

Functionalization of Fuel Cell Catalyst Supports with Nitrogen, Fluorine and Iodine

Kevin Wood,¹ Svitlana Pylypenko,^{1,2} Tim S. Olson,² Arrelaine Dameron,² Kevin O'Neill,² Charles C. Hays,³ M. A. Johnson,⁴ Bryan Pivovar,² Huyen N. Dinh,² Thomas Gennett,² and Ryan O'Hayre¹

¹Department of Metallurgical & Materials Engineering, Colorado School of Mines, 1500 Illinois St, Golden, CO 80401, US

²National Renewable Energy Laboratory, 1617 Cole Blvd, Golden, CO 80401, US

³Jet Propulsion Laboratory, Pasadena, CA

Introduction

Functionalization of carbon supports by doping with nitrogen has shown to affect the catalyst-support interactions for Pt and Pt-Ru fuel cell catalysts¹⁻⁴. In this work highly ordered pyrolytic graphite (HOPG) was used as a model system to study the effect of three different surface functionalizations (N₂, CF₄ and I₂) on the performance of Pt-Ru nanoparticle catalysts. Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) were used to analyze the chemical and structural modifications that the various dopants induced across a range of ion implantation conditions. The modified HOPG samples were then sputtered with consistently dispersed, equally sized, and alloyed nanocatalysts of Pt-Ru. Changes in morphology, coverage and migration which affect activity and durability of the Pt-Ru catalysts were then studied by comparing pre and post-cycled materials through TEM, XPS, and Cyclic Voltammetry (CV).

Experimental Setup

HOPG was modified via ion implantation doses of 4.51×10^{16} and 4.07×10^{17} ions/cm² for each of the dopants. Pt_{1-x}Ru_x nanoparticles were then sputtered onto the doped HOPG substrates from a single Pt_{0.5}Ru_{0.5} (ACI Alloys) alloyed target with a 2" Onyx magnetron sputter gun (Angstrom Sciences). The samples were positioned at a distance of 1.5" directly above the target and the deposition was done for 5 sec after establishing a base pressure below 4×10^{-6} Torr. XPS analysis was performed on a Kratos Nova X-ray photoelectron spectrometer with a monochromatic Al K α source operated at 300 W. The electrochemical durability cycling was done in an aqueous electrochemical cell using a three electrode configuration. The surface-modified HOPG substrate comprised the working electrode, with the addition of an Ag/AgCl reference electrode and a Pt wire counter electrode. The experiments were conducted in 1.0 M H₂SO₄ and the potential was cycled from 0 to 1.1 V vs. Ag/AgCl at a scan rate of 250 mV/s. A Philips CM200 Transmission Electron Microscope was used to examine the durability of both the pre- and post-cycled Pt-Ru/HOPG systems. TEM specimen preparation was performed by peeling a thin layer of HOPG and positioning it between the two grids of a Cu double grid (Electron Microscopy Sciences). Image J was used to evaluate coverage and perform particle size analysis from the TEM micrographs. Some implanted samples (before sputtering) were sent to JPL for further activity and durability testing.

Results and Discussion

Raman intensity ratios were obtained for the various dopants in order to examine the

physical/structural effects each dopant had on the surface after implantation. Results showed that as dosage increased (from 10^{16} - 10^{17} ions/cm²) the ID/IG ratio increased for fluorine, but decreased for iodine. Previous results obtained on nitrogen were confirmed while the hydrogen passivated nitrogen doped HOPG showed a decrease in ID/IG ratio compared with the nitrogen doped sample.

Analysis of TEM images of HOPG substrates with various implantation doses prior to cycling revealed even distribution of the metal phase on the surface of the HOPG. High coverages with particle sizes ranging from 1 nm to 3 nm were obtained for all samples essentially independent of HOPG doping conditions. Sputter deposition is a line of sight technique, and therefore, the entire surface of HOPG is nucleated with Pt-Ru catalyst nanoparticles. After cycling, the low dose fluorine samples showed better durability and activity when compared with the un-doped samples, while the high dose fluorine sample showed better durability than even the optimum nitrogen implanted sample. The low dose iodine sample and hydrogen passivated nitrogen sample both showed worse durability and activity after cycling. High dosages of iodine however seemed to improve durability and activity compared to the undoped sample. These results suggest promise for increasing the catalytic activity and durability of fuel cell catalysts with the use of iodine and fluorine functionalization.

Conclusions

In summary, we have utilized a model catalyst system to explore the effect of fluorine, iodine, and nitrogen functionalization on activity and durability of Pt-Ru nanocatalysts. Sputtering of Pt-Ru enabled the deposition of metal nanoparticles without preferential nucleation on defect sites or various functionalities. Activity was shown to be dopant and dosage dependent. After potential cycling, the coverage and morphology of the metal phase changed dramatically and was shown to greatly depend on the implantation dosage and surface functionalization.

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