



## Fuel Cells and Hydrogen Production: Introduction

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### Article Outline

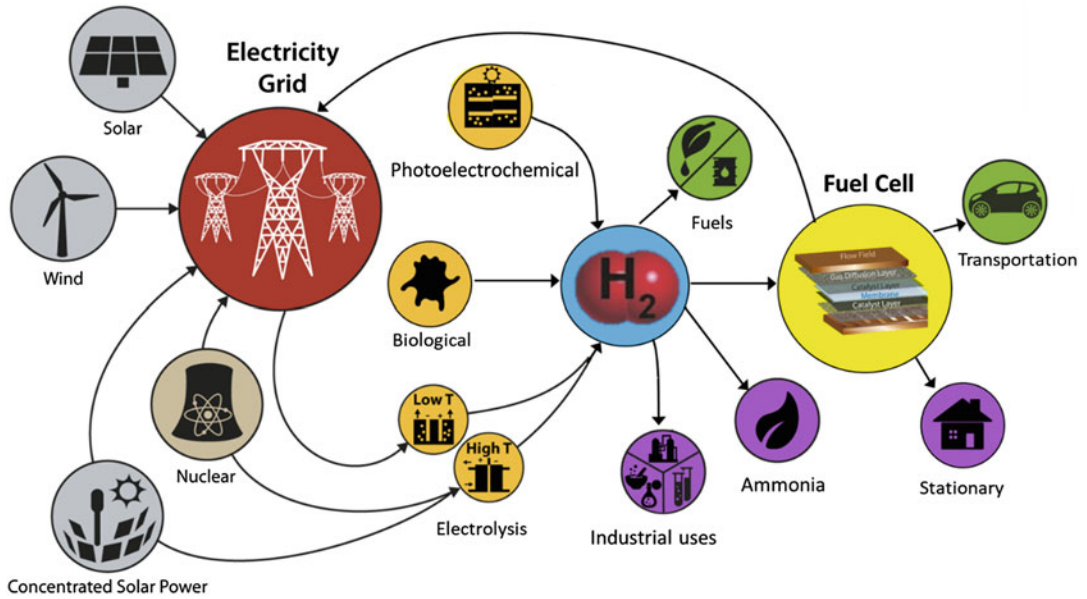
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Hydrogen is a widely produced and used commodity, now being used as an energy carrier for stationary power and transportation markets. Tens of millions of tons of hydrogen are produced each year globally, mostly for large-scale industrial uses. As awareness grows for the need to reduce greenhouse gases and enable new energy paradigms, hydrogen is being seen as playing a critical role as shown in Fig. 1 [1]. Hydrogen provides chemical storage of electrical energy and can be efficiently converted to electricity on demand for distributed applications, thus enabling the global electrification trends. The H2@SCALE initiative in the United States, the commercialization of hydrogen technologies in Japan, and the focus on power-to-gas and hydrogen utilization in Europe all point toward a renaissance for hydrogen generation and utilization based on its ability to improve efficiency and reduce emissions across many sectors.

Major uses of commercial hydrogen are for oil refining, where hydrogen is used for “upgrading” of crude oil as part of the refining process to improve the hydrogen-to-carbon ratio of the fuel, food production (“hydrogenation”), treating metals and semiconductor manufacturing, and

producing ammonia for fertilizer and other industrial uses. There are many means of hydrogen production, from established ones such as steam methane reforming, where half of the produced hydrogen comes from natural gas or biogas and half comes from steam used in the reaction, and grid-powered electrolysis that uses electricity to split water molecules in hydrogen and oxygen. Various other hydrogen production methods are becoming commercially viable and still others are emerging or being tested in laboratories. Emerging options include various pathways using biogas or other bio-feedstocks such as wood waste using gasification or pyrolysis processes, along with newly developed electrochemical, photo-electrochemical, and thermochemical processes. These include using microbial electrolysis cells as well as tailored molecules and integrated assemblies that can facilitate the splitting of water molecules into hydrogen and oxygen with lower energy requirements than conventional electrolysis. Other concepts include hydrogen production from bio-algae systems, thermo-chemical water splitting processes, and through high-temperature nuclear-power system combined processes. Concomitant with hydrogen production is its efficient utilization via fuel cells, as well as additional concepts such as power-to-gas (where hydrogen is produced from excess renewable electricity and injected into natural gas pipelines) and methanization processes to produce bio-methane.

Fuel cells are devices that electrochemically convert the chemical “free energy” of gaseous or liquid reactants into electrical energy. The basic concepts of fuel cell chemistry have been known for nearly 200 years where they were conceptually identified first in the late 1830s. Christian Friedrich Schönbein recognized and described the appearance of “inverse electrolysis” [2], shortly before Sir William Grove, the inventor of the platinum/zinc battery, constructed his first “gas voltaic battery” that is recognized as



**Fuel Cells and Hydrogen Production: Introduction, Fig. 1** Schematic illustration of hydrogen production and utilization. (Figure adapted from H2@SCALE vision courtesy of Bryan Pivovar) [1]

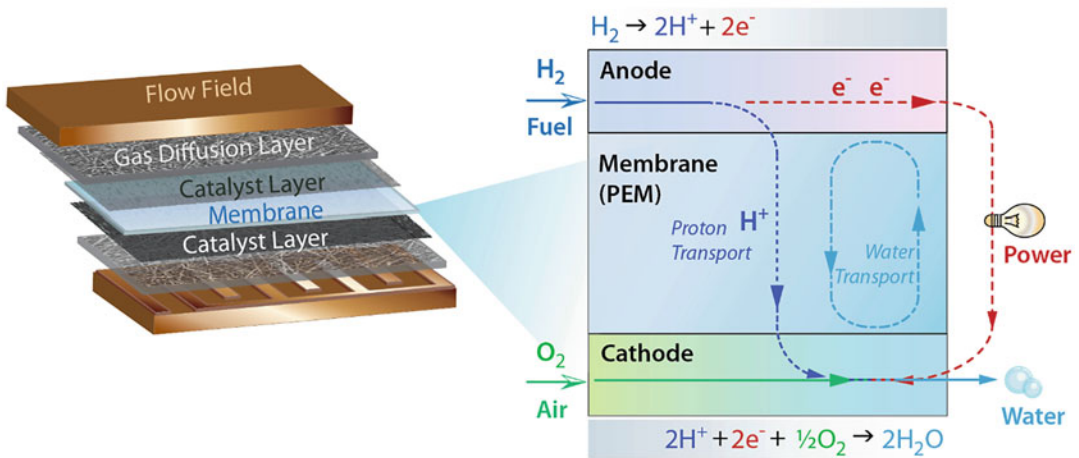
the first example of an early fuel cell device [3]. Grove had previously used platinum electrodes and a dilute sulfuric acid as a proton-conducting electrolyte. It is interesting to note that modern low-temperature polymer-electrolyte fuel cells still make use of related materials (carbon-supported platinum and perfluoro-sulfonic-acid (PFSA)-ionomer membranes).

The basic concept for high-temperature fuel cells dates back to the 1930s, about 100 years after the existence of the lower temperature concepts. In an attempt to prove the concept of “Brennstoff-Ketten mit Festleitern” (fuel chains with solid conductors), Emil Baur and Hans Preis tested different solid electrolytes [4], and they came to the conclusion that the “Nernst-Masse” is “unübertroffen” (unrivaled). At that time “Nernst-Masse” had the composition 85%  $\text{ZrO}_2$  and 15%  $\text{Y}_2\text{O}_3$ , and this is still close to what is used in current SOFCs (solid oxide fuel cell) as electrolyte material. Moreover, even in these initial experiments they tested “masses” containing Ceria ( $\text{CeO}_2$ ), and this is still discussed as a base for alternative SOFC electrolyte materials.

As in a battery or electrolysis cell, the reactants/products are prevented from chemically reacting by separating them with an electrolyte, which is in contact with electro-catalytically active porous electrode structures (Fig. 2). Apart from effectively separating the anode and cathode gases and/or liquids (i.e., fuel and air), the electrolyte mediates the electrochemical reactions taking place at the electrodes by conducting a specific ion at very high rates during operation. In the simplest case of a fuel cell, operating with hydrogen (fuel) and oxygen (air) as reacting gases, a proton or hydroxide or oxide ionic current is driven through the electrolyte and converted to electronic current at the electrodes, which can then be used to perform work (see Fig. 2). Running a similar device in the opposite direction (i.e., electrolysis) can be used to generate hydrogen. When run in both electrolysis and fuel-cell mode, a unitized energy-storage-system can be realized.

During the operation of polymer-electrolyte fuel cells, many interrelated and complex phenomena occur. These processes include mass and heat transfer, electrochemical reactions, and ionic

### Polymer-Electrolyte Membrane (PEM) Fuel Cell



**Fuel Cells and Hydrogen Production: Introduction, Fig. 2** Schematic illustration of electrochemical energy-conversion fuel-cell architecture. (Schematic designed and provided by Ahmet Kusoglu)

and electronic transport. Most of these processes occur in the through-plane direction as shown in Fig. 2. This sandwich comprises multiple layers including diffusion media that can be composite structures containing a macroporous gas-diffusion layer and microporous layer, catalyst layers, flow fields or bipolar plates, and a membrane. During operation fuel is fed into the anode flow field, moves through the diffusion medium, and reacts electrochemically at the anode catalyst layer to form hydrogen ions and electrons. The oxidant, usually oxygen in air, is fed into the cathode flow field, moves through the diffusion medium, and is electrochemically reduced at the cathode catalyst layer by combination with the generated protons and electrons. The water, either liquid or vapor, produced by the reduction of oxygen at the cathode exits the cell through either the cathode or anode flow field.

The electrons generated at the anode pass through an external circuit and may be used to perform work before they are consumed at the cathode. An electrolysis cell is essentially the same but where electrons are supplied and the reverse reactions occur within the catalyst layers. Because of the applied voltage for this process, materials are often different in terms of catalysts and backing layers in the oxygen electrode.

A fuel cell converts the intrinsic chemical energy of a fuel into electrical and heat energies, whereas an electrolyzer takes electrical energy and converts that into chemical energy. Thus, both are energy-conversion and not storage devices (i.e., a fuel cell by itself is not a battery). From the first law of thermodynamics,

$$\Delta H = Q - W_s \tag{1}$$

one sees that the net release of energy is in the form of heat ( $Q$ ) or work ( $W_s$ ). The work performed by the system is simply the power as expressed by the cell current multiplied by its operation voltage:

$$P = IV \tag{2}$$

The net energy due to the electrochemical reaction is the difference between the heat of formation of the products and reactants,  $\Delta H$ , which can be converted to an electrochemical potential, resulting in the enthalpy potential,

$$U_H = \frac{\Delta H}{z_i F} \tag{3}$$

where  $z_i$  is the charge number of species  $i$  and  $F$  is Faraday's law. Using the above power equation, the expression for the heat released becomes

$$Q = i(U_H - V) \quad (4)$$

Thus, if the cell potential equals the enthalpy potential, there is no net heat loss, which is why the enthalpy potential is often termed the thermo-neutral potential. However, the enthalpy energy is not fully accessible as it is composed of both reversible or entropic ( $Q_{\text{rev}} = T\Delta S$ ) as well as irreversible components. The maximum energy that is convertible to electrical energy is related to the free energy of the fuel,

$$\Delta G = \Delta H - T\Delta S \quad (5)$$

The potential corresponding to the Gibbs free energy is defined as the equilibrium potential,

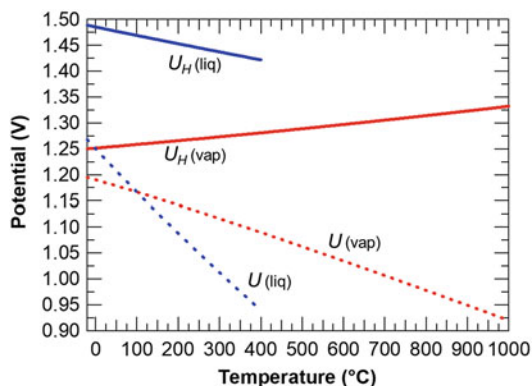
$$U^\theta = \frac{\Delta G}{z_i F} \quad (6)$$

Usually, the fuel cell is operated at a temperature greater than the standard temperature of 25 °C, which can be accounted for by integrating the state properties. For hydrogen and oxygen reacting to become water, the enthalpy and equilibrium potentials are shown in Fig. 3 as calculated from handbooks [5]. Depending on whether the product water is vapor or liquid, one arrives at different potentials due to the latent heat and free energy difference between liquid and vapor water as the reaction product. Thus, as the cell temperature increases, the amount of usable work from the fuel decreases (assuming the generated heat is expelled to the atmosphere), while the amount of heat generated increases for a given operating potential. Figure 3 clearly shows how significant the latent heat of water can be (~200 mV).

To account for local concentration changes, one can use a Nernst equation for the reaction

$$U = U^\theta - \frac{RT}{2F} \ln \left( \frac{p_{\text{H}_2} \sqrt{p_{\text{O}_2}}}{p_{\text{H}_2\text{O}}} \right) \quad (7)$$

where  $R$  is the ideal-gas constant,  $T$  is the temperature, and  $p_i$  is the partial pressure of species  $i$ .

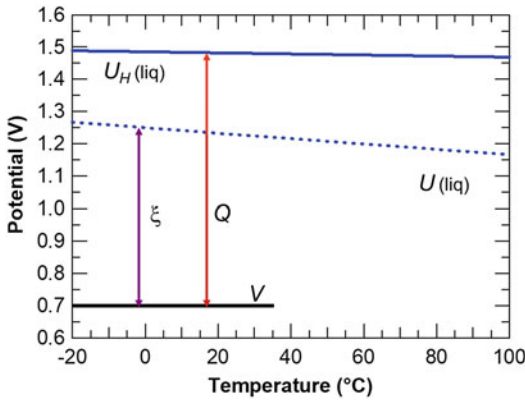


**Fuel Cells and Hydrogen Production: Introduction, Fig. 3** Thermodynamic based potentials for  $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$

Looking at fuel cells in such a principal way as above may lead one to the conclusion that they are perfect energy-conversion systems superior to any heat engine, for which the efficiency is strictly limited due to the Carnot cycle. However, the issue is more complex in practical systems, and it is still an open question what role fuel cells will play in future energy supply systems. The reason is that when current flows, the available energy or potential of the cell decreases for fuel cells due to losses in the cell. Such losses are termed overpotentials and are derived from resistances to electron and ion migration, surface concentrations that differ from the bulk due to mass-transfer limitations, and intrinsic losses in the kinetic reaction steps. Thus, the net heat lost from the cell is

$$\begin{aligned} Q_{\text{loss}} &= Q_{\text{rev}} + Q_{\text{irrev}} \\ &= i(U_H - U^\theta) + i(U^\theta - V) \quad (8) \end{aligned}$$

which is summarized in Fig. 4 for a polymer-electrolyte fuel cell. Thus, if the cell operates at a potential between the equilibrium and enthalpy potentials, the process is endothermic; whereas if the operating potential is above the enthalpy potential or below the equilibrium potential, the process is exothermic. So for fuel cells, the operation is almost always exothermic, whereas electrolyzers



**Fuel Cells and Hydrogen Production: Introduction, Fig. 4** Efficiency and heat generation of a fuel cell

(devices that convert water to hydrogen and oxygen with application of electrical current) are typically operating much closer to thermo-neutral.

Also as shown in Fig. 4, for fuel cells, the efficiency of the cell,  $\eta_{\text{eff}}$ , is typically defined relative to the maximum free energy available for electrical work,

$$\eta_{\text{eff}} = 1 - \frac{V}{U} \quad (9)$$

One must also be cognizant of whether the efficiency is defined in terms of the equilibrium or enthalpy values, and what the reference state is for the calculation (i.e., vapor or liquid water). This is especially important when comparing different fuel cells as well as with fuel cells to other systems. For example, solid-oxide fuel cells operate at temperatures (600–900 °C) where the heat generated can be recovered to electrical energy, thereby making efficiency greater than 100% possible using the definition above. Thus, it is more advisable to use the heating-value or enthalpy or enthalpy potential of the fuel as the metric for efficiency since this also allows for a better comparison among technologies (e.g., combustion engines to fuel cells). This is also often used as the efficiency value when looking at electrolysis.

Notwithstanding the above efficiency considerations, we note that the thermodynamic efficiency limits of all relevant fuel cell reactions are

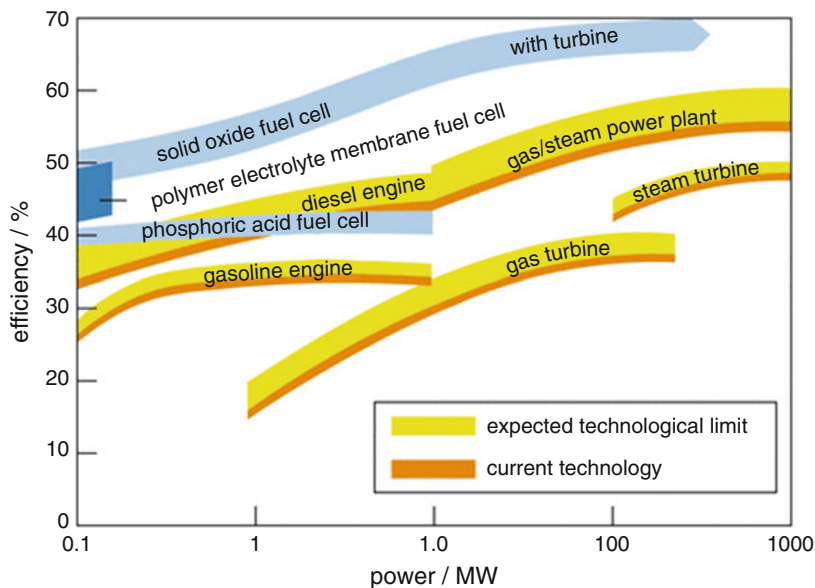
actually below unity (in the range 80–100%) and that irreversibilities (losses) occur in practically all parts of the cells as mentioned above. Nonetheless, electric efficiencies of more than 50% (hydrogen to electricity in fuel cells) and greater than 70% (electricity to hydrogen in electrolyzers) have been demonstrated commercially. Considering the fact that heat engines (e.g., steam turbines) reach such high efficiencies only for very large units operating at high temperatures, the high fuel efficiency of both large and small fuel-cell systems appears to be a unique feature (see Fig. 5) and enables distributed devices and networks.

The potential expanded use of hydrogen involves many technical and infrastructure-related challenges. For example, dispensing hydrogen to wider consumer and fleet-use markets, such as for private and fleet vehicles and for stationary power uses, includes issues related to hydrogen's low energy density (by volume) and other unusual characteristics (i.e., small molecule size, relative ease of ignition in air, metals embrittlement behavior, need for high gas purity when used in certain applications such as in polymer fuel cells, etc.). Hydrogen storage and advanced fuel dispensing and safety systems are active areas of research. Also important are ongoing efforts to study the full economics and lifecycle emissions implications of various hydrogen production and use pathways through total cost of ownership (TCO) and life-cycle impact assessment (LCIA) methods. Various analyses have shown that the capital costs and TCO of both high and low temperature fuel cells systems can be greatly reduced as a function of higher production volume, and with significant overall environmental and social cost benefits when used in different applications.

Over the past 20 years, there has been great progress in fuel-cell system cost reduction, increases in power density, and extended system durability. These improvements have brought commercial fuel cells into specialized applications (e.g., materials handling, military, and remote power applications) as well as initial entry into potentially much larger transportation



**Fuel Cells and Hydrogen Production: Introduction,**  
**Fig. 5** Efficiency versus power for different fuel cell types compared to other energy conversion technologies



(including cars, vans, buses, trucks, and rail systems) and stationary power markets. However, widespread use of the different types of fuel cell systems still requires further fundamental research and engineering efforts. This volume provides detailed insight into the current status of the diverse hydrogen-production and fuel cell technologies and identifies future directions based on critical analyses of the state of the art.

## Hydrogen Production Section

While hydrogen is the most abundant element on earth, it is not readily found in its basic molecular form and has to be produced through one of a variety of processes. This is however also a benefit as it can be produced in many different ways and using a variety of feedstocks. Major efforts are now exploring the options for expanded use of hydrogen for industrial, power generation, and transportation systems (e.g., H2@Scale by US DOE as shown Fig. 1) as well as additional recent work on hydrogen produced using renewable resources (e.g., the US DOE HydroGen – Advanced Water Splitting Materials Consortium).

As discussed above, a range of potential hydrogen production methods and pathways include reformation, gasification, electrolysis, and other

advanced processes. The most common pathway today is steam reforming of natural gas, but it is mainly produced as an industrial input; that is, hydrogen is not being used extensively as an energy carrier. Electrolysis of water to produce hydrogen is well proven at small and larger scales but remains an active area of continued research for improved efficiency and capital cost reduction (chapters ▶ “[Electrochemical Hydrogen Production](#)” and ▶ “[Hydrogen Production Through Electrolysis](#)”). There is a need to leverage the understandings gained and knowledge developed in fuel cells for further development of next-generation electrolyzer systems.

Production of hydrogen from biomass and algae sources using a variety of gasification and pyrolysis technologies is also a very active area of research, using local feedstocks and appropriate processes (chapters ▶ “[Hydrogen Production from Biological Sources](#)”, ▶ “[Biohydrogen Production from Agricultural Residues](#)”, ▶ “[Hydrogen Production Through Pyrolysis](#)”, ▶ “[Hydrogen Production from Algal Pathways](#)”, and ▶ “[Genetic Optimization for Increasing Hydrogen Production in Microalgae](#)”).

Moving forward, some countries are even considering the use of excess nuclear energy (electricity and heat) for producing hydrogen (chapter ▶ “[Nuclear-Assisted Hydrogen Production](#)”),

and others want to rely completely on renewables such as wind and solar (chapters ▶ [“Hydrogen via Direct Solar Production”](#) and ▶ [“Photo-catalytic Hydrogen Production”](#)). Making large quantities of hydrogen with sunlight, directly or indirectly, is still some years away, but this is possible at a range of scales from kilowatts to many megawatts with only solar energy and water as inputs.

Some of the latest hydrogen-generation technologies utilize electrons and electrochemical devices including more advanced concepts where they are combined with thermochemical processes (chapter ▶ [“Hydrogen Production from High-Temperature Fuel Cells”](#)). In addition to traditional electrolyzers, there has been a recent focus on utilizing solar light in an electrochemical cell (chapter ▶ [“Hydrogen Production from Photoelectrochemical Water Splitting”](#)), where efficiencies of solar to hydrogen of around 20% are now demonstrated, although longevity and associated durability concerns remain. Additional concepts include improved hydrogen production through improved chemical reactor systems that can be applied to different feedstocks and settings (chapter ▶ [“Advances on Inorganic Membrane Reactors for Production of Hydrogen”](#)).

## Fuel Cell Section

In an overall sense, fuel cells can be classified by their type of electrolyte (chapter ▶ [“Fuel Cell Types and Their Electrochemistry”](#)). The electrolyte type is highly correlated with the operating temperature regime of the fuel cell as the ions used must be mobile in order to conduct the ionic current. Lower temperature fuel cell systems tend to use relatively pure hydrogen as the reactant fuel, but for higher temperature solid-oxide and molten carbonate fuel cells, other fuels including hydrocarbon fuels can be reacted more directly (chapter ▶ [“Direct Hydrocarbon Solid Oxide Fuel Cells”](#)). Durability and reliability issues are critical for higher temperature fuel cells (chapter ▶ [“Solid Oxide Fuel Cell Materials: Durability, Reliability, and Cost”](#)) as are the main components and architectures (chapters ▶ [“Fuel](#)

[Cells \(SOFC\): Alternative Approaches \(Electrolytes, Electrodes, Fuels\)”](#) and ▶ [“Solid Oxide Fuel Cells”](#)). At the higher temperature range, molten-carbonate fuel cells also are commercially available after decades of development (chapter ▶ [“Molten Carbonate Fuel Cells”](#)), and at lower temperatures, polymer electrolyte membrane (PEM), phosphoric acid (chapter ▶ [“Polybenzimidazole Fuel Cell Technology: Theory, Performance, and Applications”](#)), and polybenzimidazole (used as a matrix for phosphoric acid) (chapter ▶ [“Polybenzimidazole Fuel Cell Technology: Theory, Performance, and Applications”](#)) types are also well established.

The most researched and deployed fuel-cell technology to date is the PEM technology that uses a sulfonic acid membrane and noble-metal catalyst material coated on the electrodes and operates traditionally at about 80 C, below the boiling point of water. While tremendous progress has been made over the past few decades, there are still several critical materials issues related to cost and durability requirements, especially for automotive applications, that must be overcome (chapter ▶ [“PEM Fuel Cells: Materials and Design Development Challenges”](#)). The electro-catalyst layers are a key cost and performance component, where there is a current need for higher performance and more durable materials (chapter ▶ [“PEM Fuel Cells and Platinum-Based Electro-catalysts”](#)). Experiments have shown that one can reduce the amount of noble catalyst, but that at least thus far this is not without drawbacks in terms of performance (chapter ▶ [“Proton-Exchange Membrane Fuel Cells with Low-Pt Content”](#)). Alternatively, non-noble metal catalysts are increasingly being researched (chapter ▶ [“Polymer Electrolyte Membrane Fuel Cells \(PEM-FC\) and Non-noble Metal Catalysts for Oxygen Reduction”](#)) to reduce overall cell cost.

A key material for realizing gains in low temperature systems is the PEM itself (chapter ▶ [“Membrane Electrolytes, from Perfluoro-sulfonic Acid \(PFSA\) to Hydrocarbon Ionomers”](#)) and its interplay with environmental conditions (chapter ▶ [“Proton Exchange Membrane Fuel Cells: High-Temperature, Low-Humidity Operation”](#)). A better ability of fuel cells systems to

adapt to local environmental conditions may help to reduce the system cost, especially by reducing the size of the cooling system, the amount of noble-metal catalyst, and the purity requirements for the fuel used (relatively pure hydrogen). Efforts are also constantly underway to find cost reductions by using non-noble metal catalysts, potentially through use of more effective anion or hydroxide exchange membranes (chapter ▶ “Alkaline Membrane Fuel Cells”). Beyond the polymer electrolyte as a membrane separator, there is an increasing focus on its existence as thin films in the catalyst layers and potential swelling of the layers over time that can inhibit performance (chapter ▶ “Ionomer Thin Films in PEM Fuel Cells”).

As noted, fuel cells are complex devices and to understand the various interplays and complexities researchers are routinely turning to mathematical modeling (chapter ▶ “PEM Fuel Cells: Modeling”). Fuel cells act as energy-conversion modules in various systems and applications (chapter ▶ “Polymer Electrolyte (PE) Fuel Cell Systems”), especially automotive for polymer-electrolyte fuel cells (chapter ▶ “Polymer Electrolyte Membrane (PEM) Fuel Cells: Automotive Applications”) and stationary for solid-oxide fuel cells. Of course, when discussing the system aspects one must be aware of the cost and design issues (chapters ▶ “PEM Fuel Cell Materials: Costs, Performance, and Durability” and ▶ “Solid Oxide Fuel Cells: Marketing Issues”), including LCA (chapters ▶ “Fuel Cell Systems: Total Cost of Ownership” and ▶ “Solid Oxide Fuel Cells: Sustainability Aspects”) and comparisons to alternative technologies (chapter ▶ “Fuel Cell Comparison to Alternate Technologies”).

We conclude this introduction by noting that various types of power systems based on

heat engines and electrochemical energy devices (mainly batteries but now including fuel cells as well) have existed side by side since the late 1800s. Over the intervening years the abundance of fossil fuels has driven the development of combustion engines and turbines and slowed the development of more efficient and cleaner energy conversion devices. As the “oil age” continues but is expected to wane over time, the transition may include an increase in the importance of an array of now commercially available systems for a cleaner and more efficient future energy system. These include solar photovoltaic, wind power, geothermal, and biomass-based renewable energy systems, as well as transitional solutions based on natural gas and nuclear power, amid which hydrogen and fuel cells have an important role to play.

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