Electrochemical Energy Engineering: A New Frontier of Chemical Engineering Innovation

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Abstract
One of the grand challenges facing humanity today is a safe, clean, and sustainable energy system where combustion no longer dominates. This review proposes that electrochemical energy conversion could set the foundation for such an energy system. It further suggests that a simple switch from an acid to a base membrane coupled with innovative cell designs may lead to a new era of affordable electrochemical devices, including fuel cells, electrolyzers, solar hydrogen generators, and redox flow batteries, for which recent progress is discussed using the authors’ work as examples. It also notes that electrochemical energy engineering will likely become a vibrant subdiscipline of chemical engineering and a fertile ground for chemical engineering innovation. To realize this vision, it is necessary to incorporate fundamental electrochemistry and electrochemical engineering principles into the chemical engineering curriculum.
ELECTROCHEMICAL ENERGY ENGINEERING

Energy has been central to human civilization. The availability of affordable, abundant fossil energy has been the primary driving force for much of the human progress made in the past 100+ years. With depleting fossil fuel reserves, increasing world population, growing expectations for high living standards, and concerns over air quality and climate change, one of the grand challenges facing humanity today is the development of an alternative energy system that is safe, clean, and sustainable, in which the combustion of fossil fuels no longer dominates.

Throughout human history, combustion has played a leading role in energy conversion. In a combustion process, reduction and oxidation (redox) reactions are coupled intimately, and electrons are transferred directly from the fuel to the oxidant to produce heat. Although this heat can be used directly, it is more often converted to mechanical energy, most often via mechanical energy to electricity, the most convenient form of energy. By contrast, in an electrochemical energy conversion process, the redox reactions are spatially separated by an electrolyte, allowing direct extraction of electrons as electricity and leading to higher intrinsic energy conversion efficiencies and milder process conditions.

Electrochemical energy engineering can be considered a subdiscipline of chemical engineering that focuses on the design and operation of electrochemical energy devices and processes. With training in chemistry, including electrochemistry, physics, mathematics, reaction engineering, transport, and thermodynamics, chemical engineers are best positioned to take the lead in electrochemical energy engineering. Electrochemical engineering with a broader scope that includes electroplating, electrosynthesis, corrosion, and energy conversion has been a part of chemical engineering programs for more than half a century. The research program established by Charles W. Tobias in the 1950s at the University of California, Berkeley, and the Lawrence Berkeley National Laboratory pioneered the field of electrochemical engineering and trained generations of electrochemical engineers (1). A significant number of today’s leading electrochemical engineers in academia, industry, and national laboratories can trace their academic lineage to the Tobias group. Another major contribution to the field of electrochemical engineering from the Berkeley group is John S. Newman’s textbook, Electrochemical Systems, which is a must-read for electrochemical engineers. As society has refocused itself on developing a safe, clean, and sustainable energy system, it has become clear that electrochemical energy devices will play a leading role, and as such, electrochemical energy engineering as a discipline is destined to grow and prosper in the twenty-first century.

A NEW GENERATION OF AFFORDABLE ELECTROCHEMICAL DEVICES

As a way to organize the research work carried out by the authors and others, an integrated electrochemical energy system is envisioned consisting of the following electrochemical energy devices: fuel cells (FCs), electrolyzers (ELs), solar hydrogen generators (SHs), and redox flow batteries (FBs) (Figure 1). Fuel cells coupled with solar hydrogen generators and/or water electrolyzers can provide clean power for mobile and stationary uses, whereas redox flow batteries are ideal for large-scale solar/wind electricity storage. With minor variations, all the aforementioned electrochemical devices share the same basic three-layer structure (electrode/membrane/electrode). Each electrode usually contains an appropriate catalyst to facilitate its designated redox reaction, and the electrode usually has a porous, thin-film structure that allows simultaneous electron conduction, ion conduction, and mass transport. One of the functions of the membrane is to
Figure 1

An integrated, safe, clean, and sustainable electrochemical energy system based on fuel cells (FCs), solar hydrogen generators (SHs), electrolyzers (ELs), and redox flow batteries (FBs). With minor variations, all the aforementioned electrochemical devices share the same basic three-layer structure: electrode/membrane/electrode.

selectively transport the common ion involved in the redox reactions between the electrodes to complete the electric circuit. The acid/base nature of the membrane fundamentally defines the electrochemical reactions at the electrodes for fuel cells, solar hydrogen generators, and electrolyzers.

This article is written as a perspective, rather than a comprehensive review, and as such it focuses on using the authors’ recent work as examples to show that by switching from proton exchange membrane (PEM, an acid membrane) to hydroxide exchange membrane (HEM, a base membrane), and by innovative designs of redox flow batteries, it is possible to eliminate the use of precious metals in fuel cells, solar hydrogen generators, and electrolyzers, which will lead to a new generation of affordable and commercially viable electrochemical systems.

**PEM**: proton exchange membrane
**HEM**: hydroxide exchange membrane
HYDROXIDE EXCHANGE MEMBRANE FUEL CELLS

Fuel Cells

Fuel cells are devices that convert chemical energy (stored in chemical bonds) to electricity through electrochemical reactions between fuel and oxygen or other oxidizing agents. Fuel cells are intrinsically superior to combustion for chemical-to-electrical energy conversion in terms of energy efficiency and environmental friendliness. Owing to the separation between reduction and oxidation reactions, fuel oxidation, oxidant reduction, ion conduction through the electrolyte, and electric load can be engineered independently, which offers excellent device- and system-design flexibility. An individual cell generally produces a relatively small voltage (e.g., 1.23 V as standard voltage for a hydrogen-oxygen fuel cell); however, fuel cells can be readily stacked in series or parallel, similar to electronics, to increase the voltage and current to meet an application’s requirements. Since the principles of fuel cells were discovered in 1839 (Figure 2), significant progress has been made, and many types of fuel cells have been designed. In the past quarter century, fuel cells have been seriously developed as possible power sources for applications ranging from buildings to

![Figure 2](image)

Evolution of low-temperature fuel cell technologies and hydroxide exchange membrane fuel cells. Abbreviations: HEMFC, hydroxide exchange membrane fuel cell; LAFC, liquid acid fuel cell; LBFC, liquid base fuel cell; PEMFC, proton exchange membrane fuel cell.
vehicles to portable electronics. In particular, hydrogen-fueled low-temperature (typically within 0–100°C) fuel cells are attractive, because hydrogen has high specific energy (34 kWh/kg, or 2.6 times that of gasoline at 13 kWh/kg), and the use of hydrogen may be free of carbon footprints if hydrogen is prepared from solar water splitting.

The nature of the electrolyte largely defines the materials selection for the other components and the operating conditions of a fuel cell; therefore, the electrolyte is usually used to categorize fuel cells. The evolution of low-temperature fuel cells has been very much driven by the development of the electrolytes (Figure 2). The principles of fuel cells were discovered in 1839 using a liquid acid solution as an electrolyte. These cells are referred to here as liquid acid fuel cells (LAFCs). The basic structure of an LAFC includes a liquid acid electrolyte, an anode, a cathode, and an external circuit (Figure 3). When hydrogen and oxygen are introduced and the electric load is applied, hydrogen molecules are oxidized on the anode electrochemically, giving electrons to the anode and protons to the electrolyte. At the same time, oxygen molecules are reduced on the cathode electrochemically, taking electrons from the cathode and protons from the electrolyte and combining them to produce water. Driven by the electrical potential difference between the two electrodes, electrons move from anode to cathode as electric current to do work through the external load. Driven by the concentration gradient established between the two electrodes, protons diffuse from the anode to the cathode to complete the electric circuit. Combining the reactions at the anode and cathode, a fuel cell transforms energy from chemical form to electrical form. Usually, electrocatalysts are used on both the anode and the cathode to facilitate the electrode reactions: The hydrogen oxidation reaction (HOR) electrocatalyst is used on the anode, and the oxygen reduction reaction (ORR) electrocatalyst is used on the cathode. The electrode reactions are as follows (based on pH = 0; SHE, standard hydrogen electrode):

Anode reaction (HOR): \(2\text{H}_2 \rightarrow 4\text{H}^+ + 4e^-\) \(E^* = 0\text{ V versus SHE}\)

and

Cathode reaction (ORR): \(\text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O}\) \(E^* = 1.23\text{ V versus SHE}\).
However, the use of a liquid acid solution as the electrolyte poses many challenges to the development of LAFCs. Strong acids are usually used for LAFCs to lower ionic resistance, but they are corrosive to most fuel cell materials (particularly metals, like electrocatalysts and containers), and their handling is also a safety concern. Besides, the liquid electrolytes tend to leak and make LAFCs bulky, which limits the power density of LAFCs.

In 1950, solid polymer electrolytes, i.e., PEMs (based on a sulfonated polystyrene polymer), were invented (2). Compared with liquid acids, solid PEMs conduct protons similarly, but they are much more convenient and safer to handle and use. PEMs are completely free of electrolyte leakage and are generally considered to be noncorrosive. PEMs were quickly adopted into fuel cells (i.e., PEM fuel cells, or PEMFCs), replacing the liquid acids in 1955 (Figure 2) (3). By switching electrolytes from liquid acids to solid polymers, PEMs offer great convenience for the use and engineering of PEMFCs. PEMFCs follow the same working principle as LAFCs (Figure 4), except for two major differences: (a) The protons are conducted through polymer PEMs instead of liquid acids, and (b) the electrolyte/electrode interfaces are dominated by polymer PEM electrolytes, not liquid acids. The real breakthrough for PEMFCs came after DuPont invented Nafion® PEM, based on a sulfonated, perfluorinated polymer, in 1962. Nafion polymer not only can be used as an excellent PEM but also can serve as a highly dispersed proton exchange ionomer (PEI) necessary to create an efficient triple phase boundary (TPB) in electrodes (4). TPB is the only place in the electrode where redox reactions occur because it allows a catalyst such as platinum (Pt) to have simultaneous access to the electron-conducting channel, proton-conducting channel, and fuel or oxidant channel. The dual function of the Nafion polymer, as well as its outstanding chemical, thermal, and mechanical stability, has enabled PEMFCs to have exceptionally high specific power (above 1 kW/kg) and good device durability (thousands of hours) (5). The success of PEMFCs has stimulated the research and commercialization interests in fuel cells in the past half century.

PEMs provide a proton-mediated environment for electrode reactions that intrinsically requires precious metals (typically Pt) as electrocatalysts for high-performance PEMFCs. The design and development of stable and active nonprecious metal–based electrocatalysts are very challenging.
for PEMFCs (6, 7), primarily owing to the fact that nonprecious metals are not thermodynamically stable in proton-mediated environments. Furthermore, nonprecious metal–based electrocatalysts generally have substantially lower catalytic activities for HOR and ORR in PEMFCs when compared with precious metals. The heavy dependence on precious metals as electrocatalysts has been largely responsible for PEMFCs’ prohibitively high materials costs, hindering their large-scale commercialization.

Nonprecious metals have much better stability and activity in alkaline media than in acidic ones, exemplified by the liquid base fuel cells (LBFCs) developed in the 1930s (Figure 2). Ni and Ag were successfully demonstrated as active but stable nonprecious HOR and ORR electrocatalysts, respectively, in KOH solutions (8). The idea of introducing HEMs, the counterpart of PEMs, to fuel cells can be traced back as early as PEMFCs. However, not much work was carried out until the concept of HEM fuel cells (HEMFCs) was brought back to the fuel cell research community in 2001 (Figure 2) (9, 10). The working principle of HEMFCs is shown in Figure 5, and electrode reactions are as follows (based on pH = 14; SHE, standard hydrogen electrode):

Anode reaction (HOR) : 2H₂ + 4OH⁻ → 4H₂O + 4e⁻  \( E^\circ = -0.83 \text{ V versus SHE} \)

and

Cathode reaction (ORR) : O₂ + 2H₂O + 4e⁻ → 4OH⁻  \( E^\circ = 0.40 \text{ V versus SHE} \).

**Key Features of Hydroxide Exchange Membrane Fuel Cells**

Similar to PEMFCs, HEMFCs use a solid polymer electrolyte and thus are also convenient and safe to handle. The single biggest advantage of HEMFCs over PEMFCs is their ability to work with nonprecious metal–based electrocatalysts, enabled by the hydroxide-conductive nature of HEMs. As representative HOR and ORR electrocatalysts, Ni and Ag metals are functional in HEMFCs (11, 12), similar to LBFCs. By contrast, those simple electrocatalysts cannot work with
PEMFCs to generate a meaningful current (13). In principle, other nonprecious metal–based electrocatalysts with similar or even lower materials costs are potentially feasible for HEMFCs. In addition to higher activities, nonprecious metal–based electrocatalysts are also more durable in HEMFCs than in PEMFCs.

Fuel crossover, the unwanted transport of fuel through polymer electrolytes from anode to cathode, leads to lower fuel cell efficiency owing to poor fuel use and, more significantly, undesirable mixed electrical potential on the cathode. In PEMFCs, the fuel crossover is aggravated because the protons move in the same direction as the fuel crossover. This makes it difficult for PEMFCs to use the thinner membranes desired for reducing PEM’s ionic resistance. The crossover is particularly significant for hydrogen because it has the smallest molecule size. By contrast, in HEMFCs, hydroxides move from cathode to anode, opposite to the fuel-crossover direction. The low fuel crossover allows for ultrathin HEMs (as thin as 10 μm, A901 commercial HEM from Tokuyama Co.) to be used without compromising the cathode potential. The ultralow thickness also helps overcome the intrinsically lower conductivity of hydroxides when compared with protons. Hydroxides have approximately half the ion mobility of protons [20.50 versus 36.25 \( \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \) in water at 25°C (14)]. For example, with one-third to one-half of the ion conductivity of PEMs, HEMs with one-half to one-fifth of the membrane thickness will have a membrane resistance comparable to that of PEMs. Low HEM membrane resistance (as low as 25 mΩcm²) makes high-performance HEMFCs possible, and power density as high as 730 mW/cm² was reported in an H₂/O₂ HEMFC at 80°C (15), close to the state-of-the-art performances of PEMFCs. The hydroxide environment of HEMFCs also favors the oxidation of more complex molecules, broadening fuels choices (16) to alcohols [e.g., methanol, ethylene glycol (17), ethanol (18), and glycerol (19)], hydrazine (20), ammonia (21), and even glucose (22).

CO₂ contamination has been a critical hurdle for LBFCs, especially for terrestrial applications (LBFCs have been successfully used for the NASA space program). CO₂ from ambient air or hydrocarbon complete oxidation can irreversibly react with the liquid bases, which lowers the electrolyte conductivity. More importantly, the CO₂ contamination brings a fatal threat to LBFCs’ porous electrodes via the formation of metal carbonate/bicarbonate crystals (23). Similar to LBFCs, CO₂ is also able to contaminate the HEM electrolytes and convert hydroxides to carbonates/bicarbonates, lowering the HEMs’ conductivity. However, unlike liquid base electrolytes, HEMs do not possess any freely mobile metal cations, eliminating the possibility of the formation of carbonate/bicarbonate crystals. Unlike that of LBFCs, CO₂ contamination has been confirmed to be reversible in HEMFCs: Bicarbonate/carbonate can be displaced from HEMs by HEMFC operations, replenishing hydroxides in the HEMs (24, 25). Owing to the outstanding advantages mentioned above, HEMFCs have been drawing increasing attention from academia, industry, and governments globally (10, 11, 26–33).

Key Components of HEMFCs

HEMs and HEIs. HEM is used between the electrodes, and its central function is to provide the medium for hydroxide transport between the electrodes to complete the cell’s electrical circuit. It also serves as an insulator to prevent electron conduction between two electrodes to avoid short circuit and as a separator between the fuel and the oxidant to avoid mixing. Hydroxide exchange ionomers (HEIs) are dispersed among the catalyst particles within the catalyst layer of the electrodes. They provide the hydroxide environment for the catalysts to mediate electrochemical reactions as well as the ion-conducting channels from the catalytic sites to the HEM.

HEMs are made by cation-functionalized polymers consisting of two main structural components: cationic functional groups that provide hydroxide conductivity and nonionic polymer
chains (main chains and/or side chains) that afford membrane robustness. The most common HEM cations are quaternary ammoniums, in which the nitrogen atoms bear one unit of positive charge and serve as the hydroxide-conducting centers. There are many polymers to choose from for the polymer main chains (27, 31, 34).

Anchoring cationic functional groups to polymer matrices is the main subject of HEM polymer synthesis. Typical synthetic recipes include direct polymerization of functional monomers, chemical functionalization of polymers, and radiation-grafting functionalization of membranes. Chemical crosslinking, physical crosslinking, and membrane reinforcement are often adopted to tune solvent resistance, dimensional stability, membrane hydration, and mechanical properties for HEMs.

The cationic functional groups are of particular importance and have profound impacts on properties of HEMs. Solubility; chemical, thermal, and mechanical stability; and the intrinsic efficiency of hydroxide conduction are all greatly controlled by HEM cations (35–37). Therefore, the design, synthesis, and characterization of cations have been some of the most important research focuses in the HEM research community. In addition to ammoniums, many new cations, such as phosphonium (35), sulfonium (38), guanidinium (39), imidazolium (40), and ruthenium (41), have been introduced and explored, bringing new features and great possibilities of designing versatile HEMs for various HEMFC applications.

HEIs are also an important component of HEMFCs. Similar to PEIs for PEMFCs, HEIs function to create efficient TPBs in electrodes necessary for high-performance HEMFC operations (35). The creation of a TPB depends on good dispersion and high hydroxide conductivity in the catalyst layer. Good solubility in low-boiling-point, water-miscible solvents is generally needed for HEI polymers to achieve excellent dispersion. High conductivity will allow for fast hydroxide transport, facilitating electrode reactions. For example, phosphonium cation-based HEI polymers (35, 42) have both desired selective solubility (in alcohols) and high hydroxide conductivity [up to 55 mS/cm at 20°C (42)], which makes them promising high-performance HEIs.

Nonprecious metal ORR and HOR electrocatalysts. ORR and HOR electrocatalysts are required to facilitate the two electrode reactions. Generally, the ORR kinetics is considered to be more facile in bases than in acids. The reason usually can be rationalized by less absorption of spectator ions (balancing anions of acids and balancing cations of bases) that physically block catalyst active sites, and/or more absorption of hydroxide that may thermodynamically favor the initiation of electron depletion from oxygen molecules (43, 44). This is particularly true for non-Pt metals. For example, Ag was shown to have 450 mV more positive ORR half-wave-potential in 0.1 M KOH than in 0.1 M HClO4 by the rotating disk method (45), which implies approximately six orders of magnitude–higher ORR exchange current density when based on 70 mV/dec of Tafel slope. Higher exchange current density means higher intrinsic catalytic activity, whereas lower Tafel slope indicates that larger activity increases with overpotential.

The complete reduction of one oxygen molecule involves the transfer of four electrons, leading to complex electrocatalytic reactions. A four-electron reaction pathway is much more preferred for ORR electrocatalysts than a two-electron reaction pathway, which produces hydrogen peroxide anions (HO2−) in alkaline media.

Owing to the inherently enhanced kinetics and improved stability, a wide range of ORR electrocatalysts have been studied for alkaline systems, among which nonprecious metal electrocatalysts are of particular interest. Typical nonprecious metal ORR electrocatalysts are based on materials including silver metal/alleys, manganese oxides, perovskite/spinel-type transition metal oxides, and macrocycle transition metal complexes (46–49). With relatively low cost and reasonably high activity, Ag has been considered an efficient ORR electrocatalyst for HEMFCs. Ag has
MEM: membrane electrode assembly

approximately 10% of the ORR-specific activity of Pt in alkaline solutions (12), but Ag has 100 times the elemental abundance of Pt in the earth’s crust (and roughly 1% of the cost of Pt). Nanostructure has a great impact on Ag’s ORR performance; for example, Ag nanowires with a certain diameter have been demonstrated to achieve higher ORR activity than simple Ag nanoparticles (50). Also, Ag was shown to be more stable than Pt during long-term operation in LBFCs (51). Other nonprecious metal–based electrocatalysts (52–55) also hold promise for HEMFC applications.

HOR electrocatalysts are also required to facilitate hydrogen oxidation. In general, HOR kinetics is widely considered much more facile than ORR kinetics in both acid and base. Ni-based nanoparticles have been introduced as nonprecious HOR electrocatalysts for HEMFCs (11, 12). Although a precious metal, Pd can be considered owing to its high HOR activity (compared with Ni) and moderate cost (compared with Pt). Together with controlled metal loadings, Pd is a potentially viable material for HOR electrocatalysts for HEMFC applications.

Key Challenges of HEMFCs

Development of highly durable HEMs/HEIs. Sufficient durability is required for HEMFCs for commercial applications. For example, a few thousand hours (5,000 h preferred) of durability are generally needed for transportation applications. However, there is a significant gap between the demonstrated and the required HEMFC durability: The state-of-the-art HEMFCs were shown to afford less than 500 h of durability with more than 1,000 μV/h of cell voltage degradation rate at 50°C cell temperature (56). Such a degradation rate of HEMFCs is at least one order of magnitude higher than that of PEMFCs. To deliver high cell performances and to reduce CO2 impact, cell temperatures higher than 50°C (e.g., 80°C) are necessary. Higher cell temperature will accelerate the degradation of HEMs and exacerbate the durability problem.

The state-of-the-art HEMs have durability in ex situ tests in pure water, for example, 2,000 h at 80°C (57) or 500 h at 90°C (58), suggesting a good potential to meet the durability target. The poor HEMFC durability observed may have been caused primarily by HEI degradation in electrodes, because HEIs work at the TPB, where they are much more stressed than the HEMs. However, the degradation mechanisms of HEIs in membrane electrode assemblies (MEAs) have not been revealed in situ yet. New in situ sensor/diagnostic techniques for MEA degradation may help uncover the HEI degradation mechanisms. Such understanding would be crucial to the design of next-generation HEIs with much higher stability. Both cationic functional groups and polymer chain structures are considered responsible for HEI degradations in MEAs; thus, both of them must be improved against both (HO2−) oxidative attacks and (OH−) nucleophilic attacks in electrodes. The authors consider this one of the most important research topics in developing high-performance HEM/HEI polymer electrolytes.

Development of highly active nonprecious metal HOR electrocatalysts. The HOR exchange current densities on many metal surfaces in base solutions are comparable to those in acid solutions (generally within one order of magnitude) (59, 60), but the HOR Tafel slopes appear much larger in base than in acid [e.g., four times on Pt polycrystalline surface: 120 mV/dec in 0.1 M KOH (61) versus ~30 mV/dec in 0.5 M H2SO4 (62, 63)]. The difference between acids and bases for HOR activity is likely to be related to hydrogen binding energy and hydroxide adsorption (60, 64, 65); however, the detailed mechanisms are still elusive.

Large Tafel slopes will inevitably require large overpotential for fuel cell operations, especially at high current densities. It is even more challenging to use nonprecious metal HOR electrocatalysts because they have much lower exchange current densities [e.g., two orders of magnitude smaller on Ni than on Pt: 10−5.5 (66) versus 10−3.5 A/cm² (63) for Ni versus Pt in 0.5 M NaOH].
One strategy to increase the HOR activity is to increase the exchange current density by tuning the metal–hydrogen binding energy, because the exchange current density on metal surfaces can be well correlated with their metal-hydrogen-binding energies (59, 67). Another possibility is to directly reduce the Tafel slope by tuning the hydroxide adsorption or completely changing the electrode reaction mechanisms. Development of nonprecious metal electrocatalysts has become another important research need for commercialization of HEMFCs.

The electrolyte/electrode interface of HEMFCs can behave very differently from LBFCs (12, 68). The characterization of interfacial structure and understanding of fundamental characteristics of the HEMFC electrode/electrolyte interface may help shed light on designing and developing highly active nonprecious metal HOR electrocatalysts.

**Fabrication of high-performance electrodes and MEAs.** Although HEMFCs share basic MEA structures with PEMFCs, there are clear differences between the two types of fuel cells. In particular, the roles of water and subsequently water management are fundamentally different. In PEMFCs, water is a simple product generated in cathodes. In HEMFCs, water serves as a reactant participating in the ORR in cathode and regenerated in the HOR in anode. The water management is considered much more complex for HEMFCs than for PEMFCs. Traditional highly hydrophobic electrode structures of PEMFCs may not be suitable for HEMFCs, as they cannot provide efficient water transport needed for HEMFC cathodes. For example, a current density as low as 50 mA/cm² was found to show apparent water transport impact on HEMFC cell voltage when traditional carbon papers designed for PEMFCs were used as electrode substrates for HEMFCs (69). There is a hurdle for HEMFC electrode design for efficient water transport for HEMFCs to compete with the state-of-the-art PEMFCs that have no appreciable water transport impact below the current density of 500 mA/cm². The hydrophobicity of the carbon backing papers must be carefully engineered and balanced for electrodes for HEMFCs to deliver high cell performances.

The fabrication method of high-performance MEAs is another challenge for HEMFCs. The traditional MEA fabrication method of PEMFCs is based on the hot-press method, because Nafion PEI polymer softens at approximately 135°C without losing its chemical integrity. The hot-press fabrication method helps to seamlessly glue the membrane and the two electrodes together, reducing overall MEA resistance and leading to very high MEA performance. Being soluble in some low-boiling-point and water-miscible solvents, many HEI polymers can easily create efficient electrodes, but none of the HEI polymers available today are suitable to a Nafion-like hot-press process. Therefore, great concerns exist for an efficient interface between the membrane and the two electrodes. Catalyst-coated-membrane technique may be helpful to improve the connection between membrane and electrodes, alleviating the need for a hot-press process. MEA engineering is urgently needed to solve these technological challenges for HEMFCs.

**SOLAR HYDROGEN GENERATORS**

**Photoelectrochemical Cells for Solar Hydrogen Production via Water Splitting**

The efficient conversion of photons in sunlight to energy stored in chemical bonds (e.g., the H-H bond in hydrogen) via photoelectrochemical water splitting is one of the most sought-after goals, owing to the clean and inexhaustible nature of solar energy. A tremendous amount of progress has been made in the field of solar-to-electricity conversion (i.e., photovoltaics) in the past quarter century (70–73). However, the intrinsic intermittency of solar energy on a daily cycle poses a serious challenge to the electric grid as the portion of electricity produced from...
Figure 6
Schematic diagram of typical single-semiconductor photoelectrochemical (PEC) cells and the mechanism for PEC water splitting. Abbreviations: CBM, conduction band minimum; E/V, potential in unit of V; SHE, standard hydrogen electrode; VBM, valence band maximum.

Solar panels becomes more substantial (74, 75). It is therefore particularly appealing that solar-to-chemical conversion via photoelectrochemical (PEC) cells not only harvests photons from sunlight but also stores the energy in chemicals for later use (76). Conceptually, the success of a PEC cell for water splitting depends critically on the following three processes: (a) light harvesting by semiconductors to generate electron-hole pairs, (b) electrocatalytic splitting of water to stoichiometric amounts of hydrogen and oxygen, and (c) transport of reactants to electrocatalysts and separation of products. Not only is it imperative that highly efficient individual processes be developed, but more importantly, these processes must be able to be seamlessly integrated and reach peak performance under identical operating conditions in a device.

Integration of Semiconductors and Electro catalysts

The recognition of the importance of integrating light harvesting and electrocatalytic water splitting processes has led to many high-performance composite photocatalysts. Figure 6 outlines the main components in a typical single-semiconductor PEC cell, along with the mechanism of photoelectrochemical water splitting. A prerequisite for any working PEC cell is that the conduction band minimum (CBM) and valence band maximum (VBM) straddle the electrochemical potentials of the hydrogen (0 V versus SHE, pH = 0) and oxygen (1.23 V versus SHE, pH = 0) evolution reaction. This condition can be satisfied by either a single semiconductor (Figure 6) or multiple semiconductors in tandem (Figures 7 and 8). Electron-hole pairs are created in the semiconductor upon excitation by photons with energy greater than the band gap. The large overpotential of hydrogen and oxygen evolution reactions (HERs and OERs, respectively) on uncatalyzed semiconductor surfaces generally results in poor overall solar-to-hydrogen efficiency, which necessitates the presence of electrocatalysts on semiconductors (77). Clearly, the synergy between the semiconductor and electrocatalysts can be achieved only when both are stable and active under the operating conditions. In addition, the interface between semiconductor and electrocatalysts also plays an important role, because electrons and holes must reach the surface of electrocatalysts.
before they can participate in the water splitting reactions. Domen and others (78–83) have made significant progress in developing semiconductors with precise control of the width of the band gap and positions of the band edges and cocatalysts for photoelectrochemical water splitting (e.g., metal nitrides and oxynitrides). Although the electrocatalysts for HERs and OERs are depicted as separate particles, in reality, they can be the same type of material, as in the case of one-step water splitting cells (Figure 6), or two different materials, as in two-step water splitting cells (Figures 7 and 8). One important limitation of the type of PEC cells shown in Figure 6 is that hydrogen and oxygen productions are not spatially separated, which clearly poses a safety challenge. Furthermore, the separation of hydrogen from the hydrogen/oxygen mixture is also an energetically costly process, which would lower the overall efficiency of the solar-to-chemical conversion. In this case, the transport of reactants (i.e., water and proton) is typically accomplished via liquid electrolyte.

PEC Cells with Built-In Product Separation

An improved PEC cell design has HERs and OERs occurring on the surfaces of a spatially separated cathode and anode (Figure 7). A PEM is employed to physically separate the anode and cathode and thus prevent the mixing of hydrogen and oxygen upon formation. Because water is present on both electrodes (PEMs must be moisturized at all times to operate), it is advantageous to engineer the CBM of the semiconductor (typically p-type) of the cathode side to be lower in electrochemical potential than that of HERs, while keeping the VBM lower than the electrochemical potential of OERs. The converse is true on the anode side. Upon illumination, electron-hole pairs are formed in semiconductors on both sides. The excited electrons in the conduction band of the n-type semiconductor on the anode move toward the ohmic contact to neutralize the holes of the p-type semiconductor of the cathode. The excited holes on the anode and electrons on the cathode are responsible for OER and HER, respectively. Therefore, hydrogen and oxygen are separated from the moment of formation in this cell configuration. An added benefit of the PEM
(~50 μm in thickness) is the reduced volume needed for proton conduction as compared with a liquid electrolyte. Lewis et al. (84, 85) pioneered PEM-based PEC cells for solar hydrogen. A vast amount of literature has been dedicated to the engineering of the position and width of band gap of both photoanodes and photocathodes (77). Moreover, the design and structure-reactivity relation of electrocatalysts to facilitate the HER and OER have also been areas of intense research.

The type of solid electrolyte employed in a PEC cell largely determines its operating environment (e.g., PEM for acidic and HEM for alkaline conditions, respectively). The stability and performance of photocatalysts depend sensitively on the pH of the operating environment (86). For example, most nonprecious metal electrocatalysts (e.g., Ni, Co, Ag) are not stable in strongly acidic media, which makes noble metals (e.g., Pt, Ru, Ir, Re) irreplaceable components of the electrocatalysts in PEM-based PEC cells. For solar hydrogen to make up a meaningful portion in the overall world energy mix, the cost of hydrogen produced via PEC cells must be competitive with hydrogen from other sources (e.g., steam cracking of hydrocarbons from fossil fuels). Therefore, precious metals in the PEC cells must be replaced by more affordable materials. Two approaches have been explored to reach this goal: (a) development of nonprecious metal electrocatalysts that are stable and active under acidic conditions and (b) switching to an HEM-based PEC cell design, because many existing nonprecious metal electrocatalysts (e.g., Ag, Ni) are stable and active under alkaline conditions (Y. Yan, lecture notes for ChE155, Caltech, 2010). We focus our discussion on the second approach in the rest of this section.

**HEM-Based PEC Cells and Perspective**

The general configuration of HEM-based PEC cells is similar to that of PEM-based cells (Figure 8), albeit with several key differences: (a) The operating environment of the HEM-based PEC cells is alkaline, and the ion that completes the electrical circuit is OH\(^-\), in contrast to H\(^+\). The potential of the water oxidation half-reaction at the oxygen-evolving electrode is 0.40 V versus SHE, and for the water reduction half-reaction at the hydrogen-evolving electrode is 0.83 V versus SHE.

---

**Figure 8**

Schematic diagram of a photoelectrochemical cell with a hydroxide exchange membrane (HEM) separating oxygen and hydrogen produced at anode and cathode, respectively. Abbreviations: E/V, potential in unit of V; SHE, standard hydrogen electrode.
the acidic environment of PEM-based PEC cells with a proton as the charge-carrying ion, and (b) under alkaline conditions, the photoanode and photocathode reactions are as follows.

\[
\text{Photoanode reaction : } 4\text{OH}^- \rightarrow 2\text{H}_2\text{O} + \text{O}_2 + 4e^- \quad E^\circ = 0.40 \text{ V versus SHE}
\]

and

\[
\text{Photocathode reaction : } 4\text{H}_2\text{O} + 4e^- \rightarrow 2\text{H}_2 + 4\text{OH}^- \quad E^\circ = -0.83 \text{ V versus SHE}.
\]

Therefore, the positions of the VBM and CBM of the semiconductors in the photoanode and photocathode of HEM-based cells must be engineered to different electrochemical potentials than those in PEM-based cells, to ensure hydrogen and oxygen are formed only on the cathode and anode, respectively. The main advantage of the HEM-based architecture is that it affords the possibility of the exclusive use of nonprecious metal electrocatalysts to achieve similar or even higher efficiency of the HER and OER, as compared with the performance of PEM-based PEC cells loaded with precious metal electrocatalysts. Our recent work has demonstrated that the combination of Ag electrocatalyst and phosphonium-based HEM shows slightly higher activity than a Pt-based catalyst under identical conditions for ORR (12), which is the reverse reaction for the anode reaction in the PEC cells. According to the principle of microscopic reversibility, Ag is likely to be an active catalyst for OER on the anode of PEC cells. Preliminary experiments have also shown several nonprecious metals that are stable and active for HER and OER under alkaline conditions.

We believe the time for developing HEM-based PEC cells has matured on both societal and technological fronts. Increasing public awareness about the undesirable impacts of our heavy reliance on fossil fuels on the environment and climatic patterns drives the search for clean and sustainable sources of energy. Furthermore, recent technological advancements have put the development of most of the key components for HEM-based PEC cells in the foreseeable future within reach, for example, the enhanced ion conductivity and stability of HEM and the active, stable, and affordable electrocatalysts for HOR and ORR under alkaline conditions. According to the principle of microscopic reversibility, Ag is likely to be an active catalyst for OER on the anode of PEC cells. Preliminary experiments have also shown several nonprecious metals that are stable and active for HER and OER under alkaline conditions.

FLOW BATTERIES

Flow batteries are rechargeable batteries that can reversibly convert electrical energy to chemical energy. The key difference between a flow battery and the traditional rechargeable battery is that the traditional rechargeable batteries store electricity internally in their redox pairs (negative and positive redox pairs) fixed on the two electrodes (negative and positive electrodes), whereas flow batteries store their energy externally in two flowing electrolytes (negative and positive electrolytes) enabled by a selective ion-exchange membrane (IEM) that on one hand isolates the electroactive redox ions and on the other conducts the balancing ions between two electrolytes. The energy storage and power delivery functions are fundamentally decoupled in flow batteries, leading to great design flexibility and system scalability. The transfer of the energy storage function into the electrical domain and vice versa is achieved by convective transport of the electrolytes across the IEM. Through this mechanism, flow batteries can achieve high energy density and power density, as well as high cycle life compared to traditional rechargeable batteries.
Comparison of proton exchange membrane (PEM)- and hydroxide exchange membrane (HEM)-based photoelectrochemical (PEC) cells.

from the internal electrodes to the external electrolytes simplifies the electrode structure and increases electrode durability. The intrinsically higher durability and greater scalability have made flow batteries particularly attractive for renewable wind/solar electricity storage applications (87). Since the principles of flow batteries were discovered in 1974 (88), significant progress has been made, and many types of flow batteries have been designed (89–92).

Flow batteries can be categorized by the electroactive elements in the redox pairs and by the number of membranes in the single cell. The significant technology milestones for flow batteries as germane to the discussion here are presented in Figure 10. The first flow battery is the two-element Cr-Fe flow battery, which uses chromium (Cr$^{3+}$/Cr$^{2+}$) as the negative pair and iron (Fe$^{3+}$/Fe$^{2+}$) as the positive pair and has a single (anion) ion-exchange membrane (AEM, a more general form of HEM). The cell consists of a liquid negative electrolyte, a negative electrode, an anion-exchange membrane (AEM), a positive electrode, and a positive electrolyte. The working principles for the two-element and single-membrane Cr-Fe flow batteries (Cr-Fe SMFBs) are shown in Figure 11. When the flow battery is being charged, Cr$^{3+}$ cations take electrons from the negative electrode and are reduced to Cr$^{2+}$ cations (cathodic reaction); Fe$^{2+}$ cations are oxidized to Fe$^{3+}$ cations and give electrons to the positive electrode (anodic reaction); the Cl$^{-}$-balancing anions move across the AEM from the negative electrolyte to the positive electrolyte; and the electrons move through the external circuit from the positive electrode to the negative electrode against the cell voltage (1.18 V standard voltage by combining $-0.41$ V of Cr$^{3+}$/Cr$^{2+}$ with $0.77$ V of Fe$^{3+}$/Fe$^{2+}$, versus SHE). The charging process converts the electrical energy to chemical energy in the redox
When the flow battery is being discharged, the reverse processes apply. More specifically, the electrons, following the cell voltage between two electrodes, move from the negative electrode back to the positive electrode, converting the chemical energy stored in the two redox pairs back to electricity. The electrode reactions of the Cr-Fe SMFB are as follows.

**Figure 10**
Evolution of flow batteries. Abbreviations: AEM, anion-exchange membrane; CEM, cation-exchange membrane.

**Figure 11**
Working principle of chromium-iron single-membrane flow batteries. Abbreviations: AEM, anion-exchange membrane; NER, negative electrode reaction; PER, positive electrode reaction.
Negative electrode reactions (charge: forward, cathodic; discharge: backward, anodic):
\[ \text{Cr}^{3+} + e^- \leftrightarrow \text{Cr}^{2+} \quad E^* = -0.41 \text{ V versus SHE} \]

and

Positive electrode reactions (charge: forward, anodic; discharge: backward, cathodic):
\[ \text{Fe}^{2+} + e^- \leftrightarrow \text{Fe}^{3+} \quad E^* = 0.77 \text{ V versus SHE} \]

Analogously, two anionic redox pairs can be separated by a cation-exchange membrane (CEM, a more general form of PEM) sharing the same cell structure. The examples conceptually include sulfur-bromide single-CEM flow battery (\(S_i^{2-}/S_j^{2-} \text{ versus } Br^{3-}/Br^-\)) (93) and zinc-iron single-CEM flow battery [\(\text{Zn(OH)}_2^{2-}/\text{Zn versus Fe(CN)}_6^{3-}/\text{Fe(CN)}_6^{4-}\)] (94). The flow batteries with a single membrane separating two electroactive elements have been the focus of the majority of the flow battery research, especially at the early stages; their successful demonstration has clearly validated the advantages and unique features of flow batteries over traditional rechargeable batteries.

However, the use of two different electroactive elements in a single-IEM flow battery often brings a significant durability concern. Currently available IEMs are not perfectly selective, and they all allow slow crossover of the electroactive redox ions. The redox ion crossover leads to a permanent coulombic efficiency loss for every cycle of operation, and more importantly, it also causes electrolyte contamination, leading to a mixed electrical potential on the opposite electrode and lowered voltage efficiency. Over time, the overall energy efficiency can be severely compromised. Frequent refreshing of both electrolytes can deal with the redox ion crossover, but the separation and regeneration of electrolytes are costly.

As early as 1981, a single-element flow battery was introduced (all-iron, \(\text{Fe}^{2+}/\text{Fe} \text{ versus } \text{Fe}^{3+}/\text{Fe}^{2+}\)) (95). The all-iron system involves a nonflowing solid phase (Fe), which is considered undesirable. In 1986, an all-vanadium flow battery system was successfully demonstrated (\(V^{3+}/V^{2+} \text{ versus } \text{VO}_2^{2+}/\text{VO}_2^{2+}\)) (96). All four vanadium redox species are soluble in the acid electrolytes. The use of a single electroactive element does not eliminate the redox ion crossover, but this crossover now reduces only the coulombic efficiency, not the voltage efficiency caused by the mixed electrical potentials. Without the interference of a different electroactive element, the single-element flow batteries have shown fast electrode kinetics and offer fast response to a changing load. Free from the redox pair contamination and with all soluble redox species, the all-vanadium flow batteries have become the most successful example of the single-element and SMFBs and have demonstrated excellent lifetime for electricity storage applications. The working principles of all-vanadium flow batteries are shown in Figure 12 and resemble those of the first-generation flow batteries. With sulfuric acid as the supporting electrolyte, HSO\(_4\)^- ions serve as balancing anions when an AEM is used, or H\(^+\) ions serve as balancing cations when a CEM is used. The benefit of transporting H\(^+\) is its lower resistance and thus higher voltage efficiency. In both cases, the electrode reactions of all-vanadium SMFBs are as follows.

Negative electrode reactions (charge: forward, cathodic; discharge: backward, anodic):
\[ V^{3+} + e^- \leftrightarrow V^{2+} \quad E^* = -0.26 \text{ V versus SHE} \]

and positive electrode reactions (charge: forward, anodic; discharge: backward, cathodic):
\[ \text{VO}_2^{2+} \leftrightarrow \text{VO}_2^{3+} + e^- \quad E^* = 0.99 \text{ V versus SHE}. \]

Other single-element-based SMFBs, such as all-neptunium (\(Np^{4+}/Np^{3+} \text{ versus } NpO_2^{2+}/NpO_2^{+}\)) (97) and all-lead (\(Pb^{2+}/Pb \text{ versus } PbO_2/Pb^{2+}\)) (98), have also been demonstrated.
However, the use of a single element in flow batteries limits their cell voltage; for example, the standard cell voltage is mostly approximately 1.0–1.5 V (0.99 V of all-neptunium, 1.22 V of all-iron, 1.25 V of all-vanadium, and 1.59 V of all-lead flow batteries). The lower cell voltage is largely responsible for their lower specific energy (e.g., 10–20 Wh/kg for all-vanadium flow batteries) when compared with traditional aqueous rechargeable batteries (e.g., 30–40 Wh/kg for traditional lead-acid batteries, 2.05 V of standard voltage). All-vanadium flow batteries also have a relatively high cost, making it a challenge to meet the low cost requirement for the renewable electricity storage applications.

By introducing one more IEM to a SMFB, our research group introduced a double-membrane flow battery (DMFB) cell configuration in 2011 (99–101). Composed of one CEM, one AEM, and an electrolyte in between, the double-membrane cell configuration is able to combine anionic redox pairs (generally having very negative redox potential) and cationic redox pairs (generally having very positive redox potential) in one flow battery cell, offering ultrahigh cell voltage. It also benefits from ultralow redox ion crossover.

**Key Features of DMFBs**

Ultras high cell voltages are possible for DMFBs, which promise to offer high power density and high specific energy. By combining an anionic redox pair of Zn(OH)$_4^{2-}$/Zn ($\sim$1.22 V versus SHE) in base with a cationic redox pair of Ce$^{4+}$/Ce$^{3+}$ (1.74 V versus SHE) in acid, Zn-Ce DMFBs offer standard cell voltage as high as 2.96 V. The working principles of Zn-Ce DMFB are shown in Figure 13. When the Zn-Ce DMFB is being charged, Zn(OH)$_4^{2-}$ anions in the negative electrolyte take electrons from the negative electrode and thus are reduced to Zn metal (cathodic reaction), Ce$^{3+}$ cations in the positive electrolyte give electrons to the positive electrode and thus are oxidized to Ce$^{4+}$ cations, Na$^+$ balancing cations move across the CEM from the middle electrolyte to the negative electrolyte, and ClO$_4^-$ balancing anions move across the AEM from Load/power source
Working principle of zinc-cerium double-membrane flow batteries. Abbreviations: AEM, anion-exchange membrane; CEM, cation-exchange membrane; NER, negative electrode reaction; PER, positive electrode reaction.

The electrode reactions of Zn-Ce DMFBs are as follows.

Negative electrode reactions (charge: forward, cathodic; discharge: backward, anodic):
\[
\text{Zn(OH)}_4^{2-} + 2e^- \leftrightarrow \text{Zn} + 4\text{OH}^- \quad E^\circ = -1.22 \text{ V versus SHE}
\]

and positive electrode reactions (charge: forward, anodic; discharge: backward, cathodic):
\[
2\text{Ce}^{3+} \leftrightarrow 2\text{Ce}^{4+} + 2e^- \quad E^\circ = 1.74 \text{ V versus SHE}.
\]

With much higher cell voltage, the Zn-Ce DMFBs have the potential to more than double the specific energy of an all-vanadium SMFB, assuming similar solubility for the redox ions. It is worth noting that the high cell voltage of the Zn-Ce DMFB is not compromised by water (solvent), as the voltage window of water electrolysis is greatly extended. For a SMFB, reversible voltage is limited to 1.23 V (e.g., 0 V versus SHE for HER and 1.23 V versus SHE for OER at pH = 0, or −0.83 V versus SHE for HER and 0.40 V versus SHE for OER at pH = 14), because the same pH is generally maintained in both negative and positive electrolytes. By contrast, a DMFB can have a much larger reversible voltage window of 2.06 V (i.e., −0.83 V versus SHE for HER at pH = 14 and 1.23 V versus SHE for OER at pH = 0), owing to the ability to combine a strong–base negative electrolyte and strong–acid positive electrolyte simultaneously.

Compared with the SMFBs, DMFBs are expected to have much lower redox ion crossover rate. For example, DMFBs can have 15–142 times slower overall redox ion crossover rate than SMFBs, based on 99% ion selectivity and 1–100 ppm of an ion contamination threshold. The lower overall redox ion crossover rate is expected to translate into much longer cell lifetime than the traditional different-element-based SMFBs.

Besides providing electrolyte continuity and serving as an ion crossover buffer, the middle electrolyte provides another significant benefit for flow batteries based on an anion/anion redox.
pair versus a cation/cation pair: cleaning of crossed-over ion-contaminated electrolytes in negative and positive electrolytes. Low-level crossed-over ions (e.g., 100 ppm) can be removed from the contaminated electrolytes by refreshing the middle electrolytes, because the crossed-over ions will rapidly diffuse back to the fresh middle electrolytes under the established ion concentration difference. Such a cleaning function helps drastically extend the cell lifetime. In addition, the middle electrolyte could manage the possible water solvent-transfer issues among electrolytes by tuning its salt concentration (a wide range of salt concentration in the middle electrolyte is allowed depending on the state-of-charge swing) and its volume ratio to the negative electrolyte or positive electrolyte.

The double-membrane configuration is not limited to the Zn-Ce flow battery, and many other redox pair combinations are possible. For example, an ultralow-cost sulfur-iron flow battery combines the two highly available elements of iron and sulfur (first- and fifth-most-produced elements worldwide, respectively). Combining a $S_2^{2-}/S_4^{2-}$ anion redox pair (-0.45 V versus SHE) and $Fe^{3+}/Fe^{2+}$ cation redox pair (+0.77 V versus SHE), the sulfur-iron DMFB has the standard cell voltage of 1.22 V (almost the same as the all-vanadium flow battery, 1.25 V). The high availability of electroactive elements endows the S-Fe flow battery with ultralow electrolyte cost.

Key Challenges of DMFBs

**Durable electrodes and IEMs.** With very high redox potential (1.74 V versus SHE of $Ce^{4+}/Ce^{3+}$), the $Ce^{4+}$ ion is a strong oxidizing agent, and the electrode potential is even higher when the flow battery is being charged. Such a high electrode potential poses a significant challenge for electrode materials (catalysts and substrates). Although carbon-based electrodes have been shown to have good activity for $Ce^{4+}/Ce^{3+}$ redox reaction, the long-term durability is still a serious concern, because carbon corrosion has very low potentials in acid (CO$_2$/C, 0.21 V versus SHE and CO/C, 0.52 V versus SHE). Pt is stable and also active as an electrode material for the $Ce$ redox pair, but it is prohibitively expensive. Stable, active, and inexpensive electrode materials are critically needed. Graphitic carbon materials, such as carbon nanotubes and graphenes, may be suitable choices.

AEMs naturally repel cations, such as $Ce^{4+}$ cations, from passing and crossing; however, AEMs are inevitably in contact with the highly concentrated $Ce^{4+}$ environment, which also brings stability concerns for AEMs against possible $Ce^{4+}$ oxidization attack. Currently available flow-battery AEMs are not specifically designed to work with such an oxidizing redox system (102, 103); therefore, novel AEMs with sufficient antioxidation ability are needed.

**Low-resistance cell design.** Compared with SMFBs, DMFBs have one more IEM and one more electrolyte, leading to increased cell resistance. High cell resistance will cause low voltage efficiency at high current density. This is particularly serious for sulfur-iron DMFBs that have relatively low reversible cell voltage and, thus, lower tolerance for voltage loss. Advanced cell design is needed to effectively lower the overall cell resistance to maintain high voltage efficiency. Ultrathin chamber design, such as a membrane electrode assembly configuration, will help reduce the electrolyte resistance, and highly conductive and thin IEMs are also helpful to reduce membrane resistance. Flow channels should be optimized to facilitate mass transport, particularly in the middle electrolyte, lowering the mass-transport resistance.

**CONCLUDING REMARKS**

Electrochemical energy conversion will be a leading path forward to a safe, clean, and sustainable energy system in which the combustion of fossil fuels no longer dominates. FCs, ELs, SHs, and
FBs are the foundation of such an electrochemical energy system, and this review discusses their fundamental operating principles, technology development challenges, and materials research opportunities. In particular, we call attention to the fact that the simple switch from an acid to a base polymer electrolyte, coupled with innovative cell design, could be a paradigm shift that leads to a new generation of affordable electrochemical energy devices and their eventual commercial implementation. Consistent with this recognition, much effort has been invested in the area of AEMs and HEMs and their related devices, and many challenging problems have been solved in the past five years. However, much work remains to be done before these devices can attain widespread commercial deployment. To strengthen this research and to supply better-trained researchers, the formal introduction of electrochemical energy engineering as a subdiscipline of chemical engineering will be of tremendous value. The incorporation of electrochemistry into the undergraduate and graduate curricula of chemical engineering programs is also a necessary and much-needed step.

DISCLOSURE STATEMENT

Y.S.Y. is a cofounder of OH-Energy Inc., which develops hydroxide exchange membrane fuel cells. S.G. and B.J.X. are not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

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LITERATURE CITED


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