

# Low-cost, non-precious metal/polymer composite catalysts for fuel cells

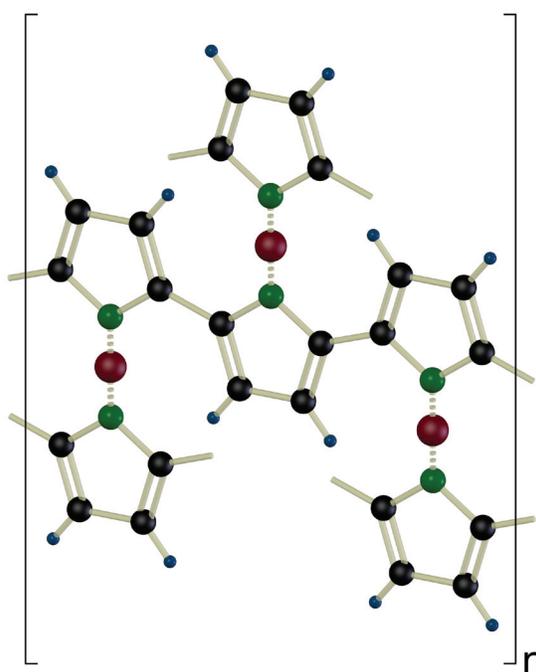
R. Bashyam and P. Zelenay<sup>1</sup>

**F**uel cells, which directly convert a fuel's chemical energy into electricity by electrochemical reactions, are a key enabling technology for the transition to a hydrogen-based economy. Of several different types under development, a polymer electrolyte fuel cell (PEFC) is generally recognized as a future power source for zero-emission vehicles. To become commercially viable, however, PEFCs must address several formidable technological and economic challenges. Only after overcoming these hurdles will fuel cells take their place as a centerpiece of a hydrogen economy and position hydrogen as a major energy carrier, lessening concerns regarding the energy security and environmental impact of fossil fuels. The high cost of catalysts due to the exclusive use of platinum and platinum-based catalysts in fuel cell electrodes is one such challenge.

We have developed a new class of non-precious metal/heteroatomic-polymer composite catalysts for oxygen reduction in fuel cells. In a recent *Nature* article we demonstrate a cobalt-polypyrrole-carbon (Co-PPY-C) composite catalyst for the PEFC cathode capable of combining high oxygen-reduction activity with good performance durability<sup>1</sup>, a result never before obtained with non-precious metal PEFC catalysts. The proposed structure, shown in Figure 1, highlights the N-Co link between the pyrrole units in the polymer and Co atoms as key to stabilizing base Co centers in the highly acidic environment of the Nafion ionomer, the most commonly used ionic conductor in low temperature fuel cells. The structure was synthesized on an electronically conducting carbon support by simple chemical methods without resorting to pyrolysis, which is universally used for inducing oxygen reduction reaction (ORR) activity in known-to-date non-precious metal.

## Fuel cell testing of the composite

Figure 2 shows a hydrogen-oxygen fuel cell polarization plot recorded after the conditioning step, with the cathode made of a newly synthesized Co-PPY-C composite. The catalyst generates  $\sim 0.2 \text{ A cm}^{-2}$  at 0.50 V and a maximum power density of  $\sim 0.15 \text{ W cm}^{-2}$ .



**Figure 1. Presumed structure of Co-PPY composite catalyst.**

the Co-PPY-C cell is more than one order of magnitude higher than that delivered by the Co/C cell. In spite of a ca. 50% surface area advantage of Co/C catalyst more than the Co-PPY-C composite, the peak power density of the Co/C cell is only  $0.009 \text{ W cm}^{-2}$ , nearly 16 times lower than that of the Co-PPY-C cell.

These results provide indirect evidence that electrocatalytic activity of the new catalyst results from entrapment of the Co sites in the polypyrrole matrix and strong Co-PPY interactions, presumably resulting in the formation of  $\text{CoN}_x$  active sites or in general Me-N active sites.

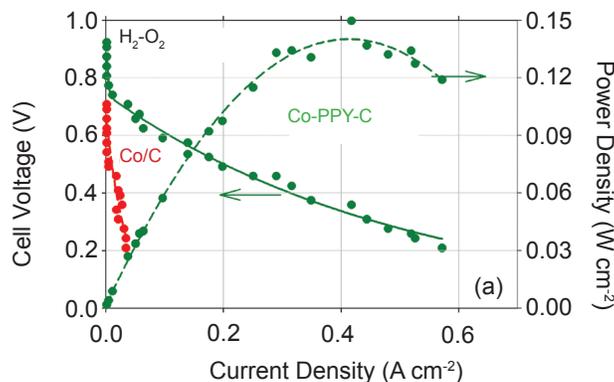
The  $\text{H}_2\text{-O}_2$  fuel cell performance of the composite catalyst compares favorably with other non-platinum cathode catalysts. The comparison becomes even more favorable when based on combining the ORR activity with performance durability.

For reference, a catalyst made by merely loading Co directly onto carbon was synthesized under the same conditions as the composite catalyst. It is evident from Figure 2 that activity of the Co/C catalyst is far lower than that of the Co-PPY-C composite. The open circuit voltage (OCV) of the fuel cell with the Co-PPY-C cathode is 0.22 V higher than that of the fuel cell with the Co/C cathode. In the voltage range between 0.50 V and 0.20 V, current density generated by

<sup>1</sup>Sensors and Electrochemical Devices Group (MPA-11), Materials Physics and Applications Division, Los Alamos National Laboratory, Los Alamos, NM 87545, USA

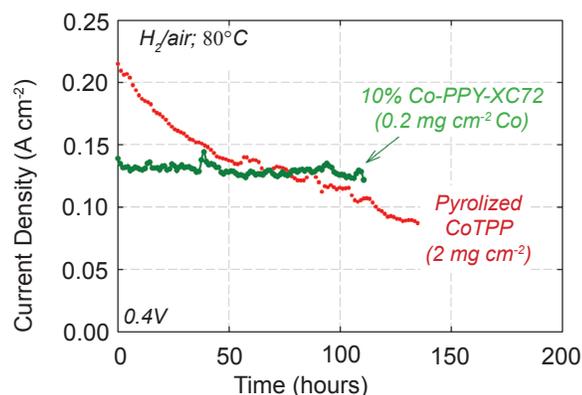
Rajesh Bashyam received his doctorate in chemistry in 2002 from the Indian Institute of Technology, joining Los Alamos National Laboratory in 2005 as a Director's Postdoctoral Fellow. He is the author of more than 15 papers in peer-reviewed journals and has presented his research at several national and international conferences. Currently his research interests include alternative catalyst, development (mainly non-precious) for polymer electrolyte fuel cell and direct methanol fuel cell and in membrane electrode assembly research.

Piotr Zelenay received his PhD and DSc in chemistry from Warsaw University, Poland. As Fuel Cell Project Leader in the Sensors and Electrochemical Devices Group, his primary responsibilities include technical leadership of direct methanol fuel cell and fuel cell electrocatalysis research. A member of the Electrochemical Society and the International Society of Electrochemistry, he has authored or co-authored more than 90 papers, more than 130 conference presentations and invited lectures, as well as several patent applications in the field of direct methanol fuel cells.



**Figure 2. Fuel cell performance of Co-PPY-C in comparison to Co/C.**

**Figure 3. Catalyst performance durability.**



### Performance durability

The most striking feature of the newly synthesized composite was the remarkable durability of the Co-PPY-C composite under fuel cell operating conditions. Figure 3 shows the stability of the fuel cell performance at 0.4 V using Co-PPY-C cathode in comparison to the well-known pyrolyzed cobalt tetraphenyl porphyrins (pyrolyzed Co-TTP). It is evident from Figure 3 that although the initial performance of the pyrolyzed Co-TTP is higher than Co-PPY-C, the continuous decline of the current clearly indicates the catalyst is not stable under fuel cell operating conditions—basically under highly acidic and oxidizing environments. On the other hand, the Co-PPY-C shows unique performance durability during a 100-hour performance test.

In addition to being made of inexpensive and environmentally benign materials, the composite catalyst's other chief advantage is that it operates in the acidic environment

of polymer electrolyte fuel cells. Ongoing fundamental electrochemical investigations will help clarify the mechanism of oxygen reduction reaction on non-precious metal/heteroatomic-polymer composites. In particular, investigation of the structure of the catalyst before and after fuel cell operation using x-ray absorption techniques will help optimize the catalyst and electrode structure to substantially improve the performance, bringing it closer to the state-of-the-art platinum-based catalysts for oxygen reduction at the fuel cell cathode.

*The United States Department of Energy's Office of Hydrogen, Fuel Cells and Infrastructure Technologies funds much of the PEFC fuel cell research at Los Alamos.*

### References

<sup>1</sup>R. Bashyam and P. Zelenay, "A class of non-precious metal composite catalysts for fuel cells," *Nature* **443**, 63 (2006).