

X-ray Absorption Spectroscopy in Fuel Cell Studies

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Introduction

The advent of synchrotron sources for the production of intense continuous wave length x-rays has made it possible to carry out a number of new experiments to probe the structure of electrochemical interfaces in particular those in fuel cells. *In situ* x-ray absorption spectroscopy (XAS) makes it possible to investigate both the electronic and geometric properties of electrocatalyst particles under the conditions that most closely resemble those of an operating fuel cell. The EXAFS (extended x-ray absorption fine structure) portion of the spectrum provides information on the near neighbor distances, composition (number of near neighbors), the particle size, and interactions with supports (1) and adsorbates (2). The XANES (x-ray absorption near edge structure) portion of the spectrum provides information on oxidation states, and structure arising from perturbations in the electronic structure due to bonding with adsorbates (3) and charging of the surface (4). The use of XAS in the study of fuel cell catalysts and interfaces will be reviewed and our recent data on the EXAFS Pt/Ru alloys will be presented.

Results and Discussion

Earlier it was established that Pt/Ru alloys have a unique activity for the electrochemical oxidation of methanol (5,6). Recent work on methanol oxidation has focused on unsupported Pt/Ru black alloys. The preparation of Pt/Ru catalyst materials has been a source of irreproducible results. The achievement of higher current and power densities as well as reducing the cell cost necessitates the use of high surface area supported catalysts. To date, the best-reported performance for direct methanol oxidation on a high surface area supported catalyst is the work of Watanabe et al. on carbon supported Pt/Ru alloys (7).

The active catalyst has been thought to be a metal oxide or a mixture of metals and oxides and not a metallic alloy. This conclusion was based on data obtained on as-prepared

catalysts (8). Here we present the XAS data for two different Pt/Ru catalyst materials: one a carbon-supported Pt/Ru catalyst synthesized by the Watanabe procedure and the second a commercially prepared unsupported Pt/Ru catalyst. Spectra obtained for the as-prepared catalysts are compared with the data from the same catalyst run as a methanol oxidation catalyst in a fuel cell for an extended period (the commercial catalyst) and with data recorded *in situ* for a catalyst held at a potential in the methanol oxidation region.

In both cases the as-prepared Pt/Ru catalysts were found to be predominately in the form of Pt and Ru oxides. When these catalysts were placed in an electrochemical cell and held in the potential region where methanol oxidation occurred the XANES data showed that the metal oxides were reduced to the metallic form (9). The analysis of the EXAFS portion of the data, shows that not only were the oxides reduced to the metallic form but they were in the form of a Pt/Ru alloy.

References

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