**Fuel Cells**

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# Nonprecious-Metal Catalysts for Low-Cost Fuel Cells**

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fuel cells · nitrogen · oxygen reduction · supported catalysts · transition metals

For a long time it has been the dream of scientists to convert chemical bond energy into electrical energy without the need for combustion. While Alessandro Volta (1799) and Michael Faraday (1832) established the scientific principles of such a process, the German-Swiss scientist Christian Friedrich Schönbein[1] and the British lawyer and scientist William Grove[2] demonstrated in 1839 that electricity could be generated from hydrogen and oxygen. Even today the device for this purpose, the fuel cell, is still considered one of the most promising energy-conversion technologies available. In recent decades, fuel cell technology has been undergoing revolutionary developments, but nearly 170 years after the first demonstration by Grove, the practical use of fuel cells in our daily life is rare when compared with the battery technology that is in widespread use.

What has held back technological breakthroughs in fuel cell technology and in effect blocked its broad application and mass production? Several technological aspects are of essence to answer the question. Active electrode/electrolyte/membrane systems with extended lifetimes are needed for an efficient conversion of hydrogen and alternative fuels; a compact process technology is needed to produce and purify hydrogen for use in fuel cells; and a meaningful strategy is required to integrate fuel cell technology into future technology concepts based on renewable resources.

The first prerequisite for the broad application of fuel cells is catalysts that accelerate the fuel oxidation and the oxygen reduction reaction (ORR) on the anode and cathode, respectively, so that electricity can be generated. The only efficient catalyst so far, at least for the proton exchange membrane fuel cell (PEMFC), is platinum, which was already used by William Grove in 1839. Platinum is one of the most expensive and rare metals in the world. From an economical and ecological viewpoint, it is not possible to equip millions of cars with platinum-based fuel cells.

In a PEMFC, the ORR is much slower than the hydrogen oxidation reaction at the anode, thus platinum is located primarily at the cathode. In 1964, Jasinski reported that a $N_4$-chelate complex with a nonnoble metal could be used to electrochemically reduce oxygen.[3] Since then, many macrocyclic transition-metal compounds, such as phthalocyanines, porphyrins, and tetraazaannulenes, have been investigated with respect to ORR activity. The common feature of these complexes is that the transition-metal atom is symmetrically surrounded by four nitrogen atoms, as shown in Figure 1a. The charge transfer from the electron-rich metal center to the $O_2$ $\pi^*$ orbital was believed to lead an overall weakening of the O–O bond and consequent reduction of $O_2$.[4] However, these macrocyclic compounds are not stable in acidic solution and cannot be used as fuel cell catalysts. Bagotsky et al. and other research groups found later that heating such compounds at high temperatures could enhance the ORR activity and, most importantly, improve the stability.[5] The performance of fuel cells based on these materials is usually quite low, although a promising system with 1.01 V open-circuit voltage and 0.33 W cm$^{-2}$ maximum output, at 0.2 MPa absolute pressure and 80 °C was reported recently.[6] The general direction was clear: the transition-metal species, nitrogen, and carbon must be present simultaneously to maximize the ORR activity.[7]

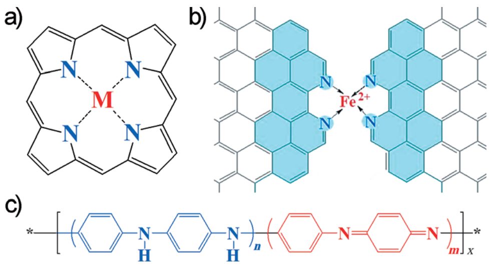

***Figure 1.*** a) Porphyrin; b) catalytic site embedded in a graphitic sheet (shaded aromatic cycles are located in the micropore of the carbon support); c) polyaniline. The drawing in (b) is adopted with permission from Ref. [10]. Copyright 2011, AAAS.

In 1989, Gupta et al. reported that, instead of the macrocycle complex, polyacrylonitrile (PAN) mixed with $Co^{II}$ or $Fe^{II}$ salts and loaded on a high-surface-area carbon support

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could yield very promising catalysts for $O_2$ reduction.[8] The nitrile groups in PAN are converted to pyridyl groups during the heat treatment, providing binding sites for the transition-metal ions, which then act as catalytic sites for oxygen reduction. This method is more economical because $Co^{II}$ and $Fe^{II}$ salts are much cheaper and available on a larger scale than macrocycle complexes. Numerous studies followed using other N-containing precursors and other reaction conditions.[9]

The performance of fuel cells based on this kind of catalyst is also low. The reported performances are mostly around and below 1 $A\,cm^{-3}$ at 0.8 V versus the reversible hydrogen electrode (RHE).[7a] One major reason is the low volumetric density of active sites. A true breakthrough was achieved in 2009 when Lefèvre and co-workers produced microporous carbon supported iron-based catalysts in which iron cations were coordinated by pyridine nitrogen atoms in the interstices of graphitic sheets (Figure 1 b).[10] This design significantly increased the volumetric density of active sites and therefore the cell performance: the ORR activity of the resulting catalyst was enhanced by more than a factor of 100. The highest current density of 99 $A\,cm^{-3}$ is equal to that of a platinum-based cathode with a platinum loading of 0.4 $mg\,cm^{-2}$ at a cell voltage of $\geq 0.9$ V.[7a,10] Unfortunately, the cell did not exhibit a stable performance: the initially very active catalyst was rapidly deactivated, losing roughly 38 % of its initial activity during 100 h of testing with $H_2$/air at 0.40 V.

Developing a nonprecious-metal ORR catalyst with high activity, practical stability, and good four-electron selectivity in acidic media remains a challenge. One of many strategies is one combining polymer precursors[11] and heat treatment.[12] The guiding concept was that the polymer, which is more ordered than the small-molecule precursors, could possibly template the formation of a more ordered and thus more stable carbon-based active layer during heat treatment. Polypyrrole was used initially, but it was soon found that polyaniline-derived catalysts (Figure 1 c) were more active and durable.[13] A breakthrough was reported recently by the Zelenay group: they used polyaniline as a template in the preparation of a catalyst incorporating iron and cobalt. The catalyst catalyzes the ORR at potentials within approximately 60 mV of that delivered by state-of-the-art carbon-supported platinum catalysts; high activity is combined with a remarkable stability of 700 h at a fuel cell voltage of 0.4 V as well as excellent four-electron selectivity (hydrogen peroxide yield < 1.0 %).[14]

The key to this success was polyaniline, which provides a favorable combination of aromatic rings connected through nitrogen-containing groups. Because of the structural similarity between polyaniline and graphite, the heat treatment could facilitate the incorporation of nitrogen-containing active sites into the partially graphitized carbon matrix. The uniform distribution of nitrogen atoms in polyaniline may guarantee a more uniform distribution of nitrogen sites in the catalyst and thus increase the density of active sites. The second key factor could be the combination of transition-metal precursors, cobalt(II) nitrate and iron(III) chloride. As shown in the fuel cell polarization test in Figure 2 a, the polyaniline-Fe-C catalyst exhibits higher ORR activity than the polyaniline-Co-C catalyst. The best-performing catalyst in fuel cell testing, with an excellent combination of high ORR activity and long-term performance durability, is the mixed-transition-metal catalyst polyaniline-FeCo-C, especially that obtained in a two-step rather than a single-step synthesis.[14]

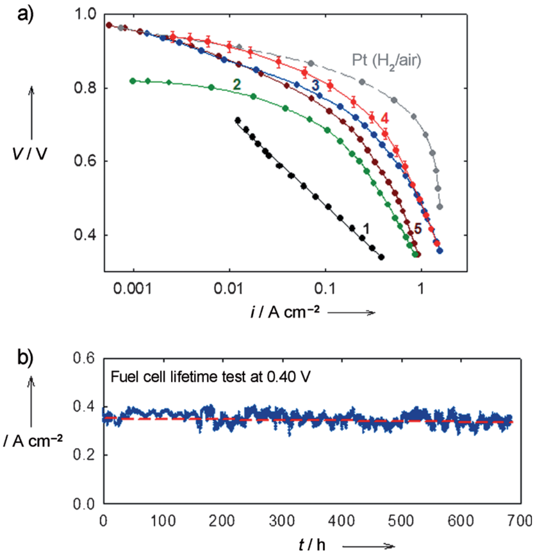

***Figure 2.*** Fuel cell and performance durability testing. a) $H_2/O_2$ polarization plots recorded with various polyaniline-derived cathode catalysts at a loading of roughly 4 $mg\,cm^{-2}$: 1) polyaniline-C; 2) polyaniline-Co-C; 3) polyaniline-FeCo-C(1); 4) polyaniline-FeCo-C(2)); 5) polyaniline-Fe-C. Performance of a fuel cell with a Pt cathode ($H_2$/air, 0.2 $mg\,cm^{-2}$ Pt) is shown for comparison (dashed line). b) Long-term stability of a polyaniline-FeCo-C catalyst at a constant voltage of 0.40 V (2.8 bar $H_2$/2.8 bar air; anode: 0.25 $mg\,cm^{-2}$ Pt; cell temperature: 80 °C). Reprinted with permission from Ref. [14]. Copyright 2011, AAAS.

In macrocyclic complexes, Fe is coordinated to four nitrogen atoms (Figure 1 a). Beck suggested that ORR on these complexes occurs by a modified “redox catalysis” mechanism.[15] In situ electrochemical X-ray absorption studies of the polyaniline-Fe-C systems show a correlation between the change in the oxidation state of the Fe species and the potential of the reversible wave in the cyclic voltammogram of the catalyst.[16] X-ray absorption analysis reveals fine structure between 2–3 Å, consistent with the known Co–Co shell distance, while the spectrum of polyaniline-Fe-C shows a peak at about 1.5 Å, which is indicative of coordination to a light element (either N or O). The role of Co in the binary catalyst, the exact ORR active site, and the reaction mechanism are still not known. It is beyond doubt, however, that addition of Co enhances the activity and stabilizes performance. The high catalyst stability and corrosion resistance are also linked to the graphitized carbon phase formed during the heat treatment.

The U.S. Department of Energy set its 2010 target performance for fuel cells not based on Pt catalysts at 130 $A\,cm^{-3}$, and the 2015 target at 300 $A\,cm^{-3}$ (at 0.8 V *iR*-free cell voltage, at 80 °C and at $O_2$ and $H_2$ total pressure of 1 bar). The performance of the catalyst reported by Lefèvre et al. in 2009 is 99 $A\,cm^{-3}$, and the performance of the polyaniline-FeCo-C system reported by Wu and Zelenay in April 2011 is

81 A cm$^{-3}$.[17] The most exciting result was reported in August 2011 in a *Nature Communication* by the Dodelet group.[18] By using a metal–organic framework consisting of zeolitic Zn$^{II}$ imidazolate (ZIF-8) as the host for Fe and N precursors [iron(II) acetate and 1,10-phenanthroline (Phen)], they prepared a Fe/Phen/ZIF-8 catalyst with a volumetric activity of 230 A cm$^{-3}$ at 0.8 V (*iR*-free), the highest reported to date for non-Pt-based ORR catalysts in PEMFCs (Figure 3). The more than twofold increase in catalytic activity compared with that reported by the same group in 2009 combined with the significantly enhanced mass-transport properties of the Fe/Phen/ZIF-8 catalysts (attributed to its interconnected alveolar carbon nanostructure) have resulted in the highest power density reported for a a nonprecious-metal catalyst for ORR.

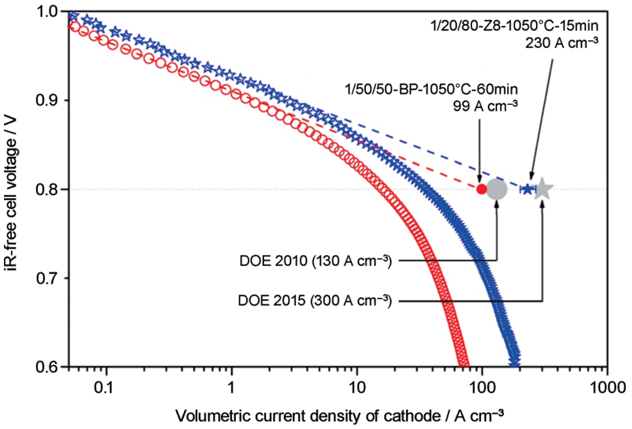

***Figure 3.*** Volumetric current density of the best non-Pt catalysts in $H_2$/air fuel cell tests at 80 °C and 100% relative humidity for cathodes,[10,18] and the U.S. DOE volumetric activity target at 0.8 V (*iR*-free). Red circles: most active iron-based catalyst from previous studies, dashed red line: extrapolation of the linear range to 0.8 V, blue stars: most active iron-based catalyst from the present study, dashed blue line: extrapolation of the linear range to 0.8 V. Adopted with permission from Ref. [10]. Copyright 2011, NPG.

Since the paper published by Jasinski in 1964, the effort to replace platinum as the ORR catalyst and thus to develop fuel cell catalysts not based on precious metals has provided encouraging results. Catalysts with good durability and stability can now be produced that are inexpensive in comparison to platinum. It seems one of the main barriers to hydrogen fuel cells may be overcome in near future. The development of anion-exchange membrane fuel cells may provide another chance to replace Pt catalysts. A better (in situ) characterization and understanding of the reaction mechanism and a knowledge-based synthesis of new catalysts are the prerequisites for further development.

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