In Situ X-ray Absorption Studies of Pt and Ru Chemistry during Methanol Oxidation

W.L. Holstein, H.D. Rosenfeld
DuPont Central Research & Development, Wilmington, DE, U.S.A.

Introduction

Unsupported and carbon-supported PtRu alloy catalysts are leading candidates for use in direct methanol fuel cell anodes. Questions remain concerning the oxidation states of Pt and Ru during methanol oxidation and their dependence on anode overpotential. The effect of changing oxidation states is of more than academic interest; some operating conditions can lead to Ru loss from the anode and a subsequent loss in catalyst activity, thereby impacting fuel cell lifetime.

Methods and Materials

X-ray absorption spectroscopy is uniquely suited to provide *in situ*, element-specific information on the catalyst oxidation state. In order to obtain information during transient operation, we developed a novel analytical technique based on the collection of absorption data at a constant photon energy. Changes in the Ru and Pt oxidation state could be monitored over times as short as 0.5 second, as compared with the 10 or more minutes needed for full scans.

Results and Discussion

20% PtRu/carbon and PtRu black catalysts, both with a 1:1 Pt:Ru ratio, were studied in an electrochemical half cell. Pt and Ru absorption were recorded while the anode potential was cycled versus a calomel reference electrode (rce) and the electrochemical current was concurrently measured. Representative plots of Ru and Pt absorption versus time for voltage cycling between -0.25 and 1.10 V at 50 mV/s for a 1 M CH_3OH + 0.5 M H_2SO_4 solution are shown in Fig. 1. Periodic changes in Ru and Pt absorption resulted from changes in their oxidation states, which lagged slightly behind the voltage. For Ru, these periodic changes are superimposed on a curve reflecting decreasing absorption due to Ru loss from the catalyst by dissolution, which occurred during cycling to high voltages. Periodic changes in Pt oxidation state were observed during the early part of the scan, but as Ru was lost, the Pt remained in the reduced state even at the higher voltages. Analogous electrochemical measurements were carried out in membrane electrode assembly half cells with solid Nafion® 117 membranes. Data recorded by using liquid electrolytes and solid electrolytes were in good agreement.

Acknowledgments

Use of the APS was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38.

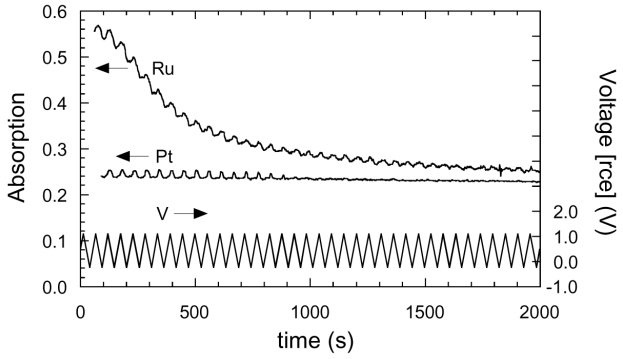

FIG. 1. Plots of Ru and Pt absorption versus time for voltage cycling between –0.25 and 1.10 V (rce) at 50 mV/s for a 1 M CH_3OH + 0.5 M H_2SO_4 solution.