Solid Oxide Fuel Cells and Membranes

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Fuel cells and membranes are similar in that they employ materials that transport ions and electrons. Both can play important roles in making clean energy a reality.

A sustainable future calls for the development of clean, efficient, and affordable energy technologies to address the world's growing demand for energy. Fuel cells, which convert chemical energy to electrical energy, have been widely regarded as a promising alternative to conventional internal combustion engines for clean and efficient power generation. Membranes are another important, closely related technology for utilizing fossil fuel resources to produce clean energy and value-added chemicals through process intensification.

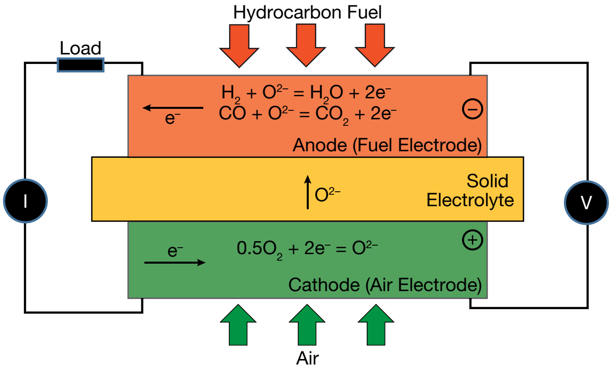
This article briefly reviews the basic working principles, system components, and applications of solid oxide fuel cells for clean power generation and membrane reactors for value-added chemical production.

Solid oxide fuel cells

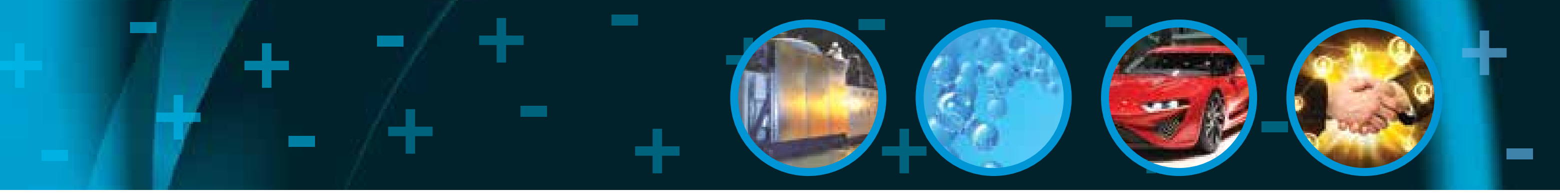
A solid oxide fuel cell (SOFC) directly converts the chemical energy in fossil fuels into electrical power via an electrochemical reaction. A SOFC (Figure 1) has three basic functional elements: cathode, electrolyte, and anode. The cathode reduces oxygen (in the form of O_2) in the air supplied to it into O^{2-}. The electrolyte transports oxygen continuously, in the form of O^{2-}, from the cathode to the anode under a gradient of oxygen chemical potential. At the anode, or fuel supply electrode, the O^{2-} delivered by the electrolyte reacts with hydrogen or a hydrocarbon fuel to produce H_2O, CO_2, and electrons. The electrons required for the cathode reaction are released by the anode and arrive at the cathode via an external load that produces electricity. The overall driving force for a SOFC is the gradient of oxygen chemical potential that exists between the cathode with a high oxygen partial pressure and the anode with a low oxygen partial pressure. References 1–3 provide a more detailed review of SOFC technology.

Like the components of a battery, each SOFC component exhibits an internal resistance to either electronic or ionic current flow, often expressed as voltage loss. The terminal cell voltage is, therefore, the open circuit voltage (or electromotive force, EMF, if no fuel is lost by any means) reduced by the individual voltage loss of each cell component.

The maximum cell voltage of a typical single SOFC with air as the oxidant is generally 1.2 V, depending on temperature, system pressure, and fuel composition. This voltage is obviously inadequate for any type of practical application. To obtain a sufficiently high voltage and power, multiple single cells are connected in series and/or in parallel by interconnects and/or cell-to-cell connectors that are electronic conductors and oxide-ion insulators.



▲ **Figure 1.** In a solid oxide fuel cell, the cathode reduces oxygen (from air) to O^{2-}, which the electrolyte transports from the cathode to the anode, where it reacts with a fuel to produce H_2O, CO_2, and electrons.



SOFC stack designs

To increase the reliability and reduce the cost of SOFCs, designers strive to obtain high performance at low operating temperatures. To achieve this goal, modern SOFCs typically contain a thin electrolyte film supported on a substrate — a porous or channeled dense layer that enables gas transport. The porous electrode (cathode or anode), dense metal or ceramic interconnect, or porous inactive insulator can serve as the substrate. The substrate can be made into either a tubular or a planar shape (Figure 2).

An important requirement for a SOFC is that oxygen must be transported across the electrolyte in the form of O^{2-}, but not as molecular O_2. To achieve this, dense barriers between air and fuel must be established. In the tubular SOFC design, dense electrolyte and interconnect layers create such a barrier, allowing air and fuel to meet only at the open end and combustion to occur only after most of the fuel has been consumed by the oxidation reaction over the entire cylindrical surface. Tubular SOFCs, therefore, do not need a physical sealing material. Planar SOFCs, on the other hand, require sealing materials along the perimeters of the interconnect/electrode and electrolyte/electrode interfaces to prevent air from mixing with fuels, which often presents a challenge to the reliability and stability of the planar SOFCs.

Certain substrate/geometry combinations have advantages. For example, a cathode substrate paired with a tubular stack design is an excellent marriage. Because cell-to-cell connections in the stack take place in a reducing atmosphere, inexpensive transition metals such as nickel and copper can be used. Otherwise, more-expensive noble metals are needed for connecting anode-supported cells into stacks in an oxidizing atmosphere. Figure 2a shows a cathode-supported tubular SOFC stack designed by Siemens/Westinghouse.

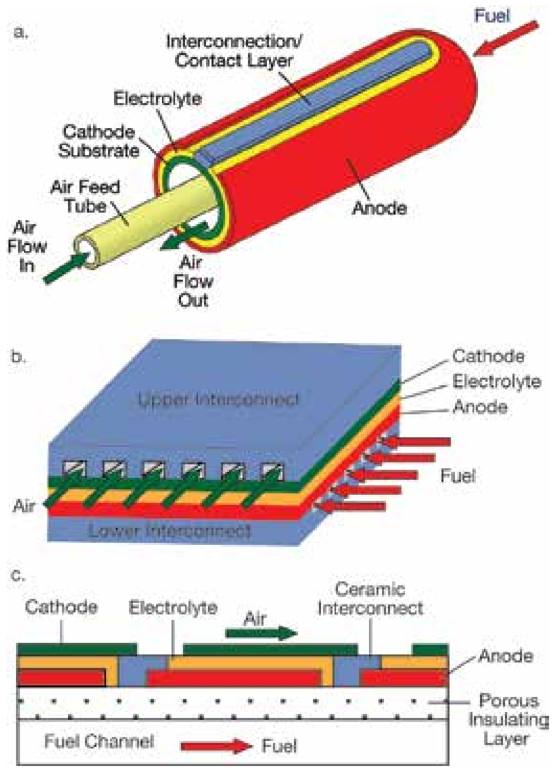
On the other hand, an anode substrate and a planar stack is a good combination. High-power-density anode-supported single cells can operate at a lower temperature, allowing economic, commercially available oxidation-resistant alloys to be used to connect single cells into a stack. The oxidation-resistant alloys provide the mechanical support for the stack and function as interconnects and current collectors simultaneously. Figure 2b shows an anode-supported planar SOFC stack designed by FuelCell Energy.

Porous metal substrates have garnered considerable interest in recent years. Potential advantages include robustness and cost-effectiveness of cells and stacks made with these materials. However, a major challenge is the fabrication of dense electrolyte and/or interconnect layers on the substrate at a temperature low enough to prevent significant oxidation and chemical reactions between underlying layers. In addition, vaporization of chromium from the chromium-containing metal interconnects during operation can degrade the cathode performance in the presence of air and moisture.

Multiple cells have also been deposited in series on an electrochemically inactive and electrically insulating substrate. This design, termed segmented-in-series, has unique advantages, including low fabrication costs. More importantly, such a SOFC stack operates at higher voltage and low current for a fixed power rating. This feature could help reduce the power losses on current connections, which is particularly important for large-class SOFC generators. Figure 2c shows a segmented-in-series SOFC designed by LG Fuel Cells.

Advantages of SOFCs

Since a SOFC operates on electrochemical principles, its efficiency is unbounded by the Carnot cycle that limits the highest achievable efficiency of conventional internal combustion engines (ICEs). Therefore, a SOFC has an inherently higher electrical efficiency than ICEs, particularly in the sub-MW range. Higher electrical efficiency infers lower CO_2 emissions per unit of electricity produced if hydrocarbons are used as fuels. A SOFC also produces virtually no nitrogen oxide emissions (collectively known as NOx) because of its low operating temperature, whereas NOx emissions are a big



▲ **Figure 2.** The SOFC substrate supporting the thin electrolyte film can be made into a tubular (a) or planar (b) shape. The segment-in-series design (c) is a special type of planar construction made by depositing multiple cells in series on an electrochemically inactive and electrically insulating substrate. Source: Adapted from *(1)*.

issue for conventional ICEs that burn fuel at much higher temperatures. And, a desulfurizer subsystem can be incorporated into a SOFC generator to reduce sulfur oxide emissions (collectively known as SOx) to virtually zero. In addition, SOFC power generators are much quieter and produce less vibration than a conventional engine during operation.

SOFCs operated at high temperatures have additional advantages. High-temperature operation, typically in the range of 600–1,000°C, provides high-quality waste heat. It also effectively activates the processes of reforming and electrochemical oxidation of hydrocarbon fuels in the presence of non-noble catalysts, which is technically important for several reasons:

- It allows SOFCs to use most hydrocarbon fuels, either in the gaseous or liquid state, provided that they are properly cleaned and reformed into simple fuels such as H_2 and CO. This is in contrast to low-temperature fuel cells, such as proton exchange membrane (PEM) fuel cells, where CO poisons the anode.
- The excess heat produced by the electrochemical oxidation of fuels can be utilized by the highly endothermic steam reforming reaction that occurs simultaneously, which makes internal on-cell reformation possible. Integration further increases the overall system efficiency.

▲ **Figure 3.** (a) Siemens/Westinghouse has demonstrated a 220-kWe SOFC/micro-turbine hybrid generator that achieved a net electrical efficiency of 53%. (b) A different unit, a 100-kWe SOFC generator, has more than 35,000 hours of operation, making it the longest-running SOFC ever demonstrated. Source: Photos courtesy of Siemens/Westinghouse.

- Co-production of heat and power, known as combined heat and power (CHP), is also possible. The recovery of waste heat to produce electricity enables CHP systems to achieve a total energy efficiency in the range of 85–90%.
- Another way to recover waste heat is to combine a micro gas-turbine with a SOFC stack to form a hybrid system. To maximize the electrical efficiency, a hybrid is often operated under pressurization, which boosts both the performance of the SOFC stack and the effectiveness of the turbine. A bottom cycle steam turbine can be added to the hybrid system to increase efficiency even further. This hybrid system is particularly beneficial for generators over 100 MWe. Siemens/Westinghouse has demonstrated a 220-kWe class hybrid SOFC generator system that achieved a net alternating-current electrical efficiency of 53% (Figure 3a).

The all-solid-state components of a SOFC system can avoid the corrosion issues caused by the liquid electrolyte in a molten carbonate fuel cell (MCFC) system, which prolongs the life of a SOFC. With over 35,000 operating hours at an acceptable degradation rate, the Siemens/Westinghouse 100-kWe unit in Figure 3b is the longest running SOFC generator ever demonstrated.

Applications of SOFCs

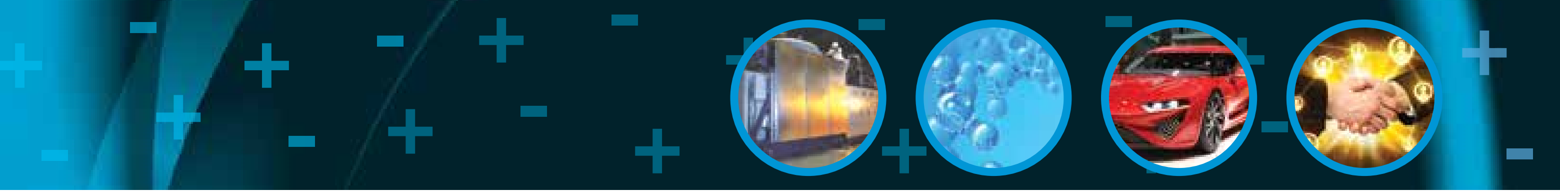
An ideal application for SOFCs is distributed stationary power generation. Depending on the size of the SOFC generator, stationary power generation can be categorized into the markets summarized in Table 1.

SOFCs: Challenges and opportunities

The two most critical challenges to the commercialization of modern SOFC technology are reliability and cost. In order to compete with ICEs, efficient and low-emission SOFC generators need to have a lifetime of 40,000 hr and cost less than $500/kWe. None of today's SOFC technologies can achieve this level of performance. However, with advances in materials and design, it is widely believed that SOFC cost and durability barriers can eventually be overcome.

An important milestone will be reducing the operating temperature of a SOFC from the current 700–800°C to below 600°C, where thermal degradation is lower and inexpensive materials can be used but the distinct advantages of a SOFC, such as hydrocarbon compatibility and CHP capability, can be maintained. The performance of such intermediate-temperature SOFCs is limited by the cathode. Thus, researchers are pursuing the development of advanced, catalytically active cathode materials with new crystal structures and morphological nanostructures.

Another recent development is the use of a SOFC as a



membrane reactor (electrolyzer) that uses electricity as the energy input to make value-added chemicals. An example of this application is the co-electrolysis of $CO_2 + H_2O$ by a SOFC electrolyzer to make syngas (primarily H_2 and CO). When combined with renewable energy, these reversible SOFCs can also be viewed as electricity storage, where the energy is stored in chemical bonds.

Membranes

To electrochemically convert fuels to electricity, solid oxide fuel cells rely on materials that transport ions and electrons. A closely related technology that is also electrochemical in nature and that employs similar classes of materials, including ion conductors and mixed ionic-electronic conductors (MIECs), is high-temperature membranes.

Ceramic membranes that transport ions, including permeation membranes and membrane reactors, play an essential role in several energy conversion systems *(4)*. Similar to SOFC electrolytes, membranes fabricated from materials that are oxygen-ion conductors and have a low electron conductivity can be used to separate oxygen from air upon application of an external voltage. This is analogous to what occurs in a fuel-cell-based electrolyzer used to split water and generate hydrogen.

MIECs function similar to SOFC electrode materials. In oxygen-ion-conducting materials, the oxygen concentration gradients drive oxygen ions from the high-partial-pressure side of the membrane to the low-partial-pressure side, while electrons are transported through the bulk of the material to participate in electrochemical surface reactions. MIEC membranes can be viewed as a short-circuit fuel cell, with electron transport occurring within the material instead of through an external circuit. In addition, the driving force for oxygen transport can be tailored by carrying out chemical reactions on the surface of the membrane.

Mixed ionic-electronic conduction can be achieved in two ways, by selecting a material that either:

- supports both ionic and electronic conduction, or
- forms a two-phase composite of an ionic conductor and an electronic conductor.

Materials of construction for equipment used for oxy-fuel combustion, production of synthesis gases, or CO_2 separation typically require mixed oxygen ion and electronic conduction.

The overall process of oxygen transport (permeation) in an MIEC membrane is divided into three steps:

1. Reduction of O_2 to O^{2-} at one surface (the feed side) by the reaction:

$$0.5O_2(g) + 2e^- \rightarrow O^{2-}$$

2. Coupled transport of O^{2-} and two electrons in opposite directions through the bulk membrane.

3. Oxidation of O^{2-} to O_2 and $2e^-$ at the other surface (the permeate side) by the reaction:

$$O^{2-} \rightarrow 0.5O_2(g) + 2e^-$$

The driving force for oxygen transport is the difference in chemical potential between the feed and permeate sides of the membrane. Figure 4 (next page) illustrates this principle for a dual-phase material consisting of an electronic conductor and an ionic conductor.

In addition to the bulk transport of oxygen ions and electrons, MIEC membranes are also subject to surface effects that impact performance. A common principle of mass transport across a membrane is that flux is inversely proportional to the membrane thickness. However, the actual

Table 1. Solid-oxide fuel cell systems can be used for power generation at different scales.

Size	Class Rating	Efficiency (Net Alternating Current, LHV)	Fuel Type	Applications
Small-Scale	<10 kWe	<35%	Pipeline natural gas Coal gas Gasoline	Residential (electricity, heating, cooling) Auxiliary power unit (APU) on heavy-duty trucks Cellular phone transmission towers Battery chargers
Medium-Scale Industrial	100–1,000 kWe	>45%	Pipeline natural gas	Credit-card data processing centers Hospitals (which cannot tolerate a power outage)
Large-Scale Dispersed	2–10 MWe	>48%	Pipeline natural gas Coal gas	Larger industrial units Small communities
Ultralarge-Scale Central	100 MWe	>60%	Pipeline natural gas Coal gas	Baseload power generation

flux is also a function of the kinetics of any reactions occurring on the membrane surface. As membrane thickness is reduced to achieve a higher gas flux, surface and interfacial effects become more important and can dramatically impact membrane performance *(6)*.

A critical thickness exists at which further reduction in thickness does not increase transport. In typical oxygen separation membranes fabricated by conventional ceramic processing techniques, this critical thickness is on the order of 80–100 µm. Surface exchange or catalyst layers are often applied to membrane surfaces to enhance the performance.

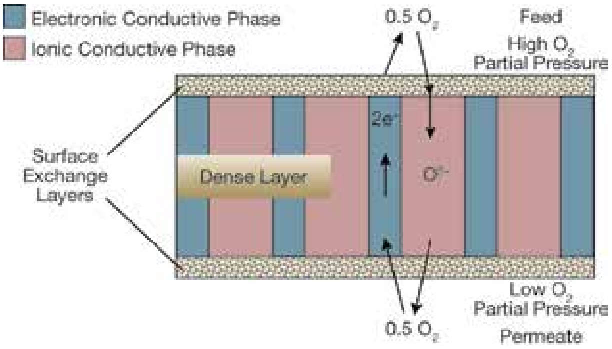
Membranes can be fabricated in a planar or tubular geometry by physical vapor or chemical deposition methods that create thin, dense layers on porous supports. Systems can be made of materials that conduct a variety of ionic species. For example, ceramic-based proton-conducting materials enable H_2 separation *(7)*, while carbonate ion conductors enable CO_2 separation *(8)*.

Applications of membranes

Membranes meet the critical need for highly efficient and environmentally friendly utilization of existing fossil fuel resources during the transition to sustainable (*e.g.*, renewable, nuclear) energy production. Applications currently being explored range from CO_2 separation to combustion in oxygen-rich environments, including partial oxidation of natural gas, oxy-combustion of coal, and oxidative coupling of natural gas upgrading to the production of higher hydrocarbons.

MIEC-based CO_2 separation membranes are composites consisting of two phases, a carbonate ion conductor and an electronic conductor. Typical configurations use a K_2CO_3 or Li_2CO_3 salt as the carbonate ion conductor within a porous metal support such as stainless steel or silver, which serves as the electronic conductor *(9)*.

Fossil fuels such as natural gas are strategically important raw materials for the synthesis of important value-added materials such as syngas *(10)*, liquid fuels *(11)*, methanol *(12)*, and ethylene *(13)*. Achieving cost-effective and large-scale hydrogen production has significant economic benefits and contributes to a cleaner environment *(14)*.



▲ **Figure 4.** A mixed ionic-electronic conductor (MIEC) membrane can be thought of as a short-circuit fuel cell, with electron transport occurring within the material rather than through an external circuit. Source: Adapted from *(5)*.

Catalytic steam reforming of natural gas:

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

has been the major route for syngas production. The reaction is strongly endothermic and requires high temperatures (~700–900°C) and pressures (~20–40 bar) to achieve the maximum conversion of CH_4 to H_2 and CO *(15)*. Furthermore, the product stream has a H_2/CO ratio of 3:1, making it unsuitable for production of liquid fuels via Fischer-Tropsch synthesis.

An alternative is the catalytic partial oxidation of natural gas:

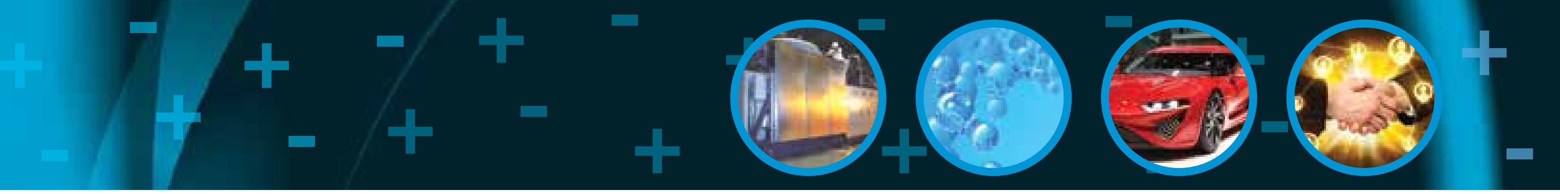
$$CH_4 + 0.5O_2 \rightarrow CO + 2H_2$$

This weakly exothermic reaction produces syngas with a H_2/CO ratio of 2:1, which is an ideal feed for making methanol or liquid fuels by Fischer-Tropsch synthesis.

However, if air is used as the oxidant, the syngas product becomes highly diluted with nitrogen. Ideally, pure oxygen would be used, but state-of-the-art pressure-swing adsorption (PSA) and cryogenic processes are highly energy-intensive and expensive. Membranes could perform both oxygen separation and catalytic partial oxidation of natural gas in a single process, at a cost that is as much as 30% lower than that of combining separate cryogenic air separation and autothermal reforming units *(16)*.

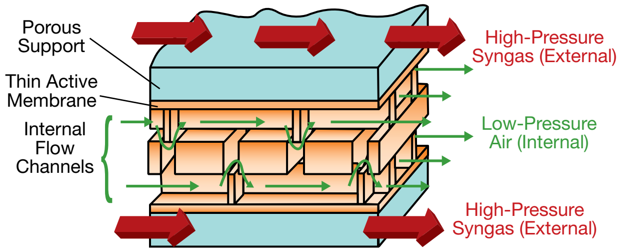
Large-scale membrane separation units have been aimed mainly at supplying oxygen for oxy-combustion of coal and production of syngas. Praxair developed an oxygen transport membrane system for coal-fired power plants that would provide oxygen for oxy-combustion and enable subsequent CO_2 capture *(17)*. Economic analysis indicated that the membrane separation unit has a higher overall efficiency than existing cryogenic air separation units.

Several material-related challenges remain in the development of membrane systems that can deliver large volumes of oxygen in harsh, real-world conditions. Since O_2 flux is inversely proportional to membrane thickness, research has focused on thin membranes on porous support substrates. These thin membranes are fragile and often prove difficult and expensive to manufacture. Research and development needs include: new materials with higher intrinsic (bulk) ion and electron conductivity, which underlies O_2 transport; materials that are stable at high temperatures and high oxygen partial-pressure gradients over long periods of time and in the presence of contaminants, such as sulfur in fluegas



from coal gasification; surface exchange (reaction) layers that can improve O_2 flux through thin membranes; and cost-efficient manufacturing techniques.

Air Products has partnered with Ceramatec to develop oxygen separation membranes for the production of syngas by partial oxidization as an alternative to autothermal reforming. The membranes combine air separation and steam reforming in a single unit, significantly reducing costs *(16)*. An additional advantage is that the use of high-pressure natural gas as the feedstock allows production of syngas with a high pressure that matches the requirements of downstream processes without additional compression. Air Products has built commercial-scale planar membranes (Figure 5) and tested them at a 27-Nm^3/hr pilot plant at syngas pressures up to 3×10^6 Pa and temperatures up to 1,323 K.



▲ **Figure 5.** An oxygen separation membrane can be used for syngas production. Source: Adapted from *(16)*.

Another application for membranes in the production of value-added chemicals is the oxidative coupling of methane for ethylene production.

The electrochemically controlled delivery of oxygen, in the form of oxygen ions, into the reaction zone minimizes the creation of byproducts, increasing selectivity and yield *(18)*.

Membrane reactors are increasingly being considered as a means to couple endothermic and exothermic reactions in thermoneutral, and thus more energy efficient, processes. Examples are the combination of partial oxidization of methane (exothermic) with steam reforming or with the thermal decomposition of CO_2 to CO and O_2 (endothermic).

Membranes: Challenges and opportunities

Research topics under investigation include membrane design; efficient, low-cost manufacturing strategies; and a variety of material science issues related to membrane stability under the required temperature, pressure, and gas-phase composition conditions. Chemical and mechanical stability in harsh environments, including ways to minimize surface poisoning and the demonstration of long-term membrane performance, are among the challenges that need to be addressed in order to move this technology into the marketplace. CEP

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