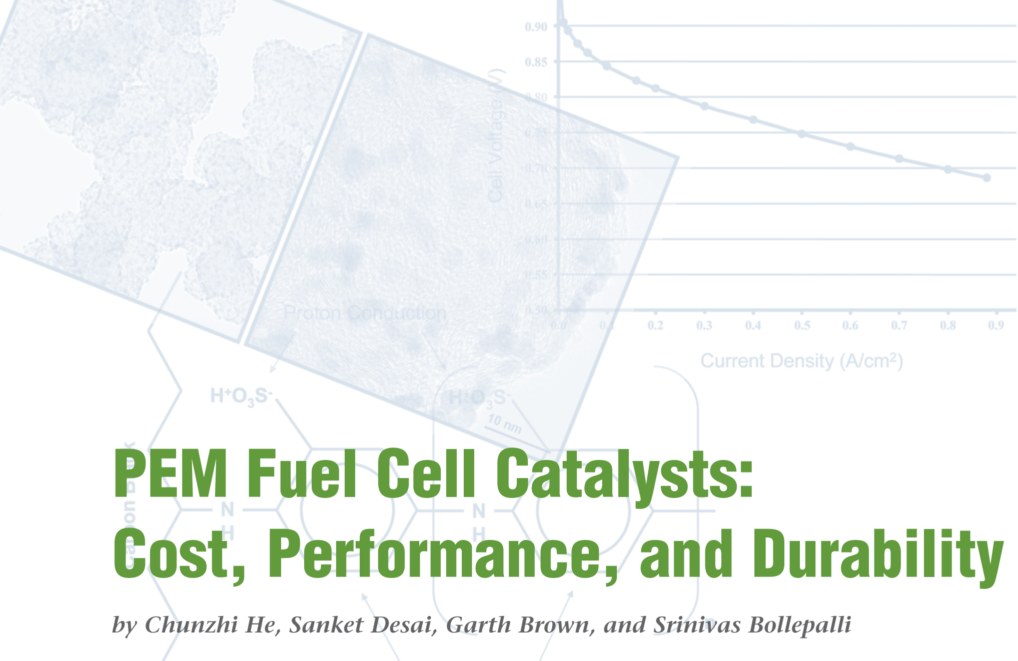

PEM Fuel Cell Catalysts: Cost, Performance, and Durability

by Chunzhi He, Sanket Desai, Garth Brown, and Srinivas Bollepalli

Proton exchange membrane (PEM) fuel cells are typically classified as methanol-based or hydrogen-based depending on the fuel used to convert chemical energy into electricity. Although direct methanol fuel cells have advantages of fuel availability and storage, long unsolved problems of poor anode kinetics and high methanol crossover limit their potential use mainly to applications with low power requirements, such as portable appliances. Hydrogen fuel cells, on the other hand, are targeted toward applications that emphasize energy efficiency and require high power densities, and may potentially replace the internal combustion engine in automobiles.

The electrochemical reactions in a hydrogen fuel cell are simple (Eq. 1-3). Hydrogen is oxidized at the anode into protons and oxygen is reduced at the cathode to produce water. Both reactions can be catalyzed by platinum.

Anode	H_2	$\rightarrow$	$2H^+ + 2e^-$	[1]
Cathode	$\frac{1}{2} O_2 + 2H^+ + 2e^-$	$\rightarrow$	$2H_2O$	[2]
Overall	$H_2 + \frac{1}{2} O_2$	$\rightarrow$	H_2O	[3]
	E	$=$	1.229 V at 25 °C	

While hydrogen oxidation over platinum is intrinsically very fast, oxygen reduction over platinum is very slow. Exchange current density is one measure of kinetics of electrochemical reactions. The exchange current density of hydrogen oxidation on platinum is almost three orders of magnitude higher than that of oxygen reduction, *e.g.*, 1 mA/cm² (H_2) *vs.* 10^{-3} mA/cm² (O_2).[1,2] The polarization loss at the anode under practical operating current densities such as at 0.4 A/cm² is about 10 mV, while that at the cathode is over 400 mV at similar current densities. A great deal of research has been focused on improving the oxygen reduction kinetics.

Oxygen reduction catalysts have evolved from platinum black to carbon supported platinum catalysts. Platinum black catalysts are not economically feasible due to their low surface areas, requiring the use of higher platinum loadings per unit area in order to attain reasonable performance. Carbon-supported platinum (Pt/C) catalysts have higher active surface areas and are the materials of choice in today's fuel cells. Pt/C catalysts are now available in loadings from around 10% to over 50% platinum. Developments in catalyst synthesis technology have allowed for production of catalysts containing over 50% platinum with very small, stable platinum particles. For example, catalysts with 55% platinum by weight can be made with an average platinum particle size of approximately 2.1 nm.

With the advances in catalyst technology has come a recognition of the importance of electrode structures. Electrodes have progressed from polytetrafluoroethylene (PTFE)-bonded[3] to Nafion®-impregnated PTFE-bonded[4] and Nafion®-bonded.[5] In PTFE-bonded electrodes, only catalyst particles at the membrane-catalyst layer interface were available for electrochemical reactions; the remaining catalyst was unusable. Introduction of ionomer such as Nafion® into the catalyst layer has improved the protonic conductivity in the electrode layer, extending the reaction zone and increasing the catalyst utilization. The use of Nafion®-bonded electrodes has been a key step in the development of electrode structures.

While significant technical advances have been made in many aspects, challenges remain toward commercialization of fuel cells. To be competitive with traditional power sources, fuel cells must improve in cost, performance, and durability. [*Editor's note*: See article by Mathias *et al.* on p. 24 of this issue.]

Cost

A key factor toward commercialization of the fuel cell technology is its cost competitiveness. The predominant cost driver is the amount of precious metal used. Researchers are striving to reduce the precious metal requirement in the cell by designing better materials and improving the overall system engineering. The move from platinum black to carbon supported platinum catalysts has significantly cut platinum requirements. Typical loadings in the electrode today are about 0.4-0.8 mg platinum/cm², which is significantly lower than 25 mg/cm² with early platinum black catalysts. The US Department of Energy (DOE) has set targets of 0.3 mg/cm² for 2010 and 0.2 mg/cm² for 2015.

Due to the fast kinetics of hydrogen oxidation, anode loadings could be lowered from 0.40 to 0.05 mg/cm² without significant loss in performance. Oxygen reduction is slow, and reducing the cathode loading results in a performance loss. Lowering the cathode loading fourfold, which is required to meet the DOE target, would lead to a loss of about 40 mV. To achieve this target, and maintain today's state of-the-art performance, alternative catalysts may have to be developed that are four times more active than

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traditional Pt/C. One alternative currently being explored is the use of Pt-X/C alloy catalysts (X = Co, Fe, Ni, or other transition metals). Pt-Co/C, for instance, has shown a twofold activity enhancement for oxygen reduction,[6,7] allowing a reduction in platinum loading from 0.40 to 0.20 mg/cm^2. A further twofold activity enhancement at the cathode is needed to meet the above mentioned target. According to a report by Technology Tracking,[8] utilizing nanostructured carbons such as nanofibers, nanotubes, etc. as supports may help realize the target. Several novel approaches being pursued in the US and abroad hold promise to boost catalytic activity and may potentially reduce the loading to as low as 0.1 mg/cm^2.

Performance

Cost reductions in fuel cells necessitate improvements in catalyst performance. Platinum particle size, crystallite geometry, metal dispersion on the carbon support, conductivity, and porosity of the catalyst layer are important features that determine the catalytic behavior in the operating environment. These features can be controlled by proper design of the catalyst synthesis process. Appropriate choice and modification of reagents and the carbon support can further influence the catalyst properties.

In a Pt/C catalyst, small platinum particles are preferentially anchored to high energy sites on the carbon surface. The density of such sites on the support influences the platinum crystallite size in the resulting catalyst. Carbon blacks typically used as supports for catalysts have surface areas between 250 and 1200 m^2/g. Supports with higher surface areas tend to have a higher number of active sites for platinum deposition and lead to catalysts with smaller particles. Specific treatments can be applied to the support to increase or decrease the number of active centers available on the surface. Carbon blacks can be chemically modified to introduce functional groups that act as sites for platinum anchoring. Besides the nature of the carbon support, the platinum particle size is influenced by the catalyst preparation process, post treatment, and handling of the catalyst.

Catalysts with smaller platinum particles have higher active surface area. While smaller particles are therefore generally desirable, the final performance of the catalyst in the operating environment is a result of many factors. Several studies have shown that the oxygen reduction reaction exhibits a particle size effect in the range of 1-5 nm, finding that an optimal particle size exists for high catalytic activity. This effect has been reviewed in the literature by Kinoshita,[9,10] Stonehart,[11] and Mukerjee;[12] and several theories have been proposed to explain this effect - absence of faceting in platinum particles in that size regime, instability of small particles, and poor platinum dispersion on such catalysts. While results differ on the optimal particle size for highest catalytic activity, they suggest that the catalyst must be designed with a specific particle size to maintain optimal catalytic activity.

The platinum particle size can be derived from an X-Ray diffraction (XRD) pattern, which also provides information on crystal phases in the catalyst. The XRD technique is generally complemented by cyclic voltammetry (CV) to measure the catalytically active surface area. The active area depends on the metal particle size and on the uniformity of metal dispersion on the carbon support. Uniform catalyst dispersion, observable by transmission electron microscopy (TEM) (Fig. 1), is essential for good platinum utilization and for resistance to platinum sintering.

A good catalyst must have optimal mass transport characteristics. During cell operation, the reactant gases — hydrogen and oxygen — traverse the porous electrode layer to reach active platinum sites. Resistance to the transport of gases must be minimized. Water, formed at the cathode and essential to the efficient fuel cell operation, can be a hindrance to the free flow of the gases. Water is a great conductor of protons through the cell, but accumulation of water in the electrode layer may lead to cell flooding that blocks access of the gases to platinum. The water that is produced must be appropriately eliminated from the cell. The catalyst layer must allow for an optimal balance of water to maintain an efficient operation.

The physical and chemical properties of the carbon substrate can alter the nature of water-catalyst interaction. Porous supports typically exhibit higher water sorption. Depending on the pore size distribution in the carbon, water may or may not accumulate within the catalyst layer. Presence of chemical functionalities on the carbon support can alter the catalyst hydrophilicity and hydrophobocity, thereby affecting the water balance. In fact, the catalyst support can be selectively treated by specifically introducing hydrophilic and hydrophobic modifications to design a material with good water balance.

Mass transport losses can also be minimized by reducing the thickness of the catalyst layers, attainable by using catalysts more concentrated in platinum. For a specific platinum loading, *e.g.*, 0.3 mg Pt/cm^2, a catalyst with 60% platinum forms a thinner layer than a similar catalyst with 40% platinum. Results show that catalysts with higher platinum concentrations offer performance advantages at high current densities where mass transport phenomena usually dominate. For a given support, catalysts with higher platinum loadings, however, also tend

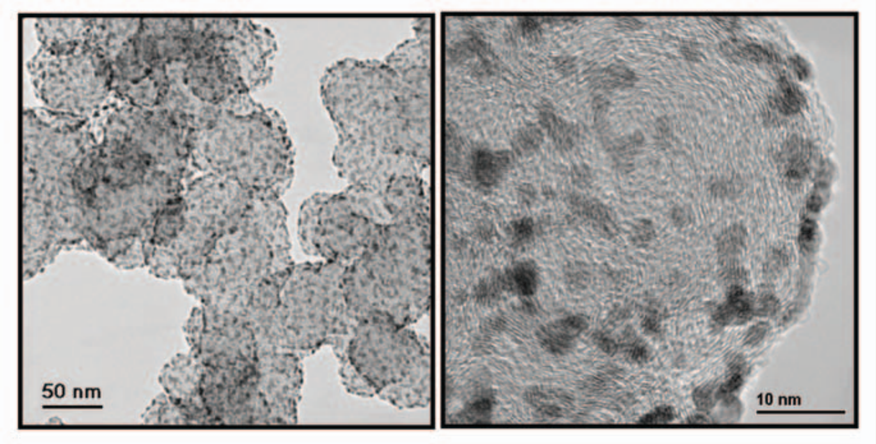

FIG. 1. Transmission electron microscopy (TEM) image of DURA-lyst™-1140 (40% Pt/C catalyst).

to have larger platinum particles, and hence lower active areas. The balance of surface area losses and mass transport losses must be weighed depending on the application under consideration.

During cell operation, electrons and protons generated or consumed at platinum sites migrate through the electrode layer. The electrode layer must exhibit good electronic and protonic conductivities to minimize resistive losses in the cell. Commonly used carbon supports (Conductex® 975 and Vulcan® XC-72) are good conductors of electrons. The catalyst by itself, however, cannot conduct protons. Presence of ionomer in the catalyst layer is necessary to conduct the protons. Therefore proton conduction may depend dramatically on the formulation of the catalyst layer. Recent advances in catalyst design have begun to address this limitation. As with electron conduction, thinner catalyst layers help reduce resistive losses due to proton conduction. Further, the surface chemistry of the catalyst support can be tailored appropriately, such as illustrated in Fig. 2, to impart protonic conductivity to the catalyst. However, such changes must be carefully performed to minimize any adverse impact on other important features of the catalyst.

The performance of the catalyst in a fuel cell is a net effect of the features discussed above. It is typically tested in a laboratory by a polarization curve, which measures the voltage produced by a cell for a range of current densities (Fig. 3).

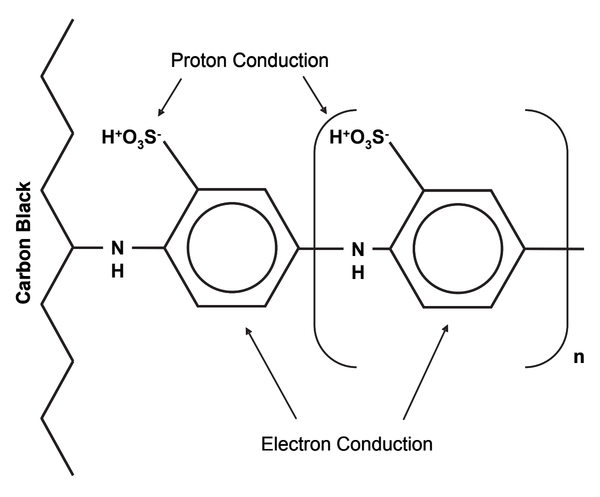

FIG. 2. Catalysts with surface modified carbon blacks show enhanced proton and electron conduction.

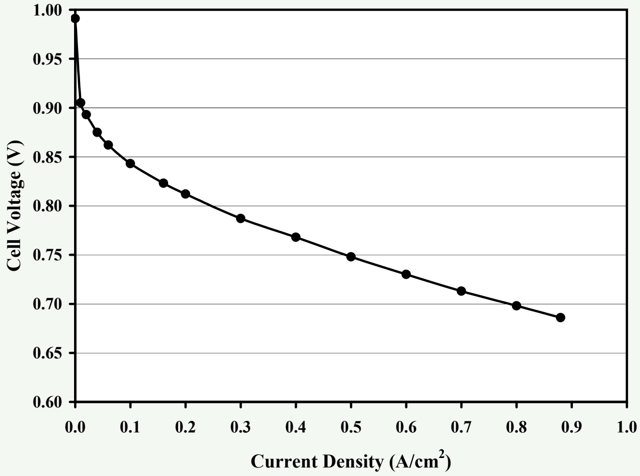

FIG. 3. Polarization curve of a H_2/air fuel cell (DURA-lyst™-2255 Pt/C, Nafion®-112, air = 2.5 stoic, constant H_2 flow rate, ambient pressure, 70°C).

Durability

In addition to cost and performance, long term stability of the catalyst is important. Often-quoted lifetime targets for fuel cells are 5,000 h for automotive and 40,000 h for stationary applications. The membrane and the catalyst must withstand these durations without significant changes in performance. The membrane may degrade over time due to attack by peroxide radicals which can form at the cathode. Presence of contaminants in the cell can accelerate the rate of peroxide generation. Contaminants such as chloride ions also may poison the platinum catalyst. Purity of fuel cell components is critical to stability, although high purity sometimes results in higher cost. The catalyst also may lose stability due to sintering of platinum particles, dissolution of platinum, and corrosion of the carbon support.

Sintering of platinum particles on the carbon support decreases catalytically active surface areas. Small metal particles of the catalyst may dissolve into the acidic operating environment, precipitating onto larger metal particles leading to particle growth; or the particles may directly coalesce with each other due to movement on the carbon surface. Both mechanisms occur to some degree, with dissolution-precipitation being more prevalent when load cycling occurs. The sintering of the catalyst may be reduced by strengthening the metal-support interaction. For example, modification of the carbon support, such as grafting polyaniline to the support surface, decreases the mobility of the metal particles. The nitrogen moiety in the polymer acts as a Lewis base that can anchor the platinum particles.[13]

Dissolution of platinum from the carbon support is less favorable under neutral pH or zero potential. In the acidic operating environment in the fuel cell, or in the presence of a potential field, platinum can dissolve from the catalyst. The dissolved metal cations can travel through the system and contaminate the polymer membrane, thus decreasing protonic conductivity and affecting cell performance. Platinum alloy catalysts show greater resistance to dissolution and sintering,[14] although care must taken to ensure that the alloying element itself

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does not leach into the cell.

Corrosion of the carbon support also may lead to performance loss.[15] When carbon corrodes, the relative percentage of conductive material in the catalyst layer decreases. The resistance of the remaining dielectric material then dominates the cell resistance. Further, as the carbon support oxidizes, the thickness of the catalyst layer decreases, decreasing electrical contact with the current collector and increasing the cell resistance. Carbon corrosion also decreases the number of sites available to anchor platinum, resulting in metal sintering.

The extent of carbon corrosion in the cell depends on the operating conditions and the specific chemistry of the support used. Higher operating voltage increases the degradation rate. The surface area of the carbon support also influences the rate of carbon corrosion. The higher the surface area of the carbon, the faster is the rate at which it corrodes. A catalyst maker may attempt to lower the available support surface area by selecting an alternative carbon. The carbon support may also be modified by graphitization. When traditional carbon blacks are heated to high temperatures (*e.g.*, ~2,000 °C), lattice rearrangements occur, increasing the graphitic nature of the material and decreasing the number of active surface sites. Graphitization produces a material which is highly resistant to oxidation and carbon corrosion. However, with fewer active sites, metal deposition on such supports is more difficult.

Conclusion

Continued developments in catalyst materials are critical to the commercialization of PEM fuel cells. Catalyst loadings have been reduced more than 50-fold in the last few decades, from early 25 mg/cm^2 to current loadings of 0.5 mg/cm^2 or less. The use of 50% or higher Pt/C catalysts in recent years has allowed for better gas transport and improved catalyst utilization. However, challenges remain to make fuel cells competitive with traditional power sources. Cathode losses with current materials are still too high to meet DOE performance targets. Stability is of particular concern for dynamic operating conditions, such as in automotive applications. Concerns of platinum dissolution and carbon corrosion must be addressed to realize the DOE targets for cell durability.

At Columbian Chemicals Company, we are investigating alternative technologies, such as tailored morphologies and surface modification of carbon nanomaterials, nanotubes, and nanofibers for improved catalyst performance and durability. Electrodes composed of catalysts with tailored supports have longer lifetimes, greater permeability of reactants, and higher protonic conductivity for enhanced catalysis. These novel carbon supports and alloy catalysts are focused to bring the technology closer toward realizing the DOE targets.

Note

DURA-*lyst*™ and Conductex® are registered trademarks of Columbian Chemicals Company; Nafion® is a registered trademark of E.I. Dupont de Nemours and Company; Vulcan® is a registered trademark of Cabot Corporation. ■

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