graph) and Ru/C (bottom graph) at various temperatures.