## **Energy Focus**

Atomic ordering in Pt-Co alloy core-shell nanoparticles boosts electrocatalytic activity and stability

One of the primary limitations to the realization of efficient fuel cells is the lack of effective and chemically stable electrocatalysts. Specifically, the slow oxidation-reduction reaction occurring at the cathode limits the practical utility of exchange membrane fuel cells. As a step toward finding a solution to this problem, researchers at Cornell University have observed an increase in activity and enhanced chemical stability of electrocatalysts made of atomically ordered platinum-cobalt alloy nanoparticles with a platinum shell.

As reported in the October 28, 2012 online edition of Nature Materials (DOI: 10.1038/NMAT3458), D. Wang, H.L. Xin, and collaborators found that structurally ordered nanoparticles have the highest reported activity for Pt-Co nanoparticle systems, and that they display a threefold increase in specific activity over both disordered Pt<sub>3</sub>Co alloy and carbon-supported platinum nanoparticles. In the study, nanoparticles were created using an impregnation-reduction method and then heated to 400°C or 700°C in a hydrogen atmosphere. While the 400°C annealed nanoparticles remained disordered, x-ray diffraction, together with atomic-resolution imaging



Annular dark-field scanning transmission electron microscopy image shows structural stability of  $Pt_3Co/C$ -700 nanoparticles after 5,000 electrochemical cycles. Reproduced with permission from *Nature Mater.* DOI: 10.1038/NMAT3458. © 2012 Macmillan Publishers Ltd.

and chemical mapping techniques, revealed the 700°C annealed nanoparticle structure to be that of an ordered alloy with a 2–3 atomic layer platinum shell.

The advantage of using the higher temperature protocol to order the Pt-Co alloy is clearly seen by using the nanoparticles as electrocatalysts in the form of thin films on a rotating disk electrode to test their activity. This demonstrated that ordered alloy nanoparticles exhibit triple the mass activity of the disordered alloy nanoparticles. In addition to the enhancement in activity, cyclic voltammetry revealed that the 700°C-annealed Pt<sub>3</sub>Co nanoparticles suffer minimal loss after 5000 cycles while the core–shell structure is preserved. The researchers attribute the increased durability and activity of these carbon-supported core– shell nanoparticles (Pt<sub>3</sub>Co@Pt/C) to the resilience of the shell and stable atomic arrangement of the intermetallic alloy.

This work presents a new approach to electrocatalyst design for applications in fuel cells, and is an important step toward a clean energy future.

**Charles M. Brooks** 

## Nano Focus

Porous graphene sieve selectively passes molecules

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Many applications rely on porous membranes to pass specific molecules while excluding others, such as industrial-scale chemical and gas purification. As reported in the October 7, 2012 online issue of *Nature Nanotechnology* (DOI: 10.1038/ NNANO.2012.162), S.P. Koenig and co-workers at the University of Colorado have fabricated molecular sieves by etching pores in bilayer graphene membranes, where the graphene membranes provide atomic thickness, mechanical robustness, chemical inertness and impermeability to standard gases.

The researchers defined an array of  $5-\mu$ m-diameter microcavities in silicon oxide using standard photolithographic techniques, and then mechanically exfoliated graphene over these wells to form suspended membranes. The as-deposited graphene flakes cling to the oxide substrate through surface forces in a gastight manner, although gases are able to enter/exit the microcavity through very slow diffusion through the oxide.

The graphene-sealed microcavities are then loaded with a desired gas species by placing them in a high-pressure (200 kPa above ambient) environment containing the charging gas and allowing the system to equilibrate for 4–12 days. When the samples are brought out to ambient conditions, the membrane bulges outward due to the pressure differential. Slow leak rates were demonstrated through the pristine membranes (on the order of minutes to hours) by using an atomic force microscope to measure the deflection  $\delta$  of the swollen blister with time.