



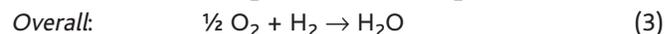
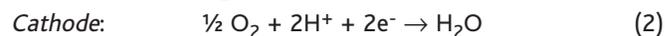
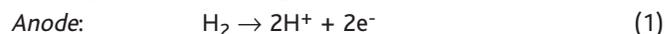
# Materials for fuel cells

by Sossina M. Haile

Because of their potential to reduce the environmental impact and geopolitical consequences of the use of fossil fuels, fuel cells have emerged as tantalizing alternatives to combustion engines. Like a combustion engine, a fuel cell uses some sort of chemical fuel as its energy source but, like a battery, the chemical energy is directly converted to electrical energy, without an often messy and relatively inefficient combustion step. In addition to high efficiency and low emissions, fuel cells are attractive for their modular and distributed nature, and zero noise pollution. They will also play an essential role in any future hydrogen fuel economy.

The primary components of a fuel cell are an ion conducting electrolyte, a cathode, and an anode, as shown schematically in Fig. 1. In the simplest example, a fuel such as hydrogen is brought into the anode compartment and an oxidant, typically oxygen, into the cathode compartment. There is an overall chemical driving force for the oxygen and the hydrogen to react to produce water.

In the fuel cell, however, this simple chemical reaction is prevented by the electrolyte that separates the fuel ( $H_2$ ) from the oxidant ( $O_2$ ). The electrolyte serves as a barrier to gas diffusion, but permits ion transport. Accordingly, half cell reactions occur at the anode and cathode, producing ions that can traverse the electrolyte. For example, if the electrolyte conducts protons,  $H_2$  will be oxidized at the anode to form protons and electrons; the protons, after migrating across the electrolyte, will react at the cathode with  $O_2$  and electrons (Fig. 1):



The flow of ionic charge through the electrolyte must be balanced by the flow of electronic charge through an outside circuit, and it is this balance that produces electrical power.

Electrolytes in which protons, hydronium ions, hydroxide ions, oxide ions, and carbonate ions are mobile are all known, and are the basis for the many categories of fuel cells under development today. Desirable characteristics of fuel cell electrolytes are not only high ionic conductivity (which results in high efficiency), but also impermeability to gases, negligible electronic conductivity, chemical stability under a

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(Image above shows detail of a fuel cell stack. Credit:  
Ballard Power Systems.)

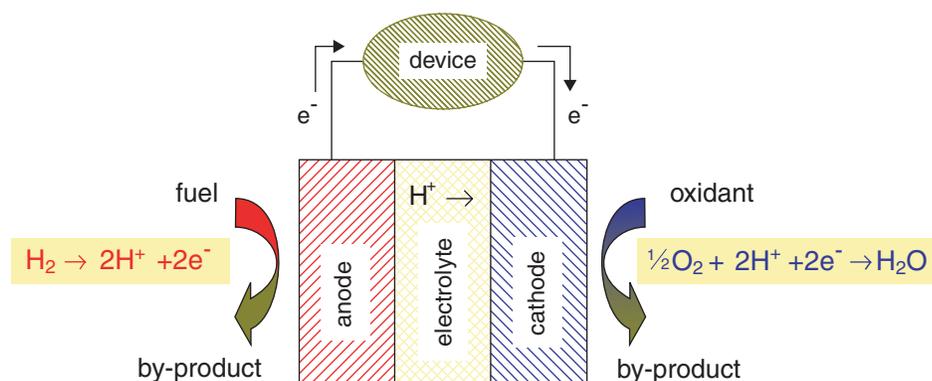


Fig. 1 Schematic of a conventional fuel cell employing a proton conducting electrolyte. Electro-oxidation of  $\text{H}_2$  occurs at the anode, creating protons that then migrate across the electrolyte and participate in the electro-reduction of  $\text{O}_2$  at the cathode. Electric power generation results from the flow of electrons through an outside circuit, necessary for charge balance. The overall reaction is  $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$ , for which there is a strong chemical driving force.

wide range of conditions, and good mechanical integrity. Because ion conduction is a thermally activated process and its magnitude varies widely from one material to the next, the type of electrolyte, which may be either liquid or solid, determines the fuel cell's temperature of operation. State-of-the-art fuel cell electrolytes are listed in Table 1, along with the mobile ionic species, temperatures of operation, and the fuels that are typically utilized. For reasons of electrode activity (which translates into higher efficiency and greater fuel flexibility), higher temperature operation is

preferred, but for portable (intermittent) power applications, lower temperature operation is typically favored. In addition, solid electrolyte systems obviate the need to contain corrosive liquids and, thus, solid oxide and polymer electrolyte fuel cells are preferred by many developers over alkali, phosphoric acid, or molten carbonate fuel cells. Nevertheless, each of the fuel cell types listed in Table 1 has been demonstrated in complete fuel cell systems, with alkali and phosphoric acid the most mature technologies, and polymer electrolyte membrane (PEM) fuel cells the most recent.

Critical to the function of a fuel cell are the electrodes/electrocatalysts. Within the electrodes, transport of gaseous (or liquid) species, ions, and electrons must all be facilitated, and at the points where all three meet, the so-called triple-point (or triple-line) boundaries, the electrocatalysts must reduce the  $\text{O}_2$  and oxidize the fuel, at the cathode and anode, respectively. Thus, the electrodes must be porous, electronically and ionically conducting, electrochemically active, and have high surface areas. It is rare for a single material to meet all of these requirements, especially at low temperatures and, consequently, a composite electrode, of which the electrocatalyst is one component, is often utilized. Desirable characteristics of fuel cell electrodes include not only high activity towards the reaction in question, but also chemical and thermo-mechanical compatibility with the electrolyte, chemical stability under reducing (anode) or oxidizing (cathode) atmospheres, resistance to poisoning by impurities in the fuel or oxidant stream, and architectural stability over long periods of operation.

Table 1. Fuel cell types and selected features<sup>1,2</sup>.

Type	Temperature °C	Fuel	Electrolyte	Mobile Ion
PEM*: polymer electrolyte membrane	70-110	$\text{H}_2$ $\text{CH}_3\text{OH}$	Sulfonated polymers (Nafion™)	$(\text{H}_2\text{O})_n\text{H}^+$
AFC: alkali fuel cell	100-250	$\text{H}_2$	Aqueous KOH	$\text{OH}^-$
PAFC: phosphoric acid fuel cell	150-250	$\text{H}_2$	$\text{H}_3\text{PO}_4$	$\text{H}^+$
MCFC: molten carbonate fuel cell	500-700	hydrocarbons CO	$(\text{Na,K})_2\text{CO}_3$	$\text{CO}_3^{2-}$
SOFC: solid oxide fuel cell	700-1000	hydrocarbons CO	$(\text{Zr,Y})\text{O}_{2-\delta}$	$\text{O}^{2-}$

\* also known as proton exchange membrane

Although substantial progress has been made in fuel cell technology over the last several decades, there is little question that today's fuel cell systems are complex and costly because of the design constraints placed on them by the materials (electrolytes and electrodes/electrocatalysts) available. For example, the extreme sensitivity of alkali hydroxides to carbon dioxide,  $\text{CO}_2$ , requires that both the fuel and oxidant be free of trace  $\text{CO}_2$  prior to their introduction into alkali fuel cells. Similarly, the extreme sensitivity of precious metal electrocatalysts to carbon monoxide,  $\text{CO}$ , necessitates the removal of trace  $\text{CO}$  from the  $\text{H}_2$  fuel stream in PEM fuel cells. Failure of one of the multitude of auxiliary components required for fuel cell operation, ranging from gas purification to pressurization to cooling systems, is more often the cause of fuel cell shut-down than failure of the fuel cell itself. We highlight here selected recent breakthroughs in both electrolyte and electrode materials for solid electrolyte systems, which are envisioned to greatly simplify fuel cell design.

### Solid oxide fuel cells

Solid oxide fuel cells (SOFCs) have shown tremendous reliability when operated continuously. For example, a 100 kW system fabricated by Siemens-Westinghouse has successfully produced power for over 20 000 hours without any measurable degradation in performance<sup>3</sup>. However, intermittent operation remains a serious challenge for SOFCs. Moreover, these fuel cells are still much too costly for widespread commercialization.

Both traits are a consequence of the high temperatures required for SOFC operation. High temperatures preclude the use of metals, which typically have lower fabrication costs than ceramics, for any of the non-electrochemical components of the fuel cell and also increase the likelihood of cracks developing upon thermal cycling. The so-called planar SOFCs are particularly prone to cracking at glass seals that keep anode and cathode chambers isolated from one another in a stacked configuration. Finally, while SOFCs offer tremendous fuel flexibility, allowing a variety of hydrocarbon fuels to be utilized, the less reactive fuels must typically be internally steam-reformed, that is, reacted with  $\text{H}_2\text{O}$  in the anode chamber to produce  $\text{CO}$  and  $\text{H}_2$ , which can subsequently be utilized in the electrochemical reactions<sup>4</sup>. Although not anticipated to prevent SOFC commercialization, internal steam-reforming requires recirculation of water, and

its elimination, again, simplifies fuel cell operation and reduces costs.

To address the challenge of high temperature operation, significant efforts have been directed towards the development of electrolytes with high ionic conductivity at approximately  $600^\circ\text{C}$ . Further reductions in the temperature of operation are generally deemed undesirable because of concomitant losses in electrode activity. Three candidate electrolytes have emerged: doped ceria ( $\text{CeO}_2$ ), doped lanthanum gallate ( $\text{LaGaO}_3$ ), and doped barium zirconate ( $\text{BaZrO}_3$ ), with the first two being oxygen ion conductors and the latter a proton conductor. The oxygen ion transport properties of  $\text{CeO}_2$  have long been known, and thus only its implementation in fuel cells (as opposed to recognition of its properties) constitutes a 'recent' materials development. The ionic conductivity of  $\text{CeO}_2$  is approximately an order of magnitude greater than that of the conventional SOFC electrolyte, yttria-stabilized zirconia (Fig. 2), but  $\text{CeO}_2$  had not been considered viable for fuel cell applications because of its high electronic conductivity. The simple solution to this problem lies again in the operating temperature. At temperatures below  $\sim 700^\circ\text{C}$  (and at  $10^{-18}$  atm  $\text{O}_2$  partial pressure), the ionic transference of  $\text{CeO}_2$  is greater than

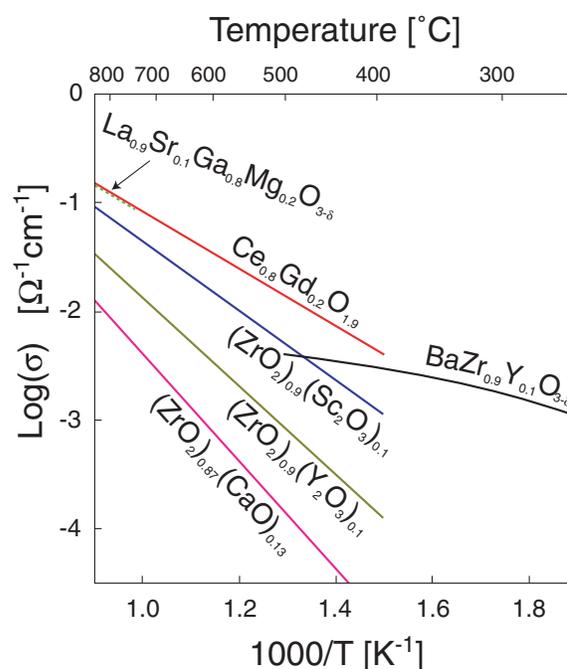


Fig. 2 Conductivities of selected oxides. Doped ceria, zirconia, and lanthanum gallate are oxygen ion conductors, whereas doped barium zirconate is a proton conductor.\*  
\*Sources: doped ceria and zirconia after Steele<sup>26</sup>, LSGM after Ishihara<sup>9</sup>, and BYZ after Bohn and Schober<sup>13</sup>.

~0.9, a value that results in good fuel cell efficiency<sup>5</sup>. An examination of the impact of various rare earth dopants on the properties of CeO<sub>2</sub> have led to the observation that the ionic conductivity is highly dependent on the ionic radius of the dopant. In particular, the conductivity increases and then decreases across the rare earth dopant series<sup>6</sup> from Yb to La, peaking at Sm. A similar observation has been made for Zr, with the peak occurring at Sc. This trend has been explained in terms of the lattice distortions introduced by the dopant, with Sm being the best-matched to the structure of CeO<sub>2</sub> and, therefore, inducing the least amount of strain and smallest variation in the potential energy landscape<sup>7</sup>.

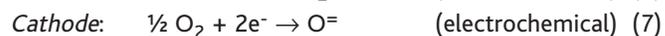
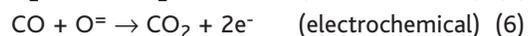
In contrast to CeO<sub>2</sub>, the development of the two perovskites, LaGaO<sub>3</sub> and BaZrO<sub>3</sub>, has occurred over just the last several years. In both cases, high conductivity is a direct result of the ability of the extremely adaptable perovskite structure to accommodate a large concentration of dopant species. Introduction of divalent dopant ions, typically Sr and Mg, onto the La and Ga sites, respectively, of LaGaO<sub>3</sub> produces O vacancies and thereby high oxygen ion conductivity. The conductivity of the particular composition La<sub>0.9</sub>Sr<sub>0.1</sub>Ga<sub>0.8</sub>Mg<sub>0.2</sub>O<sub>3-δ</sub> (LSGM), reported almost simultaneously by Goodenough<sup>8</sup> at the University of Texas, Austin, and by Ishihara<sup>9</sup> at Oita University in Japan, is comparable to that of doped CeO<sub>2</sub>. Equally significant is the fact that the conductivity is entirely ionic over an extremely wide O<sub>2</sub> partial pressure range at temperatures as high as 1000°C. The use of LSGM in fuel cells had, until recently, been hampered by the material's reactivity with Ni in the anode. However, it has been demonstrated that incorporation of a CeO<sub>2</sub> buffer layer between the electrolyte and the anode eliminates the reaction, opening the way for the use of this promising new material in commercial SOFCs<sup>10</sup>.

In analogy to the defect chemistry of LaGaO<sub>3</sub>, proton transport in BaZrO<sub>3</sub> is achieved by first doping the material with a trivalent species (such as Y) on the Zr site so as to introduce O vacancies. The material is then exposed to H<sub>2</sub>O-containing atmospheres, and hydroxyl groups are incorporated onto the formerly vacant oxygen sites, while the second proton of the H<sub>2</sub>O molecule attaches to some other O atom in the structure. The protons are only loosely bound to any particular O atom, and charge transport occurs as they jump from one O atom to the next. In comparison to related cerates (BaCeO<sub>3</sub> and SrCeO<sub>3</sub>), examined extensively by Iwahara<sup>11</sup> and others in the literature, BaZrO<sub>3</sub> offers high

conductivity and excellent chemical stability against reaction with CO<sub>2</sub>. However, BaZrO<sub>3</sub> is exceptionally refractory, and processing of dense electrolyte membranes from this material remains a significant challenge. Indeed, the high bulk conductivity of BaZrO<sub>3</sub> had, for several years, remained obscured as a consequence of the material's refractory nature, which resulted in fine-grained samples with high total grain boundary resistance<sup>12,13</sup>.

Two recent breakthroughs in electrodes for SOFCs have generated significant excitement (and some skepticism) within the fuel cell community. The first involves the apparent direct electrochemical oxidation of fuels at SOFC anodes and the second, highly selective anode and cathode catalysts that apparently enable the operation of single chamber fuel cells, or SCFCs. Direct electrochemical oxidation refers to the reaction of hydrocarbon fuels directly with oxygen ions, without intermediary reaction steps with water. The technological consequence is that excess water need not be recirculated in the anode chamber of SOFCs<sup>4</sup>. This mechanism of anode function was reported essentially simultaneously by Barnett's group<sup>14</sup> at Northwestern University and Gorte and coworkers<sup>15</sup> at the University of Pennsylvania. While the detailed reaction steps remain to be elucidated, it is evident that incorporation of CeO<sub>2</sub> into the anode cermet is essential. Moreover, minimization of the Ni content (by replacing it with a metal such as Cu) is also important in order to limit carbon deposition or 'coking'. It is noteworthy that both groups have been cautious in their discussion of the reaction pathway to allow for the possibility of *in situ* generation of water, which could then result in some unavoidable steam reforming. Establishing whether or not this occurs will be essential for understanding and, ultimately, optimizing the process.

A single chamber fuel cell, Fig. 3, relies on carefully selected anode and cathode catalysts to produce well-controlled half-cell reactions:



Ideally, simple chemical oxidation of the hydrocarbon, which would yield CO<sub>2</sub> and H<sub>2</sub>O, does not take place. Instead, partial oxidation occurs at the anode and the products of this reaction are consumed electrochemically, while O<sub>2</sub> is consumed electrochemically at the cathode. As a

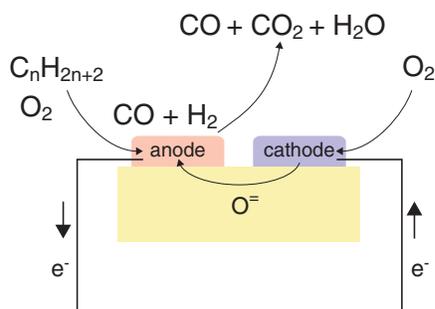


Fig. 3 Schematic of a single chamber fuel cell employing an oxide ion conducting electrolyte. A hydrocarbon fuel is partially oxidized at the anode giving rise to CO, H<sub>2</sub>, and an O<sub>2</sub> partial pressure gradient from anode to cathode which, in turn, drive the electrochemical reactions of the fuel cell.

consequence, the fuel and oxidant need not be physically separated.

Such SCFCs have been investigated over the past few years by Hibino and coworkers at the National Industrial Research Institute of Nagoya, Japan. Impressive performance of 467 mW/cm<sup>2</sup> at 500°C has been reported for cells operating on methane/air mixtures and incorporating a Pd-Ni-CeO<sub>2</sub> cermet anode and Sm<sub>0.5</sub>Sr<sub>0.5</sub>CoO<sub>3</sub> cathode<sup>16</sup>. Because complications resulting from sealing are eliminated, the SCFC greatly simplifies system design and enhances thermal and mechanical shock resistance, thereby allowing rapid start-up and cool-down. In general, both conventional stack configurations, in which the fuel cell anode and cathode are placed on opposing sides of the electrolyte, and strip configurations, in which thin strip anodes and cathodes are placed on the same side of the fuel cell electrolyte (as shown in Fig. 3) are possible in a SCFC.

## PEM fuel cells

Polymer electrolyte membrane (PEM) fuel cells rely on the relatively facile transport of hydronium ions through hydrated regions of a sulfonated polymer. Their high conductivity enables operation at close to ambient temperatures, a trait well-suited to portable applications. The challenges here arise from the sluggish reaction kinetics, precluding the direct use of hydrocarbon fuels other than perhaps methanol (direct methanol fuel cell). An additional set of complications arises directly from the hydrated nature of the polymeric electrolyte material. Because the mobile species is hydronium, high levels of humidification are required to maintain high electrolyte conductivity, yet this must be balanced by the need to remove water from the

cathode and prevent flooding of the electrocatalyst during operation. Other consequences of utilizing a hydrated polymer as the electrolyte are:

- irreversible dehydration damage if thermal excursions are experienced;
- high rates of methanol diffusion from anode to cathode in a direct methanol PEM fuel cell; and
- degradation in mechanical properties due to 'swelling' upon hydration.

Moreover, the benefits of 'warm' temperature operation, which include increased activity of the catalysts, decreased susceptibility of the anode catalyst to poisoning by impurities in the fuel stream, greater integration with high-temperature H<sub>2</sub> generators, and greater ease of thermal management, are all forgone in conventional PEM fuel cells.

Accordingly, several groups are pursuing 'water-free' proton conducting membranes. Examples of systems under investigation include polymer/inorganic composites (e.g. Nafion + silica + phosphotungstic or silicotungstic acid<sup>17</sup>), polymer/acid blends<sup>18</sup> (e.g. polybenzimidazole + phosphoric acid), and polymer/heterocycle blends (e.g. sulfonated polyaromatic polymers + imidazole, pyrazole, or benzimidazole<sup>19</sup>). Electrolyte research in the author's laboratory follows a radically different approach, in particular, we are examining inorganic (non-polymeric) solids known as solid acids. Solid acids are compounds such as CsHSO<sub>4</sub> whose chemistry and properties are intermediate between those of a normal acid (e.g. H<sub>2</sub>SO<sub>4</sub>) and a normal salt (e.g. Cs<sub>2</sub>SO<sub>4</sub>). They are typically comprised of oxyanions, for example, SO<sub>4</sub> or SeO<sub>4</sub>, that are linked together via O-H...O hydrogen bonds. Several are known to undergo a structural phase transition at slightly elevated temperatures (50-150°C), at which the proton conductivity jumps by several orders of magnitude. In the high-temperature, disordered structure, XO<sub>4</sub> anion groups undergo rapid reorientation, on a time scale of about 10<sup>-11</sup> s. The proton typically remains attached to one of the O atoms of the XO<sub>4</sub> group, but undergoes a transfer to a neighboring XO<sub>4</sub> on a time scale<sup>20</sup> of about 10<sup>-9</sup> s. A key feature of the proton transport process (Fig. 4) is that, unlike the case in polymeric systems, bare protons are truly the mobile species and hydration of the electrolyte is no longer necessary.

Proton conducting solid acids have been known for about 20 years<sup>21</sup>, but they had not been seriously considered for fuel cell applications because they suffer from solubility in water. This challenge, however, can be easily addressed

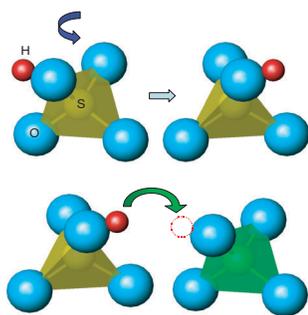
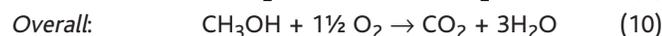
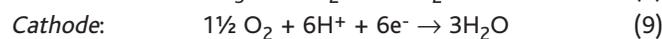
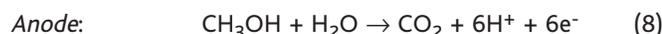


Fig. 4 Proton transport mechanism in a disordered acid sulfate compound.  $(\text{HSO}_4)^-$  tetrahedra undergo rapid reorientations with the proton attached to a particular oxygen atom (top); proton transfer from one tetrahedron to the next occurs on a much slower time scale (bottom). © Sossina Haile, Caltech.

simply by operating at slightly elevated temperatures<sup>22</sup>. A much more significant hurdle is the tendency of sulfate- and selenate-based solid acids to react with  $\text{H}_2$  to produce  $\text{H}_2\text{S}$  (or  $\text{H}_2\text{Se}$ )<sup>23</sup>, gases that poison the anode Pt catalyst when present at even the ppm level. Furthermore, fabrication routes must be dramatically improved if the Pt loadings ( $\sim 5 \text{ mg cm}^{-2}$ ) and power outputs ( $\sim 12 \text{ mW cm}^{-2}$ ) are to become competitive with state-of-the-art fuel cells.

In parallel with electrolyte development for low temperature fuel cells, laboratories worldwide are pursuing advanced electrocatalysts with the objectives of enhancing reaction kinetics, decreasing Pt loadings, and mitigating anode susceptibility to CO poisoning. Much of this research has focused on intermetallic alloys of Pt. For direct methanol fuel cells, in which the reactions are:



the most effective catalyst remains alloyed Pt-Ru. As pointed out by Gasteiger<sup>24</sup>, methanol is adsorbed onto Pt clusters and then fragmented into dehydrogenation products, essentially CO. Electro-oxidation of CO is subsequently catalyzed by oxygen-like species adsorbed onto neighboring Ru sites. In order for this bifunctional catalysis mechanism to be effective, Pt and Ru must be arranged in a specific configuration on the catalyst surface. Almost by definition, alloys, with their random distribution of atomic species, are ill-suited to provide precise chemical arrangements. In light of this fundamental limitation of alloy-based electrocatalysts, DiSalvo and Abruña have opened up a new avenue of electrocatalyst research. Specifically, they are developing intermetallic *compounds*, which have highly regular and thermodynamically stable surface arrangements, as fuel cell catalysts<sup>25</sup>. Initial cyclic voltammetry experiments in the Pt-Bi system, which includes the two compounds PtBi and PtBi<sub>2</sub>, show excellent promise in terms of both CO tolerance and electro-oxidation of formic acid (a model hydrocarbon). This approach may well lead to the next major breakthrough in fuel cell technology.

## Conclusion

In sum, the increased attention that has been directed towards fuel cells in the last few years has resulted in novel approaches and dramatic breakthroughs in materials properties for both solid oxide and proton exchange membrane fuel cells. These breakthroughs are essential to transforming fuel cells from the technology of tomorrow to the technology of today. **MI**

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