Physical Chemistry Research Toward Proton Exchange Membrane Fuel Cell Advancement

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ABSTRACT: Hydrogen fuel cells, the most common type of which are proton exchange membrane fuel cells (PEMFCs), are on a rapid path to commercialization. We credit physical chemistry research in oxygen reduction electrocatalysis and theory with significant breakthroughs, enabling more cost-effective fuel cells. However, most of the physical chemistry has been restricted to studies of platinum and related alloys. More work is needed to better understand electrocatalysts generally in terms of properties and characterization. While the advent of such highly active catalysts will enable smaller, less expensive, and more powerful stacks, they will require better understanding and a complete restructuring of the diffusion media in PEMFCs to facilitate faster transport of the reactants ($O_2$) and products ($H_2O$). Even Ohmic losses between materials become more important at high power. Such lessons from PEMFC research are relevant to other electrochemical conversion systems, including Li–air batteries and flow batteries.

Proton exchange membrane fuel cells (PEMFCs) are becoming commercially viable electric power sources for a number of applications, including materials handling (forklifts), backup power for communications, and aerospace.¹⁻³ Electric power from hydrogen fuel cells offers numerous technological advantages such as short refueling times, high system reliability, and endurance. The largest and most challenging potential market is automotive. All of the major automotive companies see PEMFCs operated with a hydrogen fuel as the next-generation electric propulsion system, but they are challenged with producing a fuel cell system that competes with highly optimized, cost-effective, long-lived gasoline and diesel engines along with hybrids and battery electric vehicles that can be recharged from an existing electric grid.¹ From our perspective, the path to the next-generation, cost-effective fuel cells lies in making more efficient, higher power systems, and this path must be forged with physical chemistry. We review the major physical chemistry advances that have helped get fuel cells to their present status and describe what research is needed to go beyond to commercially feasible systems.

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Electricity (and heat) is generated in PEMFCs from the electrochemical conversion of hydrogen fuel and oxygen to water, eq 1.

$$2H_2 + O_2 = 2H_2O$$

(1)

Equation 1 is derived from the half-cell reactions for the hydrogen oxidation reaction (HOR, eq 2) and the oxygen reduction reaction (ORR, eq 3), which are typically catalyzed on nanoscale platinum electrocatalysts supported on high-surface-area carbon (Pt/C).

Anode:

$$2H_2 = 4H^+ + 4e^-$$

(2)

Cathode:

$$O_2 + 4H^+ + 4e^- = 2H_2O$$

(3)

The protons transport from the anode to the cathode through a proton exchange membrane (PEM), typically composed of perfluorosulfonic acid (PFSA), for example, Nafion. Concomitantly, the electrons are transported from the catalyst layer (CL) to a gas diffusion layer (GDL) and then to a bipolar plate (BPP) current collector which are combined in a membrane electrode assembly (MEA). The BPP serves the additional function of providing the gases to the catalysts and transporting product water away from the GDLs and accordingly has embedded gas flow fields. MEAs are combined in series to make a fuel cell stack.

How all of these cell components (PEM, CL, GDL and BPP) work together ultimately determines the power and efficiency of the fuel cell. An increase in power density allows a smaller stack to be used and results in less stack materials, such as BPPs, GDLs, plus a smaller catalyst/membrane active area.

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Higher power is derived from higher current density per unit of catalyst area and also from using thinner membranes. An increase in stack efficiency decreases the amount of hydrogen used per Watt-hour of electricity generated and the size of the heat rejection system (assuming the same temperature of operation).

The thermodynamic efficiency of a fuel cell is calculated from the energy produced versus all of the energy in the reaction of the formation of water in eq 1. Practically, this is calculated from \( \eta_{\text{therm}} = \frac{E_{\text{cell}}}{E_{\text{theor}}} \), or the ratio of the operational voltage of the cell, \( E_{\text{cell}} \), to its thermodynamic open-circuit voltage, \( E_{\text{theor}} \). For PEMFCs, \( E_{\text{theor}} \) is near 1.229 V under standard temperature and pressure. \( \eta_{\text{therm}} \) is far below 1.229 V because of overpotentials arising from activation losses in the electrocatalytic reactions, mass-transport losses of the reactants, and ohmic (\( IR \)) losses from materials. The representative fuel cell polarization curve of the voltage versus current density in Figure 1 shows the relative contributions of these losses. The total fuel cell stack overpotential, \( \eta_{\text{FC}} \), is calculated by eq 4.

\[
\eta_{\text{FC}} = \eta_{\text{activation}} - \eta_{\text{ohmic}} - \eta_{\text{mass transport}}
\]

For a practical fuel cell stack operating near 0.7–0.8 V, the thermodynamic fuel cell efficiency is about 56–64%.

Most of the overpotential losses shown in Figure 1 derive from activation losses, mainly due to the inefficiencies of the four-electron oxygen reduction reaction (ORR), which is notoriously sluggish in the acidic (pH \( \approx 1 \)) conditions of the PEMFC cathode. The incumbent catalyst choice since 1839 is Pt, or Pt-based, and studying the ORR on Pt in acid has been a robust field of experimental and theoretical research for decades; recent reviews discuss the state-of-the-art catalysts for automotive systems.

One of the most valuable techniques for probing the fundamental chemistry of the ORR has been electrochemical studies on Pt single-crystal surfaces. The activation overpotential can then be qualitatively modeled with the Butler–Volmer equation to estimate the turnover rate of \( \text{O}_2 \). After years of Pt (111) studies, an understanding is emerging for the process for O/\( \text{OH} \) adsorption and reduction on single-crystal surfaces of Pt. The ORR entails the transfer of four protons and four electrons per \( \text{O}_2 \) molecule, which occur hetero-

![Figure 2](dx.doi.org/10.1021/jz3019012.J.Phy.let.2013,4.393-401)
illustrating both the Pt skin ligand effect and the difference in activity between nanoparticles and an extended surface. DFT has also been improved to better estimate the effect of metal segregation in the alloys and has been used to predict high-activity alternative alloys with the early transition metals scandium and yttrium, which have also shown high activity in half cells but not yet in practical fuel cells.

There is still much to be done to close the gap between theory and experiment. The apparent good correlation of theory of Pt and Pt alloys with the performance of Pt nanoparticles, and even carbon-supported alloys, is somewhat surprising due to the complexity of a practical fuel cell electrode. An optimal catalyst comprises nanoparticulate Pt, or a related material, usually on a porous carbon support, all which is interlinked with PFSA ionomer to create ample electrical conduction pathways for proton and electrons, all of which are exposed to gases and water at a range of potentials, temperatures, and relative humidities. The carbon is prone to oxidation to CO2 in the presence of high potentials, oxygen, and the Pt catalyst, thus presenting another side reaction and source of instability. However, the basic research and theory both point to the Pt–OH bond strength as an important control variable.

A new emphasis for modeling of Pt and Pt alloys might be on the basic understanding of Pt–O formation and desorption on the Pt surface as PtO formation is a gateway to loss of Pt by dissolution. The PEMFC cathode operates at potentials where the oxygen intermediates are being adsorbed and desorbed continuously during transient load operation, but start-up and shut-down transients may lead to transient potentials in excess of 1.8 V, which encourages PtO and PtO2 formation through place exchange mechanisms, which, upon subsequent reduction under high current load, may lead to enhanced Pt dissolution, a major degradation mechanism, as well as carbon corrosion. While the accepted volcano plots successfully predict reactivity at the beginning of catalyst life, they need to be adapted and refined for Pt dissolution, and more desirable compositions might emerge to predict catalysts, which maintain high activity at their end of life. Ironically, Pt alloys in particular suffer from relatively poor stability at the high potentials and acidic conditions of PEMFCs, not because of their Pt–O bond strength but rather due to the strength of O with the transition-metal additives, which are highly susceptible to oxidation and dissolution if they migrate to the nanosized surface.

Beyond alloys, promising alternatives for reducing cost include catalysts for which the Pt or other precious metals are stabilized and activated through the use of metal–support interactions via oxide-based supports or eliminated completely from the fuel cell in carbon–nitrogen-based catalysts.

There have been several reports of the increase in ORR activity of Pt when supported on oxides such as niobium oxide, tantalum oxide, iron phosphate, zirconium oxide, and cerium oxide. Pt on tantalum phosphate and carbon shows about two times the activity of Pt, as measured by rotating disk electrode (RDE) voltammetry. In most of these catalysts, carbon is also used to provide electronic conduction because it has at least 3 orders of magnitude higher conductivity than oxides. The oxide (or phosphate) also serves to protect any carbon and enhance the stability of the Pt against dissolution.

The mechanisms for the high activity of the oxide- and/or phosphate-supported catalysts can be globally attributed to metal–support interactions, but they have not been well explored and appear to vary between catalysts. For Pt on tantalum oxyphosphate on carbon (Pt-TaOPO4/VC), heating to 660 °C in an inert environment triggers the phase segregation of the tantalum phosphate into Ta2O5 and an oxyphosphate. The resulting proton-conducting phosphate layer between Pt and the tantalum oxide phase is likely to promote the ORR through its higher acidity as studies on polycrystalline platinum show that the current density of the ORR increases with increasing H+ concentration, which contributes to the formation of OH- and OOH- ions. Oxides also have high proton conductivity and acidity; therefore, the impact of a highly acidic support would translate to all phosphate- and oxide-supported catalysts. Pt on iron phosphate appears to have a completely different mechanism and relies on a redox couple between Fe2+ and Fe3+ and Pt2+ and Pt4+ ions. Also, Au on hydrous tin oxide is thought to be active in acid by a bifunctional mechanism as the SnO2 adsors O2 and thus provides the first step in the ORR, a step that the filled d-band of the Au is unable to accommodate.

None of the oxide- and phosphate-supported electrocatalysts have been modeled with the successful d-band models discussed above for alloys. The models also are not tuned to varying acidity, redox couples, spillover, and bifunctional mechanisms across materials interfaces, the mechanisms noted above for metal–support interactions. The path to modeling such complex electrocatalysts has been largely unexplored. Only recently has a water layer been added into the Pt(111) models both by DFT and periodic density functional theory, interestingly, those models showed no impact of the water in the Pt(111) models, supporting the original path of only modeling the OH bond strength. The lack of a complete model can be attributed to the extremely complex physical chemistry involved in multifunctional ORR electrocatalysts and might even require advances in computing and theory to accommodate.

The ultimate goal would be the replacement of all costly precious metals with non-noble metals or even to remove the metal entirely. This approach has been partially successful with nonprecious metal catalysts (NPMCs) based on carbon with nitrogen and iron, which come close to the kinetic performance of Pt for the ORR at very high loadings. First-principles modeling efforts of NPMCs have made some progress; although still in its early stages, there is optimism that these catalysts can be rationally designed. NPMCs that may meet cost targets and provide kinetic performance do suffer from very extensive resistive and mass-transport losses due to the thicker CLs. This means that there is still considerable effort required in CL design where physical chemistry can play an important role.
A significant problem with NPMCs is how to compare them to standard Pt/C electrocatalysts. The Pt surface area is relatively easy to measure by cyclic voltammetry (CV) as electrochemical experiments combined with surface science suggest that one H atom adsorbs per Pt; therefore, the charge from H desorbed from the Pt is directly proportional to its ECSA (see the inset in Figure 3). The area-specific activity is then determined from the kinetic current of the electrocatalyst and its ECSA.\textsuperscript{42,43} Because NPMCs have no such correlation, the ECSA and thus specific activity cannot be ascertained. On NPMCs, it should be possible to apply physical chemistry techniques to measure the active site density and hence a turnover rate for ORR if the nature of the active site were known. Most workers in the area have made assumptions about the active site and still have difficulty coming up with a truly comparative number for the activity of their catalysts.\textsuperscript{38} The low cost of the NPMCs does not necessarily mean that they are low cost to implement. The amount of catalyst on the electrodes can only be increased to a point due to mass-transport losses and resistance of thick electrodes. Therefore, the lower-activity catalyst leads to a large, low power stack that transport losses and resistance of thick electrodes. Therefore, the lower-activity catalyst leads to a large, low power stack that

A barrier to going beyond traditional Pt-based catalysts is the lack of simple methodology for electrochemical screening of catalyst activity (and stability). A success for Pt/C catalysts was the adaptation of the RDE methodology from flat single crystals to thin Pt/C films and then subsequent correlation to MEA performance.\textsuperscript{42} The preliminary methodology was based on Pt and Pt alloys, whereby the current density of the electrode at 0.9 V at 60 °C in 0.1 M HClO₄ at a rotation rate of 1600 rpm for a thin Pt catalyst film correlated well, albeit arbitrarily, to the current density of an MEA at 80 °C at 0.9 V (see the example of RDE data in Figure 3). This development stemmed from careful validation of the mathematics and physical chemistry of the RDE method to thin films and requires validation with the Koutecky–Levich methodology. Major discrepancies still exist, however, between the RDE and MEA methodologies. For RDE, the electrode must be very thin, with a loading of about 5–20 μg of Pt per cm\(^2\), while 400 μg of Pt per cm\(^2\) is standard for MEAs.\textsuperscript{44} The RDE is nominally saturated in liquid electrolyte and is thus highly susceptible to trace contaminants and assumes complete wettability. The RDE films must be of high quality for the RDE flow equations to be valid,\textsuperscript{43} and reliable methods for making high-quality, reproducible thin films have only recently been reported.\textsuperscript{55,46} Further improvements continue to be made in the data manipulation, such as background corrections for capacitive current, resulting in new mass activity values for Pt/C catalysts that are 2–4× initial reports,\textsuperscript{45,46} and they are no longer a clear match to MEA values. By changes to RDE methodology, long-established correlations between Pt nanoparticle size and ORR activity are being overturned.\textsuperscript{47} The relevance to RDE measurements in terms of predicting catalyst performance in MEAs should be revisited for Pt/C and alternative catalysts. An alternative to RDE might be flow cell configurations.\textsuperscript{48} The hydrodynamic flow is generally perpendicular to diffusion within the porous powder catalyst deposited on the working electrode, but this can lead to spurious results if the catalyst deposit is too thick. Even better would be a reliable small-scale MEA method that uses small amounts of catalyst.

As noted above, CV measurements are clearly an excellent analytical tool for measuring the Pt ECSA as well as the onset potential for OH adsorption. Although there is less certainty about the use of H adsorption for Pt alloys, which can have different H binding energies,\textsuperscript{49} hydrogen adsorption, CO stripping voltammetry, and underpotential deposition (upd) of copper adatoms must be used in combination to determine the ECSA.\textsuperscript{50} The onset potential for OH adsorption is only modestly predictive of the ORR activity of Pt/C and Pt alloys and has no correlation to the ORR activity for catalysts such as Pt on tantalum phosphate\textsuperscript{29} and NPMCs.

Catalyst physical characterization is plagued by the difficulties around measuring the O- and OH-specific coverage on a Pt electrode submerged in H\(_2\)O with regard to both distinguishing between the adsorbed species and the derivation of absolute coverages from charge measurements.\textsuperscript{7} As with half-cell mechanistic measurements, single crystals are an invaluable research tool, and research on single crystals and “extended surfaces” of Pt and Pt alloys have given indirect evidence for their interaction with OH and O. Extensive surface characterization has been carried out with low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), low-energy ion scattering (LEIS), and synchrotron-based high-resolution ultraviolet photoemission spectroscopy (UPS).\textsuperscript{15} Differential reflectance spectroscopy and second-harmonic generation have

![Figure 3. RDE voltammetry of a 20% Pt/C catalyst (ETek) in 0.1 M HClO₄ electrolyte at 30 °C. Pt loading = 15 μg/cm², rotation rate = 1600 rpm, scan rate = 20 mV s⁻¹. (Inset) CV of an electrode in O₂-free electrolyte showing regions for oxygen adsorption and desorption and hydrogen adsorption and desorption. The onset potential for O adsorption is often used as a measure of the Pt–OH bond strength. The (shaded) area of the H adsorption region correlates with the Pt ECSA. See ref 43 for more details.](image-url)
have been developed to resolve ionic and molecular absorbates on a quasi-perfect Pt(111) surface.\textsuperscript{52}

In situ physical characterization tools for practical nanoscale catalysts are few. The conductive carbon supports and nanoparticulate electrocatalysts in practical fuel cell electrocatalysts also present unique challenges as they create opacity in IR and Raman measurements. Success has been had with the $\Delta \mu$ XANES method whereby the absorption spectrum, $\mu$, from in situ X-ray absorption near edge spectroscopy (XANES) of practical electrocatalysts was taken in the potential regions for hydrogen or oxygen adsorption and then subtracted from the baseline $\mu$ in the double-layer region. The remaining $\Delta \mu$ can then be correlated to specific absorbates through comparison to models.\textsuperscript{52} The advantage of this approach is that only the H and O species that adsorb specifically to Pt sites coherently scatter X-rays, and the remaining species (for instance, in the main solution has been the avoidance of H\textsubscript{2} impurities by setting ultrahigh purity H\textsubscript{2} as the international standard for fuel cell systems. However, as anode loadings are reduced to 50-70% of those found in H\textsubscript{2} produced from reformate, natural gas, or ammonia (e.g., H\textsubscript{2}S, CO, NH\textsubscript{3}, and organic residuals\textsuperscript{54,55}). The main solution has been the avoidance of H\textsubscript{2} impurities by setting ultrahigh purity H\textsubscript{2} as the international standard for fuel cell systems. However, as anode loadings are reduced to 50-70% of those found in H\textsubscript{2} produced from reformate, natural gas, or ammonia (e.g., H\textsubscript{2}S, CO, NH\textsubscript{3}, and organic residuals\textsuperscript{54,55}).

Oxygen activation studies have been the focus of most electrocatalyst research, with anode studies largely overlooked, despite the need for poison mitigation and performance recovery strategies as impurities in H\textsubscript{2} are likely to accumulate over the thousands of hours of operation needed. The HOR is nearly 100% efficient on platinum electrocatalysts in the presence of ultrapure H\textsubscript{2}; however, the electrocatalyst performance is impeded by strongly bound blocking absorbates such as those found in H\textsubscript{2} produced from reformate, natural gas, or ammonia (e.g., H\textsubscript{2}S, CO, NH\textsubscript{3}, and organic residuals\textsuperscript{54,55}).

The advent of catalysts with higher performance brings advantages but new challenges in electrode design. With high performance from the cathode catalyst, a higher total geometric current is achieved per cell, so that less cell area and a smaller stack are needed to produce the same power at a given voltage. Such a decrease in stack size leads to necessary cost and weight reductions by reducing the amount of cell materials, such as the PEM, BPPs, and GDLs. While the local current density at the Pt surface might be increased 4-fold through implementation of some of the advanced catalysts discussed above, the mass-transport properties of the CL must also be able to deliver three reactants (O\textsubscript{2}, H\textsuperscript{+}, and e\textsuperscript{-}) and carry away products (H\textsubscript{2}O gas, H\textsubscript{2}O liquid, and heat) at four times the rate for the enhanced local current to be maintained. Presently, there is no means to design a CL structure with a greatly increased mass transport at the micro- or nanoscopic level; therefore, the activity gain of advanced catalysts may not be realized in the fuel cell.

In the CL in a fuel cell, optimization has often proven to be an empirical process rather than an engineering design process largely because it is difficult to envision the ideal CL when the structure of the state-of-the-art is so poorly understood. An array of imaging, experimental, and computational tools is being developed toward the four times (or greater) improvement of the transport properties of the CL in contact with the microporous layers (MPLs) and GDLs to the gas flow fields in the fuel cell BPPs. Macroscopic engineering models have already been developed to accommodate mixed-phase water transport (gas and liquid), heat transport, and electronic transport in the midst of transients in flow fields and GDLs.\textsuperscript{59}

Comprehensive models and understanding of the nanoscopic CL remain elusive. While empirical models have been developed,\textsuperscript{60} more accurate modeling is hindered by lack of true information about the CL, MPL, and GDL structures. The CL has, traditionally, been fabricated with simple Pt/C + PFSA ionomer ink formulations and coating process for which Pt loadings and ionomer levels and dispersion have been empirically optimized. The CL is composed of three interpenetrating networks, (i) the electronically conductive support network, (ii) the proton conductive ionomer network, and (iii) the gas pore network for diffusion of the reactant gas and product water. The reactants and products must flow effectively from the micrometer-sized structure of the GDL and the microporous structure of the CL to the nanostructure of the catalyst active sites, as shown schematically in Figure 4.

Models have been developed for water management in CLs using forms of the “flooded agglomerate model”,\textsuperscript{61} but validation of these models at a microscopic level has also been limited because of the unknown ionomer structure within the CL. Porosity has been determined by using focused ion beam and high-resolution scanning electron microscopy (FIB and HRSEM)\textsuperscript{62-64} but it is not possible to distinguish between the ionomer and carbon with this technique. A new technique, scanning transmission X-ray microscopy (STXM) has recently been developed\textsuperscript{65} and applied to ultramicrotome sections through the CL. Using this technique, it is possible to distinguish components based on the chemical composition and build a map of Pt, carbon, and the ionomer in the CL.\textsuperscript{66} A further method is transmission electron microtomography, or TEMt, which has resolution to 0.5 nm and has been used for three-dimensional reconstruction of two different Pt/C catalysts, albeit without the Nafion ionomer.\textsuperscript{67} It may be possible to use this method to build a fully three-dimensional structure of the CL in which the distribution of all components is clear mechanistic data, one attractive approach has been to establish baseline densities on the order of 235 $g/cm^2$ or less, the sensitivity to impurities and degradation will be greatly enhanced. To date, the effect of H\textsubscript{2} impurities on the anode reaction has been carried out in full fuel cells, in which the anode kinetics are obscured.\textsuperscript{55,56} Electrochemical studies of impurity adsorption on nanoscale Pt catalysts are challenging because the HOR is a fast reaction with exchange-current densities on the order of 235–600 mA cm\textsuperscript{-2} of Pt per cm\textsuperscript{-2} of Pt.\textsuperscript{56} such that the mass transport of H\textsubscript{2} to the electrode interferes with kinetic measurements. Standard RDE methodology is not applicable, and physical chemistry research has shown that electrodes on the order of 36 nm in diameter are required to minimize mass-transport effects and allow accurate mechanistic details,\textsuperscript{57} and ultralow Pt loadings are needed for meaningful transport measurements in MEAs.\textsuperscript{56} In the absence of clear mechanistic data, one attractive approach has been to develop more poison-tolerant catalysts, such as Pt supported on molybdenum oxides, which imparts CO tolerance by the conversion of CO to CO\textsubscript{2} by a water–gas shift reaction.\textsuperscript{58} Further development of the RDE and MEA methodologies above would be useful to compare the mechanisms, efficacy, and viability of alternative anode catalysts and the susceptibility of catalysts to poisons.

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The combination of advanced modeling and imaging is gradually leading to ways of designing and building CL structures with properties derived from models that will meet the demands of the high-performing catalysts of the future.

Another research frontier is the characterization of the three-dimensional dispersion of the catalyst particles themselves as they are often around 2 nm in diameter and are supported on a high-surface-area material. HRTEM has been used extensively, but it is restricted in only providing a two-dimensional projection, making full topographical characterization difficult and prone to misinterpretation (e.g., overlapping Pt particles and clusters are often indistinguishable). More recently, electron tomography has been developed to give three-dimensional images of catalyst particles, clearly showing the distribution of Pt particles on the support surface. This may prove invaluable in catalysts with noncarbon supports, which are not so transparent to electrons (e.g., oxides). Much can be learned from heterogeneous catalysis, which relies on structured catalysts or engineered supports, for high performance.

Lastly, ohmic losses contributed by bulk materials and materials interfaces have been a significant source of power/efficiency loss until recent developments of high-performance, very thin PEMs. In state-of-the-art systems with 10 μm thick PEMs and thin metal BPPs, the cell resistance is around 40 mΩ cm$^{-2}$, of which 55% of the area-specific resistance is from total contact resistance between the PEM and MPL and MPL and BPP and only 45% is from bulk materials when evaluated at 100% RH, as shown in Figure 5. At 20% RH, up to 60% of the PEM resistance is from the membrane/electrode interfacial resistance but can be decreased to around 10% with the use of certain proprietary ionomers in the electrode structure. While contact resistance between metals is generally decreased through contact of flat, corrosion-free surfaces, the contact resistance in PEMFCs is more optimal on slightly roughened BPPs to optimize contact with the porous GDL. The construction of BPPs often involves two or more sheets that must be bonded or welded together to create the plate, adding another possible source of interfacial resistance. In addition, in-plane resistances with such thin conductors may significantly impact current distribution and thermal profiles during stack operation, which will impact the dynamic operation depending on the application. With the new low resistances in commercially available thin PEMs, more attention is needed in concepts to reduce the interfacial resistances. If the contact resistance can be reduced 50% to about 10 mΩ cm$^{-2}$, the fuel cell stack will be 1% more efficient at an operating geometric power density of 1 A cm$^{-2}$, the fuel cell stack will be 1% more efficient at an operating geometric power density of 1 A cm$^{-2}$. At next-generation current densities of 4 A cm$^{-2}$, a resistance decrease of 10 mΩ cm$^{-2}$ decreases the overpotential by 40 mV, leading to a 3% increase in efficiency, a noteworthy system impact.

In summary, physical chemistry has clearly played a critical role in progressing PEMFC technology to its present state, enabling developers to understand individual fuel cells and thus build practical, controlled systems. However, much work is still needed to reach the next generation of high-efficiency, high-power, commercially viable systems. While electrochemical...
models for electrocatalysts are mostly understood for single crystals of Pt and Pt alloys, relatively little is known about the true behavior of nanoparticulate catalysts on multiple supports in contact with biphasic media over a range of potentials and Pt-free electrocatalysts. Even less is known about fundamental aspects of mass-transport losses in three-dimensional structures especially as they incorporate higher-activity nanoparticulate electrocatalysts. Research on ohmic losses is changing as well as the materials’ bulk resistances are now lower than the contact resistances, indicating that future research must be focused on interfaces between cell components from the macro- to microscopic levels. Although not a major focus of our Perspective, others have reviewed how the durability of the materials in a fuel cell, including the catalyst, is a major challenge being faced in the commercialization of this technology. The catalyst must not only perform, but it must do so sufficiently throughout the design life of the application. The stressors will vary depending on the application, and the biggest challenge is faced by the automotive sector.

New catalysts are needed, and the ability of any application to utilize the advances currently being made in catalyst development relies on the design of a CL structure that optimizes the network structure for all reactants and products for the various conditions experienced in the field by the application, be it in a vehicle, in a back-up power plant, or in an unmanned aircraft at high altitude. We envision steady progression in physical chemistry as new computational and analytical tools are developed at the nanoscale and macroscopic levels, with the ultimate goal of uniting such dynamic systems into practical stack and system models. We caution that for other electrochemical energy systems to become viable – such as Li–air batteries, flow batteries, biological fuel cells, and solar hydrogen production, the same careful details must be applied to understand the sources of resistive losses in the systems, from the fundamentals of charge transfer to the progression to the optimization of electrical and reaction/product conduction through three-dimensional electrodes.

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■ REFERENCES


(18) Stephens, I.; Bondarenko, A.; Grønlieberg, U.; Rossmeisl, J.; Chorkendorf, I. Understanding the Electrocatalysis of Oxygen


