

V.G.14 Element Specific Atomic Arrangement of Binary and Ternary Alloy Nanosized Catalysts in As-Prepared and Active State

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Program Scope

This program supports the Office of Basic Energy Sciences (X-ray scattering) mission through the application and further advancement of cutting-edge X-ray scattering techniques for determining the atomic-level structure of nanosized catalysts vital for the development of fuel cell and battery technologies, production of alternative fuels, removal of pollutants, and others. Our work focuses on chemically ordered and disordered nanoalloys, core-shell, onion-like, metal-metal oxide composites and other unconventional multi-metallic nanosystems. Structure determination is done by high-energy synchrotron X-ray diffraction (HE-XRD) coupled to atomic pair distribution function (PDF) analysis and three-dimensional (3D) computer simulations. The resulting full-scale models of nanocatalysts are used to establish the relationship between their atomic structure and performance. The relationship is then used to improve the latter through fine tuning the former. HE-XRD experiments include ex situ studies on as-synthesized and used catalysts, in situ studies on catalysts under gas-phase reaction conditions and in operando studies on catalysts as they function inside fuel cells, in particular proton exchange membrane fuel cells (PEMFCs). Resonant HE-XRD studies providing information particular about the arrangement of atomic species deemed important to the performance of metallic nanocatalysts are carried out as well. Special attention is paid to revealing the arrangement of atoms at the surface of nanocatalysts whereat chemical reactions indeed take place. Near future studies include in situ gas phase reaction HE-XRD experiments combined with diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), in operando PEMFC experiments combined with energy dispersive X-ray spectroscopy (EDX) and grazing incidence HE-XRD & PDF analysis on very thin layers of catalyst nanoparticles (NPs).

FY 2016 Highlights

In Operando PEMFC Studies on Noble Metal-Transition Metal (NM-TM) Nanoalloys

A key challenge to the viability of fuel cell technology is the development of efficient catalysts for speeding up the sluggish chemical reactions driving cells' operation, such as the oxygen reduction reaction (ORR). Indeed a number of excellent metallic nanocatalysts for ORR were developed over the last decade. Unfortunately, their superb ORR activity would decay during cells' operation, thereby limiting the cells' performance. Good knowledge of the impact of the environment inside fuel cells on the ORR activity of metallic NPs is needed to solve this problem. Recently, we studied the evolution of the atomic structure and ORR activity of Pd-Ni and Pt-Ni-Co nanoalloy catalysts as they function at the cathode of an operating PEMFC (shown in Figure 1). Studies showed that under actual operating conditions, NM-TM nanocatalysts can undergo structural changes that differ significantly in both length-scale and dynamics and so can suffer ORR activity losses that differ significantly in both character and magnitude. In particular, we found that highly dynamic (see Figure 2) structural fluctuations occurring at the Ångstrom length-scale and irreversible large scale structural changes such as a gradual growth in the order of a few nm, can indeed be equally responsible for the losses in the ORR activity of metallic nanocatalysts during cells' operation. Hence, we argue that, to be fully successful, efforts to reduce these losses should strive to achieve control

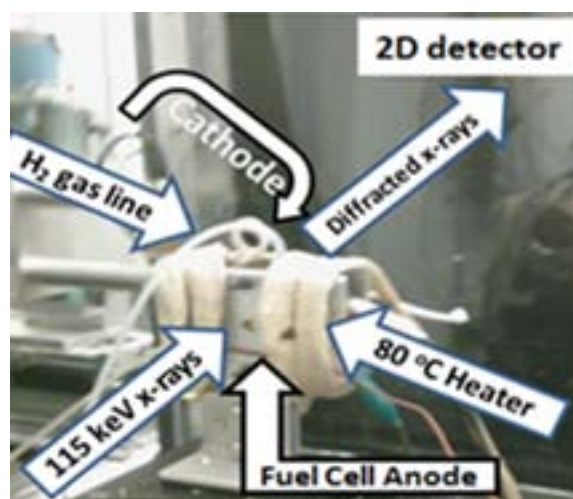


FIGURE 1. Custom-made PEMFC as used at the beamline 11-ID-C, APS.

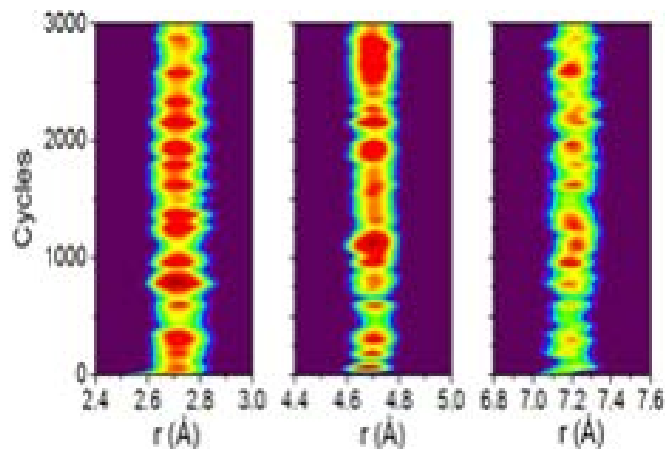


FIGURE 2. Color maps of the low-r peaks in the in operando PDFs for Pd-Ni nanocatalyst obtained in interval of 3 min while the nanocatalyst is undergoing 3,000 voltage cycles (0.6 V-1.2 V) inside the PEMFC. The maps emphasize the presence of local structural fluctuations in the nanocatalyst during the voltage cycling.

not only over the irreversible but also over the rapidly fluctuating structural changes that metallic nanocatalysts indeed undergo inside operating fuel cells (PEMFCs).

3D Atomic Arrangement at Functional Interfaces Inside Nanocatalysts by Resonant HE-XRD

Using Ru core-Pt shell NPs as an example, we demonstrated that precise atomic-level knowledge of functional interfaces inside metallic nanocatalysts can be obtained by resonant HE-XRD (K edge of Pt at 78,400 keV) coupled to element-specific PDF analysis. Moreover, using the unique structure knowledge obtained, we scrutinized the still debatable influence of hcp(Ru)\fcc(Pt) interface on the catalytic activity of Ru core-Pt shell NPs for CO oxidation, “reformat” hydrogen oxidation (HOR) at the PEMFC anode and ethanol/methanol electro-oxidation. In particular, we evaluated the importance of so called ligand and strain effects induced by the interface and, based on the experimental data for the evolution of surface Pt-Pt distances (see Figure 3) with the thickness of Pt shell, concluded that strained metal-to-metal bond lengths (~ 2 %) and not heterometallic (Ru-Pt) interactions at the interface are the likely reason for the superb catalytic activity of Ru core-Pt shell NPs for the foregoing reactions.

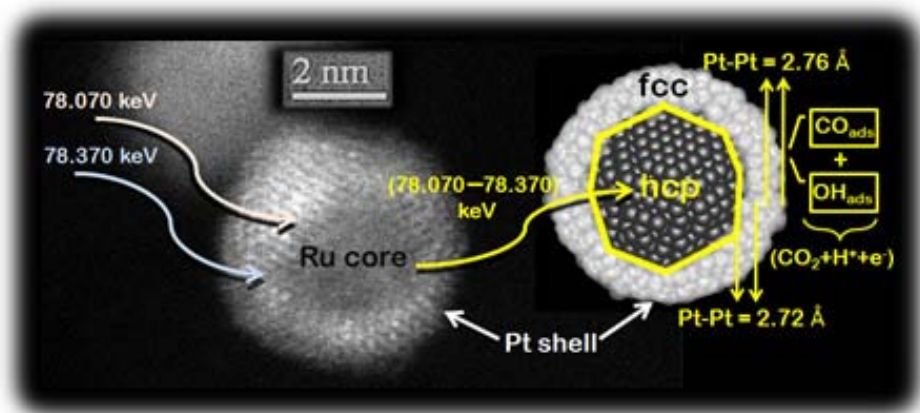


FIGURE 3. Influence of the hcp\fcc interface inside Ru core-Pt shell NPs on their catalytic properties as deciphered by resonant HE-XRD coupled to element specific atomic PDF analysis.