Hydrogen Production from Fossil Fuels with High Temperature Ion Conducting Ceramics

by Eric D. Wachsman and Mark C. Williams

Hydrogen is the most abundant chemical-energy resource in the world, but unlike oil and natural gas it is an energy carrier not an energy source. There are no H_2 wells available in the world. Further, we do not have a hydrogen infrastructure. The longest pipeline in the world is only 950 miles long. The largest plant operating today produces only 250 million standard cubic feet per day of H_2. Therefore, the hydrogen infrastructure must be created and production must be increased an order of magnitude to meet the U.S. Department of Energy (DOE) 2015-2018 projections.[1,2]

Historically, hydrogen has been produced from fossil fuels and for the foreseeable future will continue to be so. The major source of H_2 is steam reformation of natural gas. Therefore, improvements in the efficiency and cost of H_2 production from natural gas are necessary in the near term. Gas separation membranes and membrane reactors based on ion conducting ceramics may provide the technological advance necessary to increase the efficiency and reduce the cost of H_2 production from natural gas.[3-5]

However, other sources of H_2 must be developed for the envisioned hydrogen economy, and coal provides the greatest U.S. domestic resource-based option. The U.S. DOE is developing a FutureGen plant based on coal gasification, solid oxide fuel cells (SOFCs), and ion conducting membranes that will produce H_2 and electricity with zero emissions and carbon sequestration; thereby, not contributing to global warming.[6-8]

The future production of H_2 from fossil fuels requires advances in membranes and fuel cells. The importance and potential of ion conducting ceramics in SOFCs and ceramic membranes to hydrogen production, and their ultimate integration in a coal-based FutureGen plant are discussed.

Ion Conducting Ceramics

SOFCs, oxygen and hydrogen separation membranes are based on high temperature ion conducting ceramics. These ceramics are metal oxides with typically a perovskite or fluorite structure. In the oxygen-ion conductors, an oxygen ion moves from a filled (O_O^x) to a vacant ($V_O^{\bullet\bullet}$) oxygen site through a fixed cation lattice (M_M^x), as shown in Fig. 1a. Therefore, the actual charged solid-state ionic species involved in oxygen-ion transport is $V_O^{\bullet\bullet}$. In the proton-conducting oxides the proton is associated with an oxygen site ($OH_O^\bullet$) and hops between adjacent oxygen sites, as shown in Fig. 1b. Because oxygen and hydrogen are transported through lattice sites (*vs.* porous membrane diffusion) the gas separation selectivity is infinite.

Ionic transport is a thermally activated process and high ionic conductivities, ~1 S/cm, are achieved in the 600-1000°C temperature range. While these high temperatures create several materials issues, they are compatible with typical industrial gas processing (*e.g.*, catalytic oxidation and steam reforming) temperatures. Thus, ion conducting ceramics thermally integrate well with most conventional processes to convert hydrocarbon fuels to H_2.

Ion Transport Membranes and Membrane Reactors

Membrane reactor technology holds the promise to circumvent thermodynamic equilibrium limitations by *in situ* removal of product species, resulting in improved chemical yields. Recent advances in mixed-conducting oxide-
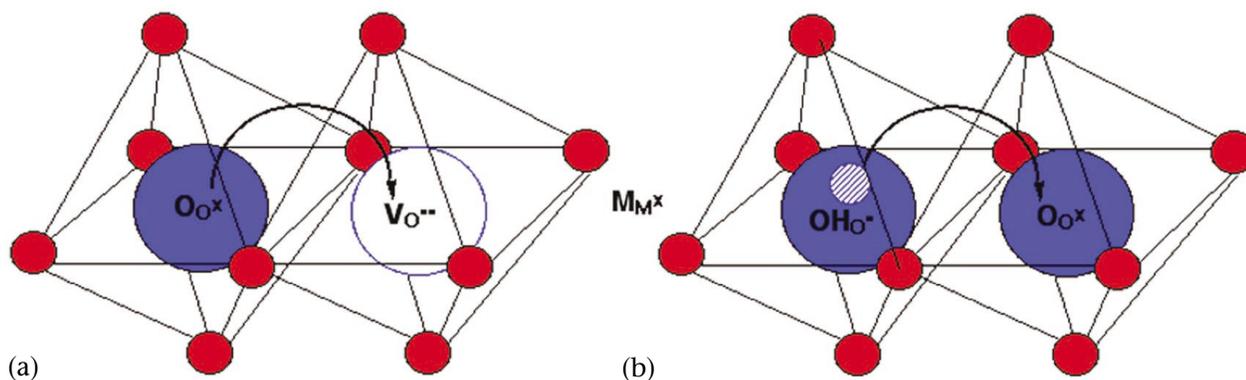

(a)   (b)

FIG. 1. (a) Oxygen ion transport; and (b) proton transport, in high temperature ion conducting ceramics.

membrane technology present the possibility for a dramatic reduction in the cost of converting petroleum and coal-derived feed stocks to hydrogen and other value-added hydrocarbons. Because of this potential, several major corporations (such as Air Products, BP, and Praxair) are actively pursuing development of this technology.

The major functional components of these reactors are the oxygen-ion and proton transport (or O_2 and H_2 separation, respectively) membranes and the oxidation, steam reforming, and water gas shift catalysts. The membranes are based on metal oxides (such as $La_{1-y}Sr_yCo_{1-x}M_xO_3$ perovskite-type oxides) that exhibit both ionic and electronic (mixed) conductivity. Because of their significant electronic conductivity, these mixed ionic-electronic conductors (MIECs) have an internal electrical short and the ionic species selectively permeates through a dense film of the material under a differential partial pressure. The potential permeation flux rates of these materials are extremely high. For example, based on the results of Teraoka et al.[9] and assuming the flux is bulk diffusion limited, calculated O_2 flux rates through a 50 µm thick membrane of $La_{0.6}Sr_{0.4}Co_{0.8}Cu_{0.2}O_3$ at 600°C are 22,400 L (STP) h^{-1} m^{-2} of membrane surface area under a 0.21 atm P_{O_2}-gradient.

Oxygen-Ion Transport Membranes

The perovskite-type oxides typically used are p-type semiconducting oxides so that a high degree of electron-hole (h•) conduction is obtained under oxidizing conditions. Because of the potential high O_2 flux of these materials under a simple air P_{O_2}-gradient, major industrial gas suppliers are developing what they have termed ion transport membranes (ITMs) to produce pure O_2 from air. By siting one of these ITM units next to a hydrocarbon processing unit, dramatic improvements in conversion efficiency are achieved because N_2 is removed prior to reaction of O_2 with the hydrocarbon feed stream.

Due to the thermal compatibility of these membranes with, for example, catalytic oxidation processes, membrane reactors are under development to integrate the partial oxidation of hydrocarbons, such as natural gas, to syn gas using an oxygen-ion transport membrane, as shown in Fig. 2a. The integrated process further improves efficiency and reduces cost.

Proton Transport Membranes

A series of perovskite-type oxides (e.g., $BaCe_{1-x}M_xO_3$, where M is a metal dopant) have been shown to have high proton conductivity at elevated temperature.[10,11] These materials are receiving considerable attention because of their numerous applications as H^+ electrolytes in fuel cells, hydrogen pumps, electrolyzers, and gas sensors.[12] $BaCe_{1-x}M_xO_3$-type protonic conductors have sufficient ionic conductivity to obtain comparable flux rates to the oxygen-ion conductors. However, they have insufficient electronic conductivity. The electronic conductivity is necessary to balance the transport of charge through the material, as shown conceptually for H_2 permeation in Fig. 2b. Further, it is desirable that the electronic conductivity is n-type (e' conduction) so that electronic conductivity is obtained under low P_{O_2} conditions. If comparable electronic conduction were obtained with the $BaCe_{1-x}M_xO_3$-type protonic conductors, they would be excellent H_2 permeation membrane materials, equivalent to palladium alloy films, but with the potential advantages of higher temperature operation (for thermal integration) and lower cost.

Because of the dramatic potential of these materials in H_2 production, several groups including Argonne National Lab, Georgia Tech, and the University of Florida, have been developing mixed protonic-electronic membrane materials. Most of the earlier work focused on
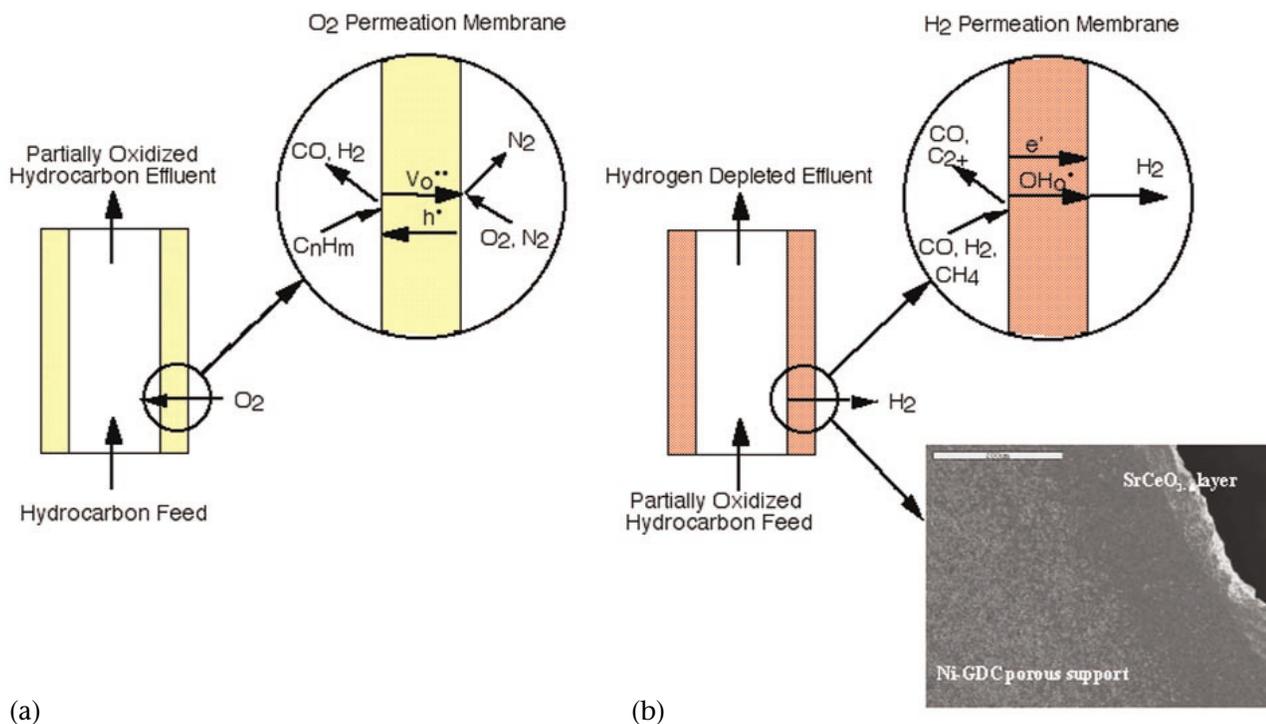

FIG. 2. (a) Integration of oxygen-ion; and (b) proton transport membranes (including SEM of actual membrane under development at the University of Florida) in conversion of hydrocarbon fuels to H_2.

developing composite membranes of the proton conducting oxide and a metal phase for electronic transport;[13] however, more recent work has shown that using a multivalent dopant cation, n-type electronic conduction may be achieved in a single phase material.[14-16]

This work has been supported by the Department of Energy (DOE) (through Argonne National Lab), CANMET, and the National Aeronautics and Space Administration (NASA). The latter being a Florida-based NASA initiative to develop a H_2 production facility at Kennedy Space Center (KSC). The reason for this initiative is not only the futuristic hydrogen economy, but the current reality that every time a space shuttle launches 50 tanker trucks of liquefied H_2 travel 600 miles from the petroleum refineries near New Orleans to KSC to provide fuel for the shuttle (Fig. 3).

Ultimately these two MIEC membranes can be combined in series, and integrated with partial oxidation, steam reforming, and water gas shift catalysts, also in series, to optimize the thermodynamics of hydrogen production. The first membrane separates O_2 from air (with infinite selectivity) and reacts any of the hydrocarbons in the feed to form CO and H_2, facilitated by an oxidation catalyst. The second membrane separates the H_2 (also with infinite selectivity) providing a pure H_2 gas stream. As the process gas stream continues through the reactor, any hydrogen that has not been separated tends to oxidize to H_2O. A water gas shift catalyst, with the introduction of additional H_2O, in the latter part of the reactor could push the conversion to higher H_2 yields.

F<small>IG</small>. 3. Supplying H_2 fuel for a space shuttle at Kennedy Space Center. Photo courtesy of Air Products and Chemicals, Inc.

| Table I. Solid Oxide Fuel Cells – Attributes.	
High electric conversion efficiency (%)	• Demonstrated 47 • Achievable 55 • Hybrid 65
Superior environmental performance	• No NO_x • Lower CO_2 emissions • Sequestration capable • Quiet; no vibrations
Cogeneration – combined heat and power (CHP)	• Coproduction of hydrogen with electricity • High quality exhaust heat for heating, cooling, hybrid power generation, and industrial use • Compatible with steam turbine, gas turbine, renewable technologies, and other heat engines for increased efficiency
Fuel flexibility	• Low or high purity H_2 • Pipeline or liquefied natural gas • Diesel • Coal gas • Fuel oil • Gasoline • Biogases
Size and siting flexibility	• Modularity permits wide range of system sizes • Rapid siting for distributed power
Transportation and stationary applications	• Watts to megawatts
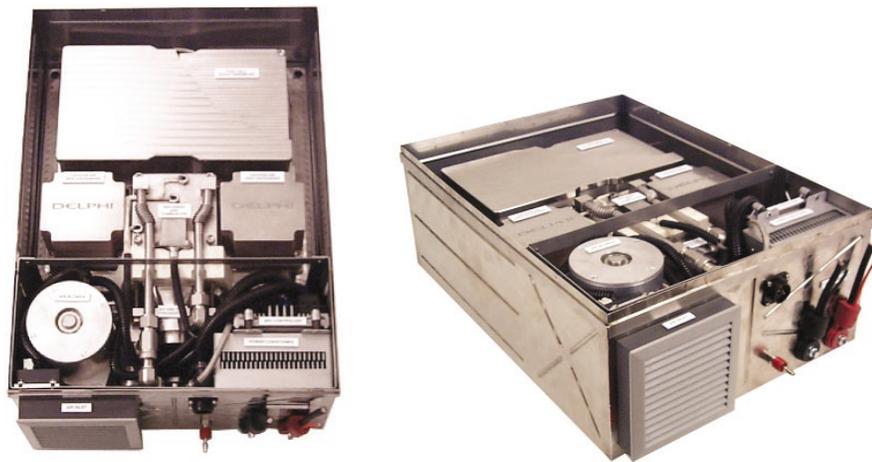
FIG. 4. Delphi SOFC APU.

Solid Oxide Fuel Cells

Fuel cells are electrochemical devices that use hydrogen and air to produce electricity and water with virtually no pollution.[17] The use of fuel cells is expected to bring about the hydrogen economy. Hydrogen fuel cell cars using low temperature proton exchange membrane (PEM) fuel cells could create the demand for the hydrogen infrastructure. However, commercialization of fuel cells is expected to proceed first through high temperature fuel cells such as SOFCs in portable and stationary applications, because they have more potential for combined heat and power (CHP) and the ability to use conventional fuels now. Two hurdles, fuel cell reliability and cost reduction, could occur through distributed generation (DG) deployment first, especially in buildings because buildings use two-thirds of all electricity.

SOFCs have many desirable attributes as shown in Table I that will help the long-term development of coal-based hydrogen systems.[18] They can operate on today's conventional fuels and thus provide a bridge to the hydrogen economy. Their potential for cost reduction with given mass customization is predicated on similar reductions achieved by the computer chip industry. Nevertheless, developing SOFCs that meet both performance and cost targets is a matter of complex trade-offs. That is why the U.S. DOE and industry have undertaken the ambitious Solid-

State Energy Conversion Alliance or SECA.[19-21]

SECA

SECA is the flagship stationary fuel cell program for the DOE. Its goal is the development and commercialization of modular, low-cost, and fuel flexible SOFC systems. Through advanced materials processing and system integration, R&D will bring SOFC costs to $400/kW for stationary and auxiliary power unit markets by 2010. Six industry teams, including Acumentrics, Cummins, Delphi, General Electric, FuelCell Energy, and Siemens Westinghouse, are working on designs and manufacturing schemes. SECA industry team needs may be different for the various system alternatives and their design, *i.e.*, anode supported, cathode supported, and electrolyte supported; planar, radial tubular.

While progress has been made in power density and utilization, the cathode remains an important area of research if low temperatures are to be achieved. To achieve low overpotentials at reduced temperature requires optimization of composition and structure. Mixed ionic and electronic conducting cathodes with sufficient catalytic activity are being considered. Seals are a long-standing issue in some SOFC designs. The requirements on the seal are demanding to ensure thermal cyclability and gastightness. The use of low-cost metallic interconnects is highly desirable for some designs. These issues

are being addressed by the industrial teams and by universities and national labs in the SECA Core Technology Program.

There has been early interest from auto manufacturers in SECA type fuel cells as evidenced by BMW's arrangement with Delphi, a SECA industry team developer, to put a compact SOFC for auxiliary power in BMW vehicles by 2007. A mock-up of the Delphi auxiliary power unit (APU) is shown in Fig. 4.

While these APUs are being designed to run on conventional fuels, such as gasoline, another important attribute of the SOFC APU is its ability to improve the efficiency and emissions of internal combustion engines (ICEs) through H_2 enrichment of the fuel mix. The SOFC operates on partially reformed gasoline as a fuel. The fuel is electrochemically converted to electricity and into lower hydrocarbons in an internally reforming SOFC. The resulting H_2-rich fuel in the anode exhaust is injected into the ICE resulting both in lower emissions and greater overall system efficiency. BMW is evaluating ICEs running on H_2-rich fuels; thus, this is another way SOFCs help transition toward a hydrogen economy.

The longer term goal is to aggregate SECA fuel cells into larger systems and to produce a very high-efficiency fuel cell-turbine hybrid module by 2020. The SOFC hybrid is a key part of the FutureGen plant where it will produce electric power and other parts could produce H_2 and sequester CO_2. The H_2 produced can be used in fuel cell cars and for large SOFC DG applications. The fuel cell or hybrid could operate on syngas or H_2 and segregation/isolation of CO_2 if operating on syngas is possible with some fuel cell designs. The key SECA/SOFC hybrid hurdles will be aggregation and integration.

Today, fuel cells are already operating on coal gas. Under the SECA Program, Delphi ran 2 x 15 cell, 100 cm^2, stacks at the Power Systems Development Facility in Alabama in June 2003. A FuelCell Energy (FCE) molten carbonate fuel cell (MCFC) ran on coalmine methane from September to December 2003 in Cadiz, Ohio. A much larger FCE 2 MW MCFC unit is being installed in Indiana. It will be operating on a coal and petroleum coke blend slipstream at the Wabash River gasifier this year.

Hydrogen from Coal - FutureGen

One way in the U.S. to produce H_2 should be with coal. Coal is an abundant resource in the U.S. and for energy independence should be used as the primary energy resource. Over 50% of the electricity in the U.S. comes from coal, and coal use is increasing.

FutureGen, the Integrated Hydrogen, Electric Power Production, and Carbon Sequestration Research Initiative, is a partnership to design, build, and operate a nearly emission-free, coal-fired electric and H_2 production plant. No coal-to-gas plant in the world today is configured to optimize H_2 production or to capture carbon. The FutureGen prototype plant would be the world's first. The 275 MW prototype plant will serve as a large scale engineering laboratory for testing new clean power, carbon capture, and coal-to-hydrogen technologies. It will pioneer advanced H_2 production from coal, as well as capture and permanently sequester CO_2. The captured CO_2 will be separated from H_2 by novel membranes currently under development. Two primary goals for FutureGen are as follows:

- Design, construct, and operate a nominal 275 MW (net equivalent output) prototype plant that produces electricity and hydrogen with near-zero emissions. The size of the plant is driven by the need for producing commercially relevant data, including the requirement for producing one million metric tons per year of CO_2 to adequately validate the integrated operation of the gasification plant and the receipt of geologic formation.

- Validate the engineering, economic, and environmental viability of advanced coal-based, near-zero emission technologies that by 2020 will (1) produce electricity with less than a 10% increase in cost compared to nonsequestered systems; (2) produce H_2 at $4.00 per million Btu (wholesale), equivalent to $0.48/gallon of gasoline (wholesale).

A representative FutureGen plant is shown in Fig. 5.[22] This configuration integrates all the ion conducting ceramic components: SOFCs, oxygen and hydrogen separation membranes. It consists of an O_2 blown advanced transport reactor (ATR) with hot gas cleanup followed by a shift unit and a high temperature membrane unit. This membrane unit separates the H_2. The tail gas from the membrane unit consisting primarily of CO, CO_2, portion of the H_2 that is not separated, H_2O, and inert gases such as N_2 are fed to the anode side of a SOFC. Air to the cathode side of the SOFC is supplied by the compressor of a gas turbine. The anode exhaust gas after heat recovery is fed to a second shift unit where additional H_2 is formed by shifting the remaining CO. The shifted gas, now mainly CO_2 with some small CO and H_2 content goes to a H_2 membrane separator to capture the 80% of the H_2 for recycle to the SOFC. Alternately, a membrane shift unit can be utilized. The non-permeate is fed to a catalytic combustor using O_2 from the ITM oxygen plant to fully remove the
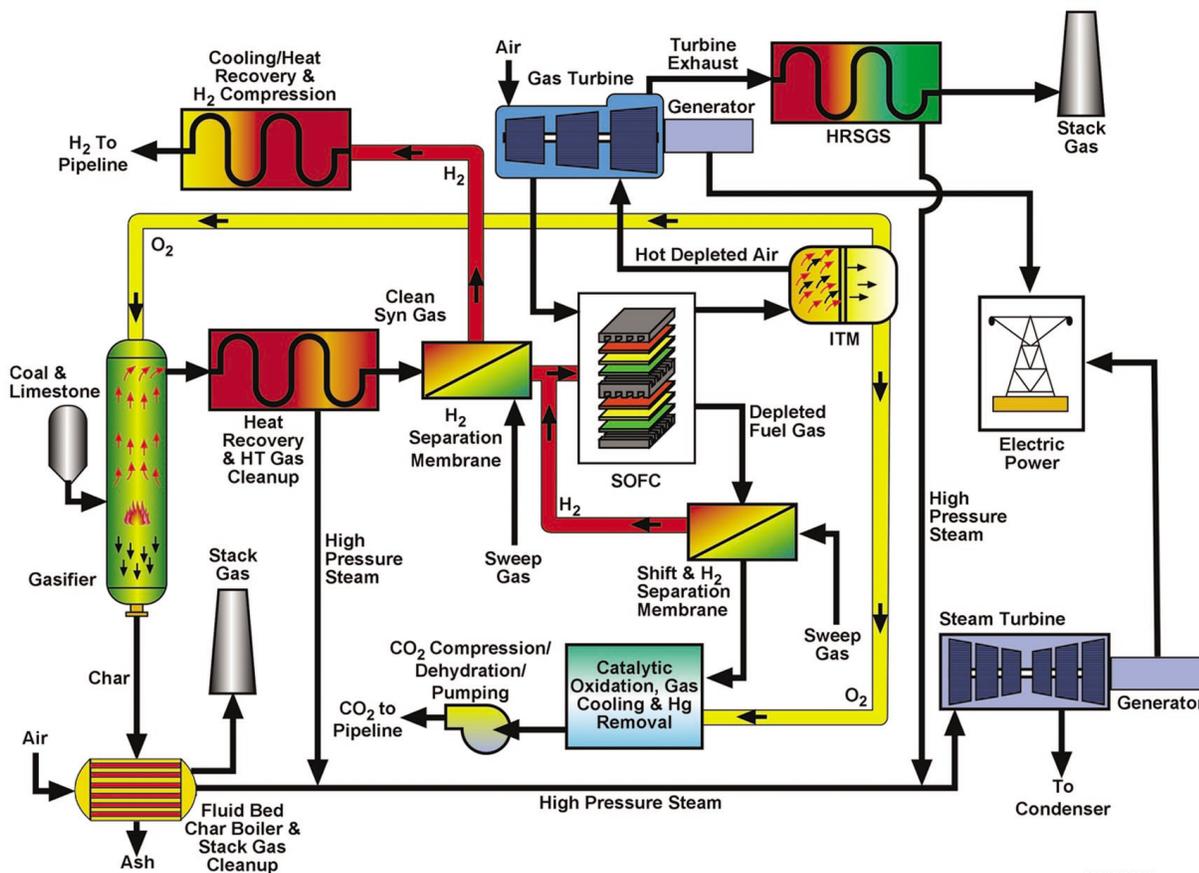

Fig. 5. FutureGen plant, converting coal to H_2 and electricity using ion conducting ceramic fuel cells and membranes.

small amounts of any remaining CO and H_2, leaving only CO_2, H_2O, and a very small amount of O_2 in the stream. This stream is cooled and pressurized to 2000 psi, for CO_2 sequestration.

On the cathode side, the compressed air, at approximately 20 bar, is heated in a regenerator (not shown in the diagram) prior to entering the SOFC. The hot depleted air exiting the cathode enters the hot side of the regenerator and is cooled to 900°C, the temperature required by the ITM unit for air separation. In this membrane unit, O_2 is removed from the already vitiated air and exits the unit at subatmospheric pressure. The 100% O_2 is cooled and compressed to gasifier pressure with a small side stream going to the catalytic cleanup burner. The non-permeate, now reduced in mass flow and pressure, is expanded in the turbine and exhausts to a heat recovery steam generator (HRSG) where it is cooled to 66°C.

Conclusion

Ion conducting ceramics play a major role in the production of H_2 from fossil fuels. Ongoing R&D on SOFCs and ceramic membranes will result in cost competitive and efficient systems for using and separating hydrogen. Collaborations among government, industry, and universities like SECA and FutureGen will provide systems testing and verification. Hydrogen from coal with zero emissions and electric power is a viable reality. ∎

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