doi: 10.1017/S1431927609098961
Microsc Microanal 15(Suppl 2), 2009

Pt-Co Bimetallic Catalysts for PEM Fuel Cell Cathodes

K.L. More,* K.S. Reeves* and R. Borup**

*Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN
**Institute for Hydrogen & Fuel Cell Research, Los Alamos National Laboratory, Los Alamos, NM

Polymer electrolyte membrane fuel cells (PEMFCs) are being developed for future use as efficient, zero-emission power sources. However, the performance of PEMFCs degrades rapidly as a function of time at temperature (≤ 80°C), potential cycling, and a corrosive operating environment, during electrochemical aging. Much of the performance degradation can be attributed directly to the limited durability of the electrocatalyst, especially on the cathode side where the catalysts are subjected to extremely harsh oxidative conditions. Pt nanoparticles supported on carbon black (CB) continue to be the most used cathode catalyst, but bimetallic catalysts are being investigated to replace Pt. The most important reasons to replace Pt are cost and a limited supply of Pt, but improved activity for the oxygen reduction reaction (ORR) and enhanced durability are also desired. Pt alloyed with transition metals (M=Co,Cr,Ni, etc.) have shown enhanced activity compared with Pt-only catalysts, which may be attributed to changes in the atomic nature of the nanoparticles, including Pt-Pt and Pt-M bond lengths, the atomic coordination, a change in the electron density of states in the Pt-5d orbital, the nature of the particle morphology and surface, and ordering of the atoms within the particle [1-4]. Thus, it is important to characterize the nature and uniformity of the atomic-scale crystalline structure of catalyst nanoparticles in order to determine the effects of catalyst microstructure, morphology, and composition on performance.

A commercially-available 20 wt% 3Pt:1Co supported on (Vulcan XC-72) CB is the focus of this study (compared with a similarly loaded Pt/CB). As shown in Fig. 1, the stability of this 3Pt:1Co/CB is clearly enhanced over Pt/CB (lower loss of catalyst electrochemically-active surface area). Typical particle dispersions of the Pt-only and Pt:Co catalysts are compared in the TEM images shown in Figs. 2a and 2b, respectively. The Pt:Co nanoparticles are clearly larger and have a higher degree of surface faceting. Particle size distributions, measured from TEM images, are compared in Fig. 2c. X-ray diffraction data (not shown) indicates that the Pt:Co nanoparticles are larger and more crystalline (less peak broadening); the 3Pt:1Co sample exhibited peak shifts to higher 2-theta, indicative of a contraction of the Pt lattice due to the incorporation of Co and the formation of a Pt_3Co disordered fcc alloy. In addition, a small (110) superlattice reflection for the $L1_2$ fcc Pt_3Co lattice was observed, indicating limited ordering of the Pt_3Co nanoparticles.

To further characterize the crystalline structure of individual Pt_3Co nanoparticles, high-angle annular dark-field (HA-ADF) STEM images were recorded on a JEOL 2200FS equipped with a CEOS GmbH aberration-corrector on the probe-forming lenses. Typical HA-ADF images of individual Pt_3Co particles are shown in Fig. 3. Many of the smaller nanoparticles were identified as disordered Pt_3Co (Fig. 3a), where Co randomly substitutes for Pt in the fcc crystallographic lattice creating a solid solution (alloy) of Pt_3Co. A much smaller number of fully ordered Pt_3Co particles were identified having the $L1_2$ fcc structure, where Co substitutes for Pt atoms only at the cube-corners (Fig. 3b), consistent with our XRD data. A more common Pt_3Co nanoparticle structure observed consisted of a Pt_3Co alloy "cap" on an ordered Pt_3Co "base", which were easily identified by the interface formed between the cap/base (Fig. 3c). In general, many larger particles (>5 nm) having distinct crystallographic facets exhibited some degree of structural ordering, whereas the smaller particles (<5 nm) were Pt-rich and disordered (alloyed). Characterization of electrochemically-aged Pt_3Co/CB (i.e., membrane electrode assemblies with Pt_3Co/CB cathodes) is ongoing [5].

References

[1] Stamenkovic et al., *J. Phys. Chem. B* **106** (2002) 11970.

[2] Xiong and Manthiram, *J. Mater. Chem*. **14** (2004) 1454.

[3] Mun et al., *J. Chem. Phys.* **123** (2005) 204717.

[4] Gasteiger et al., *Appl. Cat. B* **56** (2005) 9.

[5] Research sponsored by the U.S. Dept. of Energy's (1) HFCIT Program, Office of EERE, and (2) ORNL's SHaRE User Program, Scientific User Facilities Division, Office of Science.

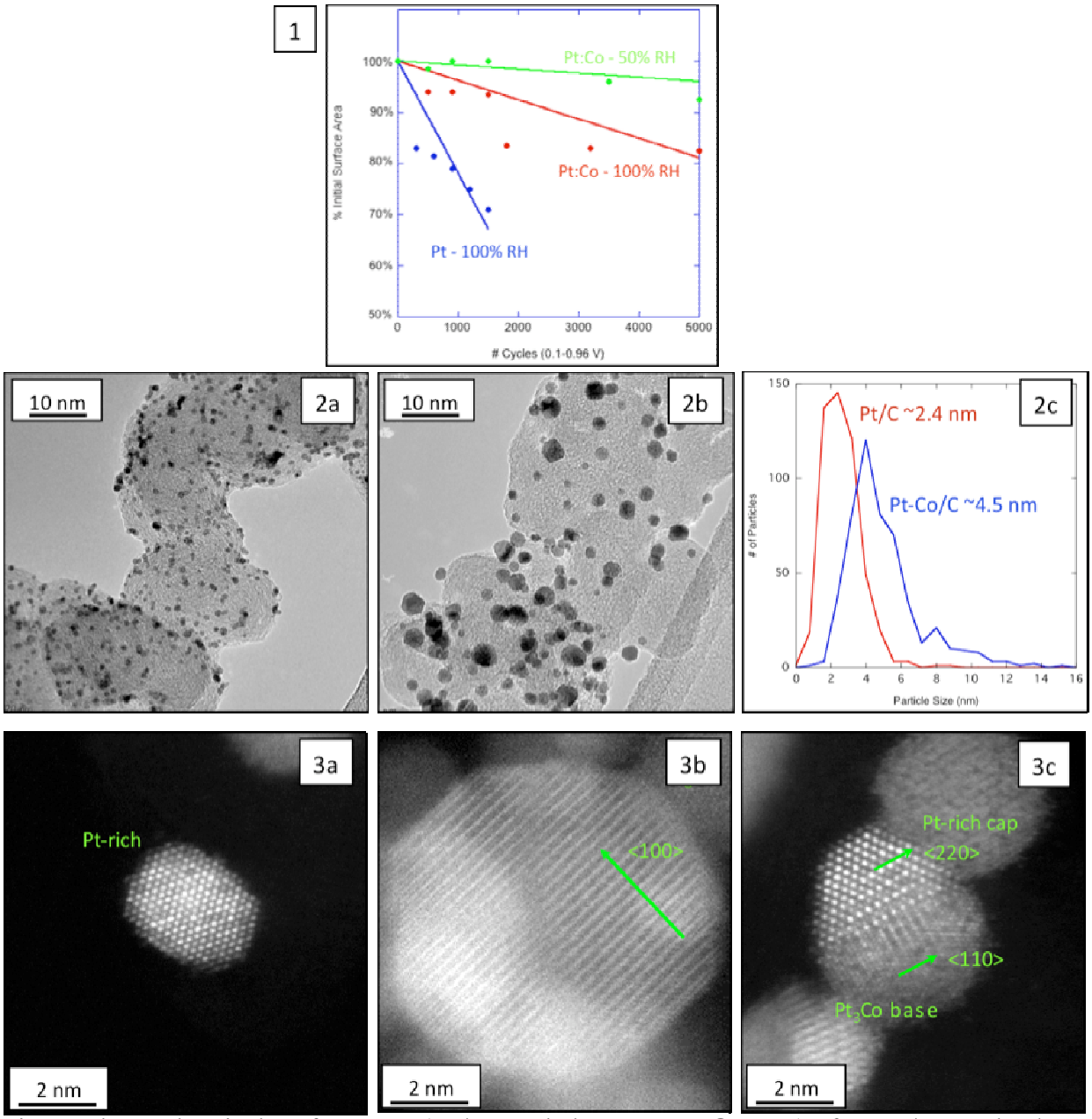

Fig. 1. Electrochemical performance (H_2/N_2 cycled 0.4-0.96V @ 80°C) of Pt:Co/CB and Pt/CB.

Fig. 2. TEM images comparing (a) Pt-only catalyst, (b) 3Pt:1Co catalyst, and (c) particle size distributions.

Fig. 3. HAADF-STEM images of individual Pt_3Co nanoparticles: (a) Pt_3Co disordered fcc alloy particle, (b) fully-ordered $L1_2$ fcc Pt_3Co particle, and (c) Pt_3Co alloy "cap" on Pt_3Co ordered "base".

https://doi.org/10.1017/S1431927609098961 Published online by Cambridge University Press