

FUELING SURFACE STUDIES FOR CATALYTIC SCIENCE

Coating platinum (Pt) nanoparticles with a sub-monolayer of ruthenium converts the normally bulk-sensitive x-ray absorption spectroscopy into a surface-sensitive technique. This new approach can then reveal critical details about the mechanisms of catalytic reactions at the surface, simulating Pt/ruthenium (Ru) catalysts, and allowing researchers to see how the catalyst accelerates the electrochemical oxidation of methanol in a fuel cell with a view to boosting catalyst efficiency. This important process could underpin future electricity generation for portable devices and vehicles.

Fuel cells were first invented in the nineteenth century and use the reaction of an energy-rich organic molecule such as methanol or ethanol, flowing over a catalytic metal reacting with oxygen to produce an electric current as well as releasing water and carbon dioxide as byproducts with no toxic pollutants. Essentially, a fuel cell is a battery with a chemical fuel supply. As such, these devices have become the focus of twenty-first-century clean power technology. They might one day displace the internal combustion engine or allow us to recharge mobile devices, such as cell phones and computer tablets, with a canister of liquid fuel as simply and easily as one might refill a cigarette lighter without the need to connect to an electrical power outlet.

Direct methanol fuel cells (DMFCs) are among the most promising class of these devices. However, their wider adoption for commercial applications has been stymied somewhat by the Pt catalysts used in experimental designs. Platinum is an expensive noble metal. Moreover, the two-step reaction that converts methanol to water and carbon dioxide leads to poisoning of the catalyst as carbon monoxide and methanol intermediates are formed that fill up the reactive sites on the catalyst surface. It was known that addition of a less expensive metal might impede this poisoning process. The most effective additive is Ru metal, which almost wholly precludes the poisoning reaction and so maintains the catalytic activity of the Pt almost indefinitely.

In order to develop the optimal approach to incorporating Ru as an additive to work with the Pt catalyst requires new insights into how different arrangements of the two metals might affect the catalytic process and electricity

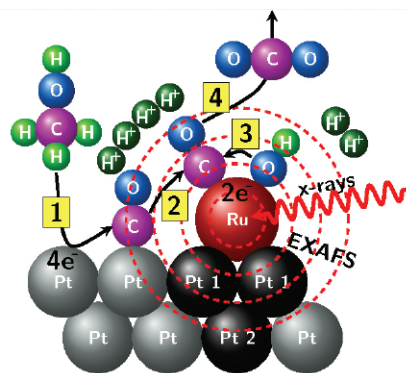


Fig. 1. A novel experimental setup allows *in situ* Ru K-edge XAS to be carried out using a sparse layer of Ru atoms coating nanoparticles Pt electrocatalyst in order to study the mechanism of methanol oxidation in a fuel cell. Graphic: C. Pelliccione (IIT) et al.

generation in a DMFC. Researchers from the Illinois Institute of Technology and at Argonne have investigated platinum nanoparticles coated with sub-monolayers of Ru as a model catalyst for x-ray absorption spectroscopy (XAS) studies of the methanol oxidation mechanisms. They collected *in situ* XAS data at Ru-K edge on the MR-CAT beamline 10-ID-B at the APS. Because of the low concentration of Ru in the sample, they had to use fluorescence mode with a Lytle detector ion chamber in continuous scan mode.

The team's unique way of coating the Pt nanoparticles with Ru lent itself to a clear view using XAS of the methanol electrochemical oxidation reaction. Specifically, the layer of Ru atoms is very thin — approximately a single atom thick and covering a little less than a third of the platinum surface, simulating the surface of bimetallic catalyst. Having Ru only at the surface of the catalyst, the team explains, means that whereas XAS is

usually a “bulk” analytical technique for investigating solids by correlating the x-ray absorption fine structure data at the Ru K-edge of the spectra, the team was able to exploit it as a surface analytical technique instead. This provided a unique view of the methanol oxidation process. (The team also investigated the morphology and atomic distribution of as-prepared Ru@Pt catalyst using scanning electron microscopy at the Argonne Electron Microscopy Center [EMC]).

The team recorded data at various oxidation potentials, with a solution of methanol and with background electrolyte lacking methanol as a control experimental setup. This revealed significant differences between the behaviors of the Ru-metal ions in those environments. In the methanol system, the Ru exists as metal and Ru(III) ions regardless of potential. In this state, it absorbs and processes the unwanted carbon monoxide and keeps the Pt active. By contrast, in the control experiments, the metallic Ru was all oxidized to a mixture of Ru(III) and (IV) oxides. The results suggest how to optimize the catalysts for optimal use in DMFC (Fig. 1). — David Bradley

See: Christopher J. Pelliccione¹, Elena V. Timofeeva², John P. Katsoudas¹, and Carlo U. Segre^{1*}, “*In Situ* Ru K-Edge X-ray Absorption Spectroscopy Study of Methanol Oxidation Mechanisms on Model Submonolayer Ru on Pt Nanoparticle Electrocatalyst,” *J. Phys. Chem. C* **117**, 18904 (2013). DOI:10.1021/jp404342z

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