Structural Characterization of Novel Nanocomposite Catalysts for Fuel Cell Applications

Chuan-Hsio Chang (張川修), Chun-Hsia Liu (劉君夏), and Chia-Min Yang (楊家銘)

Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan

One of the great challenges in the twenty-first century is unquestionably energy storage. In response to the needs of modern society and emerging ecological concerns, it is now essential to explore new energy conversion and storage systems. Fuel cells are very promising in these respects because they convert chemical energy directly into electrical energy with high efficiency and low emission of pollutants. The performance and the improvement of fuel cell systems, such as direct methanol fuel cells (DMFCs), depend intimately on the properties of their materials. One of the developments has been focused on the electrocatalyst with better activity and stability. The electrochemical reactions at the electrodes involves solid-phase catalysts catalyzing either liquid-phase or gas-phase reactions. These heterogeneous catalysts should be designed to facilitate both the molecular transport and catalytic processes, and new opportunities arise in light of architectures designed and fabricated from the appropriate nanoscale building blocks, including the use of void space (pores) and deliberate disorder as design components.

We have chosen ordered mesoporous materials as suitable scaffolds to build up the catalytic architectures. Mesoporous materials have ordered and uniform pores with diameters in the range of several to hundreds of nanometers. These pores allow fast diffusion of guest molecules and they also provide an excellent spatial confinement to deposit or assemble catalysts and other species with limited sizes. The pore diameter, pore wall thickness and even the surface properties can be tuned and modified by controlling the synthesis condition and the post-synthesis treatments. For the DMFC applications, we have applied mesoporous carbon materials to prepare bimetallic PtRu catalysts for methanol oxidation. The bimodal mesoporous/micropores SBA-15 silica was used as a hard template, within which the metal salts were first impregnated into the micropores of the silica host followed by the infiltration of carbon precursor. After the pyrolysis of carbon at high temperature, the silica was dissolved by hydrogen fluoride solution without dissolving the nanostructured metals. By using this novel templating method, PtRu@CMK nanocomposites with bimetallic PtRu nanoparticles deposited preferentially on the surface of mesoporous carbon scaffold were prepared without disturbing the its mesoscopic structural ordering of the resulting materials.

The PtRu@CMK nanocomposites were characterized by powder X-ray diffraction, and very broad and weak reflections attributed to the metal nanoparticles with dimensions smaller than 2 nm were observed. In addition, nitrogen physisorption measurements suggested that the ordered void space between carbon rods of the CMK scaffold was largely preserved without significant blocking. The images obtained by using Transmission electron microscope also showed that small and relatively uniform metal nanoparticles of 1-2 nm were well distributed on the CMK carbon scaffold. The coordinations and distributions of both Pt and Ru metals were further analyzed by using in-situ X-ray absorption spectroscopy at Beamlines 17C and 01C, and the XANES and EXAFS spectra of one of the catalysts are shown in Figure 1. The data also suggested the small sizes of the nanoparticles. In addition, from the derived coordination numbers of Pt and Ru, the bimetallic nanoparticles in PtRu@CMK seemed to have a Pt-core/Ru-shell morphology, which may be beneficial for the catalytic performance of the nanocomposite. Indeed, the nanocomposite PtRu@CMK catalysts were found to have comparable or better activities for methanol oxidation than commercial catalysts, but some of them were found to have lower onset potentials than the commercial ones. The results show that the as-prepared PtRu@CMK nanocomposites were promising for DMFC applications.

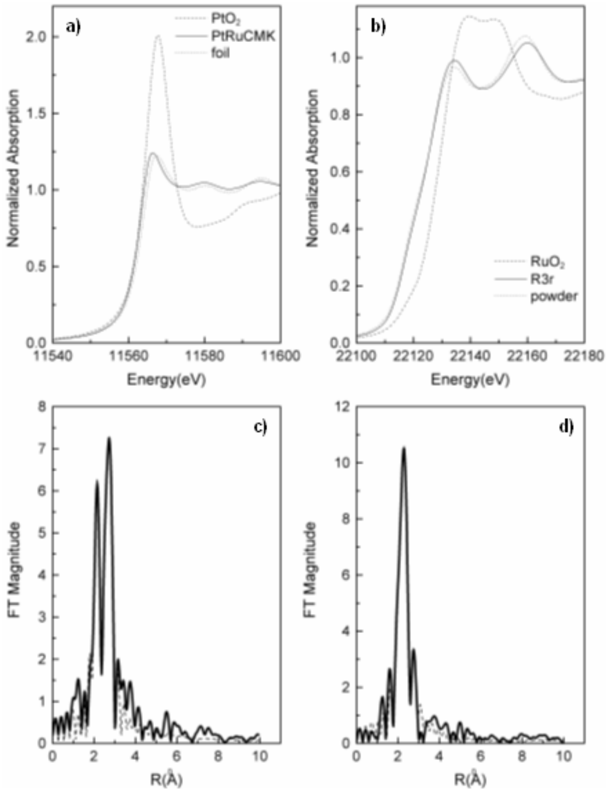

Figure 1. XANES (a and b) and k^3-weighted EXAFS spectra (c and d) of Pt (a and c) and Ru (b and d) for a PtRu@CMK nanocomposite catalyst.