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Electrochemical Impedance Spectroscopy of PtRu/C Thin Film Electrodes

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PtRu/C is a promising anode catalyst for use in direct-methanol fuel cells. Ru is widely known as a second metal that promotes the CO electro-oxidation. In order to prepare active electrocatalysts, it is important that the fundamental electrocatalytic activity of CH_3OH and CO_{ad} oxidation is understood. In particular, for understanding reactions with different rates, it is essential that the reaction rates of the electro-oxidations of CH_3OH and CO_{ad} are characterized. Electrochemical impedance spectroscopy has been utilized to probe the anodic processes for CH_3OH electro-oxidation using a MEA with H_2 passed on the cathode side to act as the counter and reference electrode.[1,2] In this work, we studied the CH_3OH electro-oxidation on a $Pt_{50}Ru_{50}/C$ thin film electrode by electrochemical impedance spectroscopy and compared the results with CO_{ad} stripping voltammetry.

The $Pt_{50}Ru_{50}/C$ (30 mass% metal) electro-catalyst was prepared by a co-impregnation method reported previously.[3] All electrochemical measurements were conducted at 60°C. A beaker-type electrochemical cell equipped with the working electrode, a platinum mesh counter electrode, and an Ag/AgCl reference electrode was used. The working electrode was a thin film electrode composed of a mirror polished Glassy Carbon rod (0.196 cm^2 surface) modified with 40 μg of the active material (12 μg metal) and stabilized with Nafion ionomer. Impedance measurements were conducted in 1.0 M CH_3OH + 0.5 M H_2SO_4 solution in a constant voltage mode by sweeping frequencies from 5,000 to 0.050 Hz at an amplitude of 10 mV. The electro-oxidation behavior of CO_{ad} was measured by CO_{ad} stripping voltammetry in 0.5 M H_2SO_4 solution at a scan rate of 10 mV s^{-1}. Gaseous CO was purged into the cell while maintaining a constant voltage of 300 mV vs. RHE.

The complex-plane impedance plots of CH_3OH electro-oxidation on PtRu/C at various electrode potentials are shown in Fig. 1. At 300 mV vs. RHE, an arc is evident in the complex-plane plots and a deviation from the 90° phase angle in the Bode plots is observed (Fig. 2). This indicates the presence of a resistive component. A pseudo-inductive behavior is clearly observed above 400 mV vs. RHE. With increasing electrode potential, the transition frequency of the change in the sign of the slope of the phase angle in the Bode plots is observed at higher frequency, indicating that the overall CH_3OH electro-oxidation rate is kinetically favored. CO_{ad} stripping voltammetry on PtRu/C revealed that the electro-oxidation of CO_{ad} begins at approximately 300 mV vs. RHE. This is in good agreement with the impedance data showing a resistive behavior at 300 mV vs. RHE and a pseudo-inductive behavior above 450 mV vs. RHE.

The impedance data was fitted using an equivalent circuit shown in Fig. 3. The value of CPE_2 was approximately 8 μF cm^{-2}, which is a reasonable value for the electrical double-layer capacitance. The reaction resistance R_0 and the inductance L of CO_{ad} electro-oxidation decreased with increasing electrode potential, which can be attributed to the faster reaction rate of CO_{ad} electro-oxidation to CO_2 at higher electrode potentials.

1. J.T. Mueller, P.M. Urban, *J. Power Sources*, **75**, 139 (1998).
2. J.T. Müller, P.M. Urban, W.F. Höderich, *J. Power Sources*, **84**, 157 (1999).
3. Y. Takasu, T. Fujiwara, Y. Murakami, K. Sasaki, M. Oguri, T. Asaki, W. Sugimoto, *J. Electrochem. Soc.*, **147**, 4421 (2000).

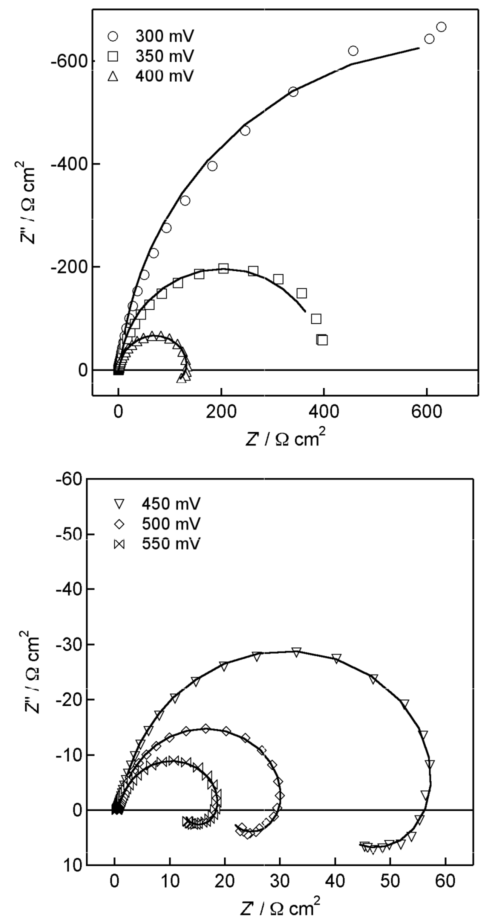

Figure 1. Complex-plane impedance plots of PtRu/C in 1.0 M CH_3OH + 0.5 M H_2SO_4 (60°C) at various electrode potentials. The solid lines represent the fitted data to the equivalent circuit Fig. 3.

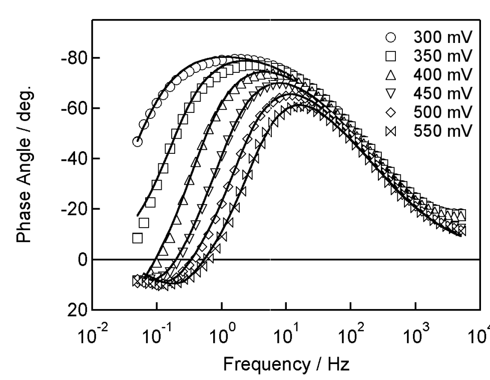

Figure 2. Bode plots of PtRu/C in 1.0 M CH_3OH + 0.5 M H_2SO_4 (60°C) at various electrode potentials. The solid lines represent the fitted data to the equivalent circuit Fig. 3.

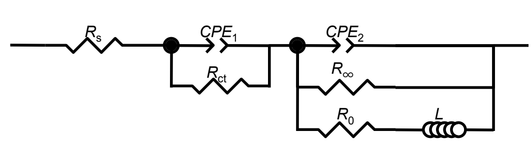

Figure 3. Equivalent circuit used for modeling the Faradaic impedance on PtRu/C anode.