NEXAFS Study of Chemisorption on Carbon-Supported Pt and Pt/Ru Fuel Cell Catalysts in an Electrochemical Cell

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Introduction

Differences in the transitions excited in the Pt L2 and L3 absorption spectra allow them to be appropriately subtracted to reveal information concerning the antibonding orbitals of chemisorbed species on the Pt surface.[1] Using an electrochemical cell designed for *in situ* x-ray absorption spectroscopy, we have studied chemisorbed species on carbon-supported Pt and Pt/Ru alloy direct methanol fuel cell catalysts in 0.5M H_2SO_4 electrolyte at various electrochemical potentials, with and without methanol in the electrolyte. We find that alloying with ruthenium affects the binding energy of the 2p core states. We further find that this binding energy is affected by applied electrochemical potential and by the addition of 1M methanol to the electrolyte solution. Variation of the binding energy as a function of potential and methanol presence is similar for the alloyed and unalloyed Pt catalysts. In spite of these similarities, bonding of chemisorbed species as a function of applied electrochemical potential is quite different. The Pt/Ru alloy shows a greater resistance to oxidation at high potentials and a higher energy Pt-H antibonding state (suggesting a stronger Pt-H bond) than does unalloyed Pt. X-ray absorption spectroscopy was performed at beamline 5-BM-D, DND-CAT, the Advanced Photon Source, Argonne National Laboratory.

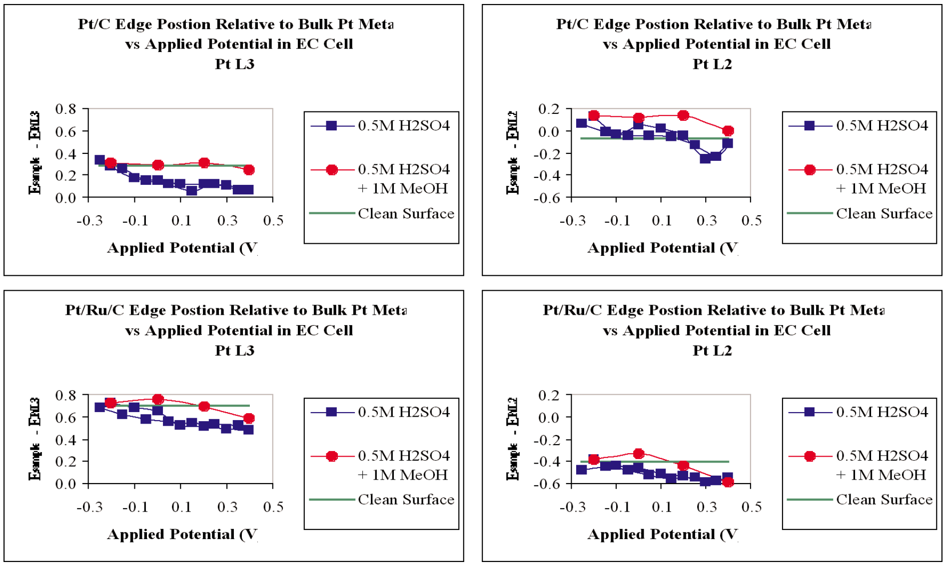

FIG. 1. Absorption edge threshold energy relative to that of bulk Pt versus applied electrochemical potential.

Methods and Materials

Carbon-supported Pt and Pt/Ru alloy catalysts were formulated into a Nafion® ionomer ink and applied to a conductive carbon paper strip at a loading of approximately 0.3 mg Pt/ 1.5 cm^2. The carbon paper strip was placed over a 10 mm x 5 mm rectangular hole cut in the lower left corner of one face of a square 125 ml polyethylene bottle, with the catalyst facing the inside of the bottle. Glassy carbon electrodes were placed in contact with the carbon paper on either side of the hole. The catalyst/carbon paper/electrode assembly was secured to the bottle with 1 mil Kapton® polyimide adhesive tape. The screw cap for the bottle was modified to accept a Pt counter electrode and a calomel reference electrode. The bottle was filled with 0.5M H_2SO_4 electrolyte and placed in the 7 mm x 1 mm x-ray beam in fluorescence geometry. A Lytle cell containing Xe gas at atmospheric pressure, equipped with a 6 absoprtion length filter of either Ge (Pt L3 edge) or Se (Pt L2 edge), was used for fluorescence detection. Sufficient intensity was transmitted through the electrochemical cell to utilize a Pt reference foil downstream for energy calibration. The electrochemical cell was attached to a poteniostat for control of applied electrochemical potential. The electrolyte was deaerated with He at 50 sccm for 1hr before beginning any electrochemistry. The catalyst was cycled 30 times between –0.25 V and +1.1 V (relative to the calomel reference electrode) at a rate of 50 mV/s to "clean" the catalyst surface. The final cycle was ended at –0.25 V and the catalyst held at that potential for collection of the first set of Pt L3 and L2 spectra. Subsequent spectra were obtained at constant potentials of –0.15, -0.05, +0.05, +0.15, +0.25, +0.35, +0.40, +0.30, +0.20, +0.10, 0.00, -0.10, and –0.20 volts in that order. Methanol was then added to the cell to a concentration of 1M in the electrolyte solution. And spectra were obtained at potentials of –0.20, 0.00, +0.20, and +0.40 volts. Finally, the catalyst was removed from the electrochemical cell, placed in a gas reactor cell, heated to 75°C in 50 sccm H_2 for 20 minutes and cooled in 50 sccm He to room temperature, to provide spectra from a clean (free from chemisorbed species) catalyst surface.

Spectra were energy calibrated based on peak fitting the maximum in the first derivative of their associated Pt foil reference spectra (assumed 11564 eV). They were corrected for dark currents, background was subtracted, and they were normalized. Sample spectra edge positions were found using linear interpolation to identify the energy at which absorption had risen to 0.6, and the zero of the energy scale shifted to that edge position. Near-edge features associated with chemisorbed antibonding orbitals were extracted by first subtracting clean surface spectra from the sample L2 and L3 spectra, then subtracting each samples L2 difference spectra from its L3 difference spectra.[1]

Results & Discussion

Sample absorption edge positions relative to bulk Pt foil are shown in Fig. 1. Both Pt/C and Pt/Ru/C show Pt L3 edge positions for a clean surface that are higher than that of bulk Pt. Their clean surface Pt L2 edge postions are lower than that of bulk Pt. Trends of absorption threshold versus applied potential are similar for both catalysts. Note that addition of methanol tends to raise the threshold energy.

Figure 2 shows near-edge difference spectra showing features arising from chemisorbed species. Gas phase experiments on these catalysts indicate that the negative peaks near 0 eV and 5 eV correspond to transitions to Pt-H antibonding orbitals. Note that this feature occurs at higher energy in the Pt/Ru/C catalysts, which may indicate a stronger Pt-H bond for that catalyst. Gas phase experiments also indicate that the structure seen at +0.4 V without methanol in the Pt/C catalyst is that of Pt-O bond formation, while that with methanol is a combination of Pt-O and Pt-CO bonds. This is in marked contrast to the Pt/Ru/C catalyst in which there is no evidence for formation of anything other than Pt-H bonds at any potential studied, with or without methanol.

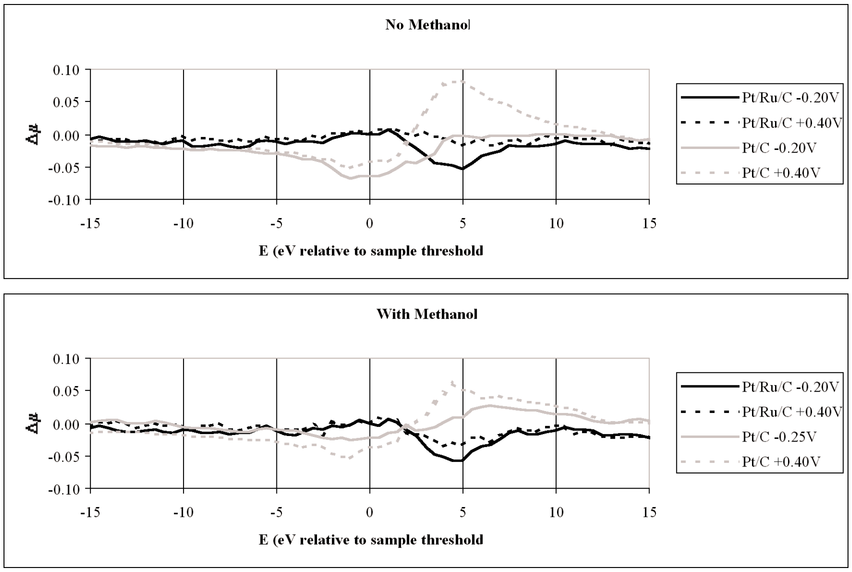

FIG. 2. Near-edge difference spectra for Pt/C and Pt/Ru/C at –0.20 V and +0.40 V with and without methanol.

Acknowledgments

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Reference

[1] D. Konigsberger, B. Mojet, J. Miller, D. Ramaker, J. Synchrotron Rad. **6**, 135-141 (1999).