

# NEW MATERIAL NEEDS FOR HYDROCARBON FUEL PROCESSING: Generating Hydrogen for the PEM Fuel Cell

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■ **Abstract** The hydrogen economy is fast approaching as petroleum reserves are rapidly consumed. The fuel cell promises to deliver clean and efficient power by combining hydrogen and oxygen in a simple electrochemical device that directly converts chemical energy to electrical energy. Hydrogen, the most plentiful element available, can be extracted from water by electrolysis. One can imagine capturing energy from the sun and wind and/or from the depths of the earth to provide the necessary power for electrolysis. Alternative energy sources such as these are the promise for the future, but for now they are not feasible for power needs across the globe. A transitional solution is required to convert certain hydrocarbon fuels to hydrogen. These fuels must be available through existing infrastructures such as the natural gas pipeline. The present review discusses the catalyst and adsorbent technologies under development for the extraction of hydrogen from natural gas to meet the requirements for the proton exchange membrane (PEM) fuel cell. The primary market is for residential applications, where pipeline natural gas will be the source of H<sub>2</sub> used to power the home. Other applications including the reforming of methanol for portable power applications such as laptop computers, cellular phones, and personnel digital equipment are also discussed. Processing natural gas containing sulfur requires many materials, for example, adsorbents for desulfurization, and heterogeneous catalysts for reforming (either autothermal or steam reforming) water gas shift, preferential oxidation of CO, and anode tail gas combustion. All these technologies are discussed for natural gas and to a limited extent for reforming methanol.

## INTRODUCTION

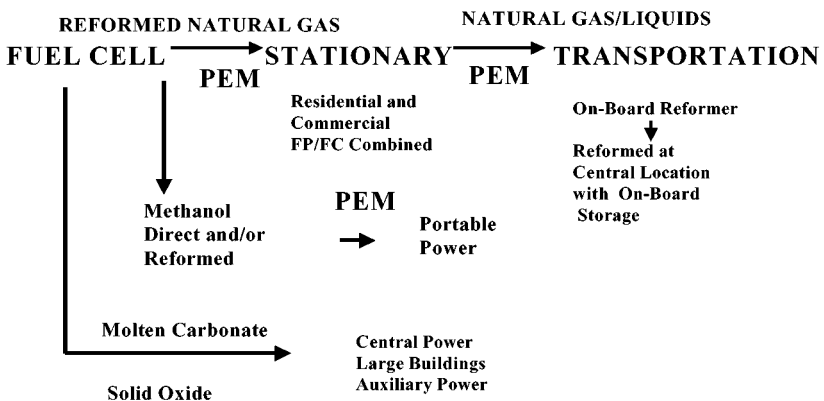
PEM (proton exchange membrane) fuel cells promise to be an efficient and clean alternative to fuel combustion for primary power generation for stationary and mobile source applications. They are about twice as fuel efficient as the internal

combustion engine and produce virtually no CO, HC, or NO<sub>x</sub>, and a reduced level of CO<sub>2</sub>. They operate on the basic principle of direct conversion of chemical energy into electrical energy, avoiding the mechanical steps and thermodynamic limitations of traditional combustion energy generation cycles. Hydrogen gas is electrochemically oxidized to hydrogen ions at the anode, which pass through a proton-conductive membrane to the cathode, where they combine with electrochemically reduced O<sub>2</sub> (from the air) producing H<sub>2</sub>O. The electrons flow through the external circuit providing power. The cells are stacked in series to produce the desired power.

A critical question involves the source of hydrogen. The ultimate hydrogen economy predicts that it will be generated from water via electrolysis with the power provided by the sun or wind. These technologies will be developed over a long term, so a transitional approach is necessary, the most likely would be to reform readily available hydrocarbon fuels to fuel cell quality hydrogen.

The goal of using fuel cells to power vehicles, given the cost and size requirements, will require major breakthroughs in new technologies. Some major car companies (Honda and Ford) have stated that cost-effective fuel cell vehicles for the mass market are 15 to 20 years away. The issue of H<sub>2</sub> infrastructure, for providing hydrogen to vehicles, is also a major complication that must be addressed. However, Toyota, Honda, Ford, and others have recently announced they will have fuel cell vehicles available for limited use by early 2003, but it should be understood that these vehicles are not cost effective or sufficiently reliable for the mass market. Clearly, there is a strong commitment to bring this new technology to commercial fruition.

The earliest market will be for stationary power generation. Fuel cells must first be successful for this before they can be applied to transportation applications. Figure 1 shows that stationary application is on the critical path for transportation.



**Figure 1** The road to commercialization for fuel cells.

Also shown is the parallel path to commercialization for portable power applications, where methanol is the likely fuel of choice. Molten carbonate and solid oxide fuel cells are also being developed for high-power applications (>250 kW); however, they do not require extensive fuel reformers because this function occurs within the anode compartment (1).

Distributed power applications will use the current natural gas and commercial propane infrastructure to generate H<sub>2</sub> in homes and at industrial sites. High efficiencies can be realized by combined cycle electricity and heat generation. Once this technology is implemented in the mass market, transportation applications will be more feasible, but breakthroughs in cost, size, and infrastructure are essential. It is expected that automotive applications will require on-board storage of H<sub>2</sub> distributed from a centralized location (equivalent to your local service station). The H<sub>2</sub> will be generated from natural gas or from a liquid fuel designed specifically for fuel cells (low sulfur, high paraffin content, without the necessity of optimizing octane or cetane numbers). On-board reformers, using liquid fuels, are viewed as a transitional solution until new H<sub>2</sub> storage technologies are developed.

The portable power market for laptop computers, cellular phones, and personal digital equipment is another potential application for fuel cells. Devices containing direct methanol or reformed methanol appear to be the approach to replace the heavy and cumbersome battery currently required. A small cartridge of methanol can provide sufficient power and can easily be replaced.

This review addresses the catalyst and adsorbent requirements and materials availability for reforming natural gas for stationary applications. The importance of the reactor design and its effect on the catalysts is also discussed. The technology developed will eventually be applicable to vehicles; however, this will require significant breakthroughs in cost, size, and applicability to the transient operation of a vehicle.

## PEM FUEL CELL

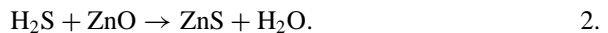
The PEM fuel cell is a solid polymer electrolyte, which operates at about 80°C, and is the most promising fuel cell system for residential and transportation due to its high-energy density (2). The proton-selective membrane is a fluorocarbon polymer of sulfonic acid called Nafion<sup>TM</sup>. The anode and cathodes are primarily Pt-containing materials.

At present, H<sub>2</sub> is the only fuel that can be electro-catalytically oxidized at the anode. Because there is no infrastructure available for hydrogen, the strategy is to use natural gas, liquefied petroleum gas (LPG), and heating oil from which H<sub>2</sub> can be generated for stationary applications. Liquid fuels, specially formulated for fuel cells, could be made available at centralized service stations for transportation applications.

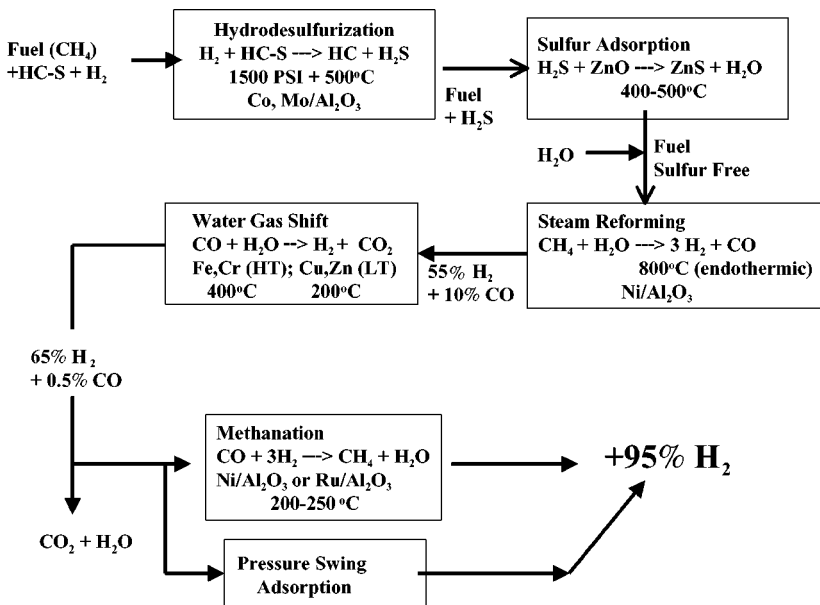
## CONVENTIONAL CATALYSTS AND PROCESSES FOR THE SYNTHESIS OF INDUSTRIAL GRADE HYDROGEN

The catalytic synthesis of  $H_2$  from hydrocarbons has been practiced in the chemical industry for many years (3, 4). The unit operations for natural gas fuel processing are summarized in Figure 2. In the next section the limitations of this technology for fuel cells are addressed.

The first step for desulfurizing natural gas is catalytic (Co, Mo) hydrodesulfurization (Reaction 1) of the sulfur-containing hydrocarbon (R-S) at  $\sim 200^\circ\text{C}$  and at pressures up to  $\sim 300$  (20 bar). The  $H_2S$  produced is adsorbed on particulate ZnO (Reaction 2) at  $\sim 400^\circ\text{C}$ . Sulfur levels can be decreased to 0.02 ppm or 20 ppb (volume).



Sulfur removal is necessary owing to the sensitivity of the Ni-based catalysts for the primary steam reforming reactions shown in Reaction 3.



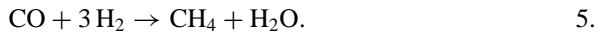
**Figure 2** Conventional unit operations for generating hydrogen from natural gas.

The reaction is highly endothermic and requires high-energy input (inlet temperatures exceed 800°C).

The exit from the steam reformer contains about 10–12% CO, which is fed to a high-temperature water gas shift (WGS) reactor containing an Fe-Cr catalyst (~350–400°C). This further increases the H<sub>2</sub> content and decreases the CO to about 2%, as governed by the thermodynamics of the exothermic reaction. The product gas is fed to a low-temperature WGS reactor containing a catalyst such as Cu, Zn, Al, (~200°C), where the CO is further decreased to less than about 5000 ppm thus generating more H<sub>2</sub>.



The remaining CO, which poisons downstream ammonia or methanol synthesis catalysts, is removed by pressure swing absorption or in some case methanation (Reaction 5) over a Ni- or Ru-based catalyst at about 250°C.



## LIMITATIONS OF CONVENTIONAL PROCESSES AND CATALYSTS FOR HYDROGEN GENERATION FOR PEM FUEL CELLS

Weight, size, transient operations, and consumer safety are critical considerations for fuel cell applications, thus new technologies will have to be developed to meet these requirements. The limitations of the traditional technologies are

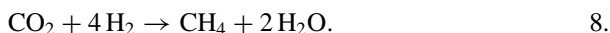
- Nickel steam reforming catalysts are extremely sulfur sensitive and deactivate readily in the presence of traces of sulfur.
- Hydrodesulfurization operates with pressure far in excess of that available from the existing infrastructure of natural gas.
- Nickel in its active state is pyrophoric; if exposed to air it will generate excessive amounts of heat that causes sintering and can be a fire hazard.



- Steam reforming is an endothermic process requiring complicated engineering for heat management.
- Cu- and Fe-based WGS catalysts require slow and careful reduction, not to exceed 300°C, to avoid loss of activity caused by sintering. After activation, the catalyst is highly reactive toward air, and therefore can be a fire hazard to the consumer.



- Methanation of CO requires removal of CO<sub>2</sub>.

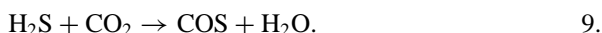


- Ni methanation catalysts are pyrophoric.
- Pressure swing adsorption requires high pressure.
- Large H<sub>2</sub> plants operate at steady state. They are not designed for the numerous start-ups and shut-downs that are required for fuel cells. Frequent departures from steady-state operation are chemically and physically damaging to catalysts and other materials in the reformer.

## ALTERNATIVE CATALYSTS AND ADSORBENTS/ PROCESSES FOR GENERATING H<sub>2</sub> FOR PEM FUEL CELLS

### Sulfur Removal

Natural gas composition varies by region and locality due to differences in its source, processing, and the choice of sulfur odorants. Before introduction to the pipeline, natural gas from the ground is processed to meet limits on hydrogen sulfide, water, hydrocarbon condensibles, energy content, and inert gases (CO<sub>2</sub> and N<sub>2</sub>). The sulfur content of pipeline natural gas in the United States is 4 to 8 ppmW (ppm on a weight basis) and usually contains H<sub>2</sub>S, COS, methylmercaptan, and trace amounts of dimethylsulfide (5). The COS is the product of the reaction between CO<sub>2</sub> and H<sub>2</sub>S:



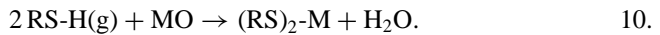
The local natural gas distributor will add a sulfur odorant package from 5 to 20 ppmW. The odorants are typically blends of butyl- and propylmercaptan isomers, sometimes containing dimethylsulfide or methylethylsulfide (6). Blends containing tetrahydrothiophene are also used. In Europe the preferred odorants are dimethylsulfide and tetrahydrothiophene. European natural gas has extremely high concentrations of COS (20 ppmW) because of its higher H<sub>2</sub>S concentration and the reaction with CO<sub>2</sub>. Japan imports liquified natural gas and controls the addition of odorants in a systematic manner making adsorbent designs more simple than in other parts of the world.

Sulfur compounds, present as odorants, are poisons for many downstream catalysts especially for the anode. They are also poisons for any base metal oxide catalysts present in the processor. Consequently, it is necessary to decrease the sulfur levels to the <10 ppb to maximize durability.

In the plant scale production of synthesis gas, hydrocarbon desulfurization is performed upstream of the Ni steam reforming catalyst because this catalyst is extremely sensitive to sulfur poisoning. The process uses a hydrodesulfurization (HDS) catalyst, typically Co-Mo/Al<sub>2</sub>O<sub>3</sub>, to convert the organo-sulfur compounds to H<sub>2</sub>S, followed by H<sub>2</sub>S scrubbing with ZnO to S concentrations in the hydrocarbon feed of less than 0.02 ppmvol (ppm on a volume basis). Hydrogen (H<sub>2</sub>) partial

pressures of up to 200 bar (3000 psig) and temperatures up to 500°C are required for HDS of liquid fuels, and with ZnO scrubbing of the H<sub>2</sub>S at temperatures of 300 to 400°C (7). Because the sulfur compounds in natural gas and LPG are non-aromatic and of low molecular weight, HDS can be performed at lower H<sub>2</sub> partial pressures, typically 1 to 20 bar (15–300 psig), depending on the catalyst, and temperatures of 200 to 400°C (8).

The adsorption of sulfur-containing odorants or native organo-sulfur species in natural gas needs to be accomplished with specially designed materials at atmospheric pressure and essentially room temperature. No single adsorbent will remove all sulfur compounds under these mild conditions. Activated carbons will adsorb only the higher-molecular-weight species (C<sub>3</sub> and higher), but have low capacity (typically <1 gS/100 g). Their capacity and adsorptivity for H<sub>2</sub>S and ethylmercaptan is improved by impregnation with alkali earth or transition metals, typically potassium, copper, iron, chromium, or some combination thereof. The reaction of mercaptans and hydrogen sulfide with the metal oxide probably proceeds by the formation of the metal sulfide:



Metal-impregnated carbons have an extremely low capacity for COS and dimethylsulfide (<0.5 gS/100 g). Zeolite adsorbents trap dimethylsulfide and higher-molecular-weight sulfur species with high capacity (1.5 to 3 g/100 g). Typical organo-sulfur adsorbent bed volume for United States application is about 20 liters for average power for a 1-year time on stream. Removing COS from the hydrocarbon stream remains a difficult task. This is not as severe a problem in the United States as it is in Europe, where COS concentrations can be extremely high.

An alternative to trapping sulfur compounds upstream of the reformer is to remove them downstream of the reforming catalyst but upstream of the WGS catalyst. This is a viable approach for precious metal–reforming catalysts owing to their tolerance to sulfur. Base metal (i.e., Ni) steam reforming catalysts are irreversibly poisoned by sulfur, and therefore sulfur trapping must be accomplished upstream. For precious metal catalysts used in autothermal reforming (ATR) (see below), the sulfur compounds are converted to H<sub>2</sub>S, which is removed in a bed of ZnO at the exit of the ATR reformer. However, the high steam concentrations in the reformat severely decrease ZnO capacities for sulfur below 0.1 gS/100 g. This is in contrast to the 10 to 20 gS/100 g capacity observed for ZnO in pre-reformer HDS scrubbing applications with little or no steam present.

The sulfur removal task for LPG is even more challenging than it is for natural gas. Sulfur levels in special-duty propane (HD-5 of GPA Standard 2140), designed for internal combustion engine use, can be up to 120 ppmW without the addition of the odorant. Heavier hydrocarbon (C<sub>4</sub><sup>+</sup>) concentrations can be as high as 2.5% and that of propylene up to 5%. Because of the higher sulfur levels, adsorption bed volumes will need to be proportionally higher. Atmospheric pressure HDS, using precious metal catalysts and ZnO H<sub>2</sub>S adsorption bed pre-reformer, is an attractive alternative for use with LPG.

Improved adsorbents and/or alternative processes for removing sulfur are needed to minimize size and expense of current strategies.

## REFORMING

### Steam Reforming

Catalytic steam reforming process (Reaction 3) operates at high temperature (above 800°C for CH<sub>4</sub>) and low space velocity (GHSV at 3000 to 8000 1/h) owing to slow kinetics (4). These conditions are not desirable for a reformer involving transient duty cycles. However, it produces the highest yield of hydrogen compared with partial oxidation and ATR processes, thus overriding many of its disadvantages. The endothermic heat can be supplied by the proper reactor design and/or use of heat exchangers. The particulate catalyst can be present in a series of tubes surrounded by a combustion gas that transfers heat through the tubes to supply heat to the endothermic reaction. One can also envision a steam reforming catalyst applied to one wall of a heat exchanger, the other side coated with a combustion catalyst to provide the heat. However, this requires a much more active catalyst than the Ni-based materials because less catalyst material can be deposited on the wall compared with that of a packed bed.

Ni-based catalysts are cost effective and commercially available but have a number of drawbacks when considered for fuel cell applications. For instance, they have a high propensity toward coke formation and thus require careful operational control (e.g., high H<sub>2</sub>O-to-C ratios). In an active state, Ni-based catalysts are pyrophoric (reaction with air is highly exothermic) and thus pose potential dangers for the consumer market. They are intolerant to sulfur, which puts greater demand on upstream sulfur removal processes. Finally, as a particulate they are prone to attrition and dusting, especially in vehicular applications.

Finding more cost-effective active catalysts with diminished tendencies to form coke, a greater tolerance to sulfur, and safe handling properties continues to be an issue.

Precious metal catalysts are candidates because of their intrinsic high activities, tolerance to sulfur and non-pyrophoric nature. They are far more active than Ni-based materials (4, 9), which permits decreased reactor size and/or lower temperature operation.

Rh on Al<sub>2</sub>O<sub>3</sub> (10) or MgO (11) as a support displayed high and stable activity. A 0.5 wt% Ru on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> showed comparable activity to a 15 wt% Ni on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (12). Pd, when supported on ceria, showed good steam reforming activity for CH<sub>4</sub> (13) and light hydrocarbon fuels (14). The higher activity of Pd/ceria than that of Pd/silica and Pd/alumina was attributed to ceria's ability to facilitate oxygen transfer needed for the steam reforming (15). Ce-supported Pd also demonstrated a greater resistance to coke formation when operating at lower H<sub>2</sub>O/C ratios.

Catalytic steam reforming of methanol as a hydrogen source is drawing interest for portable power fuel cell application.





The reaction is only moderate endothermic, therefore it requires relatively low-process temperature (200 to 400°C) with low steam-to-carbon ratios to produce a reformat with high H<sub>2</sub> concentration. Using a 1.5 H<sub>2</sub>O/C ratio improves the methanol conversion. The excess water also decreases the reverse WGS reaction that converts H<sub>2</sub> and CO<sub>2</sub> to H<sub>2</sub>O and CO. Its low-operating temperature makes it a suitable candidate for providing H<sub>2</sub> for portable power systems.

Commercially available methanol steam reforming, Cu-based catalysts deactivate when exposed to liquid water during a shutdown mode. Furthermore, the catalysts' pyrophoric nature makes them unattractive candidates for portable power applications. Recent studies show that Pd-supported catalysts have high activity for methanol reforming and high selectivity toward H<sub>2</sub> formation (16–18). The activities of Pd-containing catalysts are enhanced by formation of Pd-Zn alloys (19).

## Autothermal Reforming of Natural Gas

The reforming technology that appears the most suitable for mobile applications is ATR because of the adiabatic design permitting a compact smaller reactor, with low-pressure drop. The design combines a partial oxidation reaction, which provides the energy for the endothermic steam reformer.

The ATR process has been widely used as a secondary reformer in hydrogen plants producing ammonia. A given amount of methane is burned homogeneously to produce heat for the subsequent steam reforming reaction inside the reformer (20). In the late 1970s, several autothermal reformers (21, 22) were developed to produce hydrogen from diesel oil for fuel cell applications, and these reformers used catalytic combustion and steam reforming catalysts to convert diesel oil over metal oxide and/or Ni/Al<sub>2</sub>O<sub>3</sub> catalysts. In early 1980s, Engelhard developed a catalytic autothermal reformer (23–25) to produce synthesis gas from diesel oil, jet fuel, LPG, and natural gas. The unique feature of this system is the use of a monolithic-supported Pt/Pd partial oxidation catalyst to produce CO, H<sub>2</sub>, and heat in the first reaction zone at a very high space velocity (>125,000/h). The product gas and heat is then passed through a supported Pt/Rh catalyst where the steam reforming reaction occurs at a space velocity of <6000/h. This reformer was demonstrated to produce CO and H<sub>2</sub> synthesis gas for the production of ammonia, methanol, and liquid hydrocarbons (26–29).

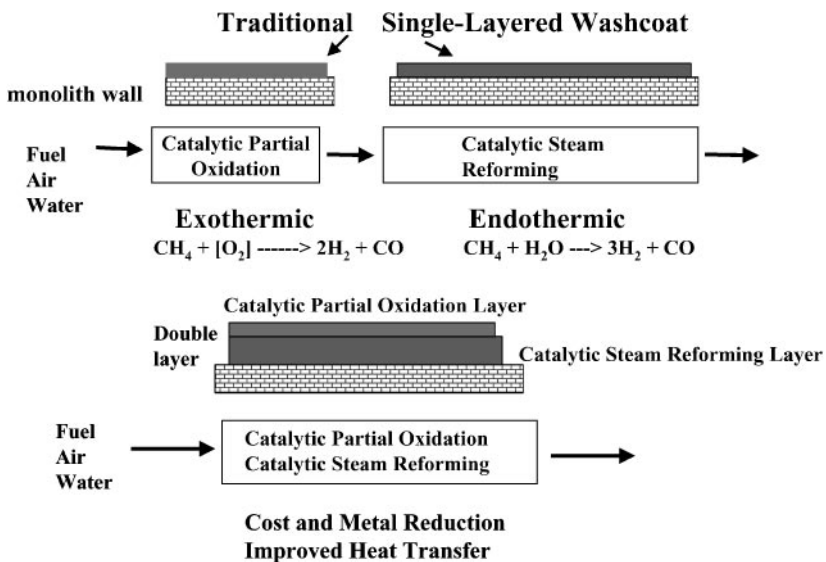
To produce H<sub>2</sub> from natural gas for the PEM fuel cell application, an autothermal reformer, which utilizes the monolithic Pt/Pd CPO and monolithic Pt/Rh SR catalysts, was incorporated into an integrated fuel processor system (30). As shown in Table 1, about 45 to 49% of equivalent H<sub>2</sub> could successfully be produced from natural gas, LPG, gasoline, and diesel oil even in the presence of large amounts of sulfur. For example, Table 1 shows that diesel fuel with up to 2000 ppm sulfur can be processed with ATR without coke formation or permanent deactivation. Clearly the performance is much better in the absence of sulfur, but its function continues, albeit with some inhibition, with sulfur present. However, when a Ni/Al<sub>2</sub>O<sub>3</sub> steam reforming catalyst is used with diesel fuel, it is completely deactivated in the presence of sulfur and large amounts of coke are formed in less than 100 h of operation (24).

**TABLE 1** Typical catalyzed ATR reformer outlet gas composition (30)

	Natural gas	LPG	Gasoline	Diesel 2000 ppm S
H <sub>2</sub>	40.1	42.0	37.2	36.7
CO	11.1	12.9	14.8	15.1
CO <sub>2</sub>	11.7	7.5	10.5	10.9
CH <sub>4</sub>	1.1	0.4	1.1	0.9
N <sub>2</sub>	36.0	37.2	36.4	36.4
Equivalent H <sub>2</sub>	46.1	46.6	45.3	45.0

The first generation of ATR catalysts was developed using the sequential reaction zone concept. Recently, a second generation of ATR catalysts was developed that is based on the overlapped reaction zone concept (31).

As shown in Figure 3, the double-layer ATR catalysts consist of a Pt/Rh steam reforming catalyst in the bottom washcoat layer and a Pt/Pd CPO layer as the top layer. The CPO reaction is very fast relative to the SR reaction. As the heat is released in CPO, it is consumed by the SR reactions immediately without going through any heat transfer barriers. The large heat release drives the rate of SR reaction. This phenomenon moderates the maximum temperature in the catalyst thereby decreasing the overall thermal stress on the catalyst. Therefore, a double-layer catalyst can manage the reaction heats more efficiently when the CPO and the SR are in intimate contact with each other (32).



**Figure 3** Autothermal reforming: double-layer monolith technology.

The HotSpot Hydrogen Generator was introduced in 1988 for producing hydrogen from methanol by using two sequential layers of pellet catalysts (33, 34). For cold start, a noble metal oxidation catalyst in the second layer was used to initiate a total oxidation reaction, and the heat generated was transferred back to the first base metal oxidation layer. This reformer could produce hydrogen automatically from methanol primarily by using the CPO reaction at 600°C. Recently, a more efficient radial flow autothermal reformer, which uses Cu/SiO<sub>2</sub> and Pd/SiO<sub>2</sub> for CPO and SR reactions, was used to produce hydrogen from methanol and hydrocarbons fuels (35, 36).

To obtain the maximum thermal efficiency it is important to match the catalysts and the ATR's operating conditions. Selecting the proper O<sub>2</sub>/C and H<sub>2</sub>O/C coupled with inlet temperature gives the engineer great flexibility to optimize the design. Other designs are also under investigation (37–43).

## Water Gas Shift

The product from the reformer contains up to 12% CO for steam reforming and 6–8% CO for ATR, which can be converted to H<sub>2</sub> via the WGS (Reaction 12). The shift reactions are thermodynamically favored at low temperatures, but the kinetics are so slow that large volumes, i.e., low space velocities <2000 h<sup>-1</sup>, are required. The product gas is typically no greater than 2000 ppm CO for low-temperature shift.

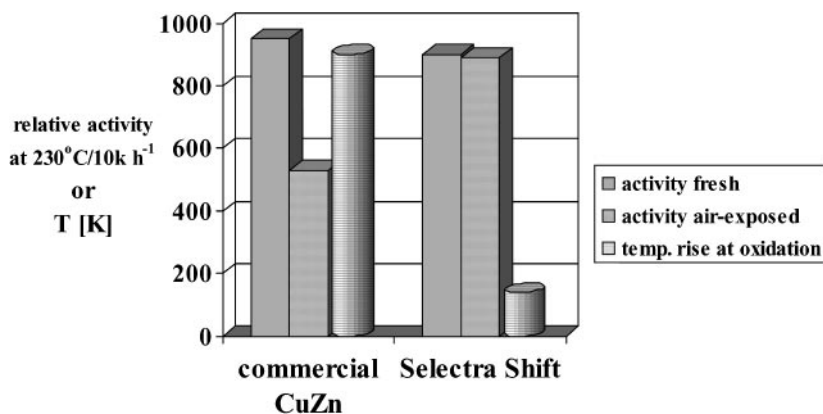


A critical property that must be designed into all shift catalysts is the absence of pyrophoricity, a property that makes the conventional Fe,Cr high-temperature shift (HTS) and especially the Cu-Zn low-temperature shift (LTS) catalysts impractical and dangerous for fuel cell applications. Exposure to air as a result of an accident or a maintenance mistake will render the conventional catalysts completely unsafe because an exothermic reaction of over 650°C is typical (44). Furthermore, because of the exothermic nature of the reduction of the conventional catalysts and their sensitivity to sintering, the activation in reducing gas must be carried out with very slow heating and careful temperature control that is impractical in the field. Discharging a pyrophoric catalyst from the processor also requires very careful passivation with dilute air to avoid excessive and unsafe temperatures.

## Base Metal Catalysts—Pro and Con; Examples of New Materials

Despite increasing research efforts in the area, few examples of base metal WGS catalysts suitable for fuel cell applications have appeared in the literature (Figure 4). A non-pyrophoric base metal catalyst, SELECTRA,<sup>TM</sup> was published by Ruettinger et al. (44). The catalyst has activity comparable to that of the industrial LTS catalyst composed of Cu-Zn-Al, but it does not need controlled activation protocols and requires no special care when exposed to air.

A copper/ceria catalyst was demonstrated (45) to have better enhanced thermal stability than Cu-Zn; however, it had much lower activity than the commercial LTS



**Figure 4** Activity and stability toward air exposure for a non-pyrophoric base metal WGS particulate versus commercial CuZnAl.

catalyst and had to be operated at higher temperature (46). In addition, copper/ceria catalysts have the same inherent sensitivity to sulfur as all copper-containing WGS catalysts. Table 2 shows a comparison of kinetic data for various Cu-containing catalysts. It is clear that Cu-Zn-Al is still the most active material in this group.

A new class of catalysts for the WGS reaction are the transition metal carbides and nitride (47).  $\text{Mo}_2\text{C}$  shows activity similar to that of commercial LTS catalysts and may be less sensitive to sulfur. However, the difficult synthesis of these materials and the fact that they may be pyrophoric make them less likely candidates for fuel cell reformer use.

Another class of WGS catalysts that has seen a renaissance in research activity are Co-containing materials. Co-Mn, Co-Cr (48), and new cobalt metal oxide catalysts (49) all show better activity than Fe-Cr above  $300^\circ\text{C}$ . Co-Mo catalysts (50) seem to have lower activity, but are highly sulfur tolerant. The main advantage of cobalt catalysts seems to be that they show relatively higher stability toward sulfur than do other base metal catalysts and therefore a cost advantage over precious metal materials. However, the low activity between 200 and  $300^\circ\text{C}$  makes them less useful for LTS applications.

**TABLE 2** Rate data for WGS catalysts (46) at  $200^\circ\text{C}$

	8%CuO/CeO <sub>2</sub>	8%CuO/Al <sub>2</sub> O <sub>3</sub>	Cu-Zn-Al
Rate $\text{mol} * \text{g}_{\text{cat}}^{-1} * \text{s}^{-1}$	0.11	2.9	7.6
Rate $\text{mol} * \text{g}_{\text{Cu}}^{-1} * \text{s}^{-1}$	1.73	45.6	21.7

Cu-exchanged zeolites have been explored for the WGS reaction as well (51–53). The idea of ion-exchanging zeolites with Cu cations is appealing because this would essentially produce a 100% dispersed Cu. Activities of these materials have been moderate to low and as such have not gained much further attention.

## Precious Metal Catalysts

Precious metal catalysts have obvious advantages over base metal catalysts in that they are non-pyrophoric, stable at high temperatures, and more tolerant of catalyst poisons such as sulfur. However, the high cost of such catalysts, together with the relatively low activity of alumina-supported precious metal versus copper (54), has made them unattractive for industrial use. Furthermore, the zero order CO kinetics limits their effectiveness to low CO (<3%) concentrations. Nonetheless, the advent of residential and automotive fuel processor development has led to a renewed interest in these materials, especially as monoliths.

It was realized at least 20 years ago that ceria-supported platinum has good activity for the WGS reaction (55). Indeed, Pt/ceria catalysts have about 15 times higher activity than Pt/alumina for the WGS reaction at identical Pt loadings (46). Ceria-containing, automotive three-way catalysts are taking advantage of the WGS reaction to reduce CO emissions (56). Studies by Gorte's group (57, 58) have shown that the catalytic activity of these materials is largely independent of the nature of the precious metal but depends on the crystallite size of the ceria support. A bi-functional mechanism for the WGS reaction was invoked, where the ceria surface is reduced by CO spilling over from the Pt surface. The reduced ceria is then re-oxidized by steam. This mechanism appears consistent with data collected under model conditions (57, 58) but may not explain data collected under realistic fuel processing conditions (46). Tests of initial activity of Pt/ceria catalysts versus commercial Cu-Zn-Al point to an advantage at high-space velocities. Whereas the base metal catalyst showed a mass-transfer limited rate, the Pt/ceria catalyst does not and therefore can be operated at high temperatures (where kinetics are sufficiently fast) using a small catalyst volume. However, the low-temperature activity is insufficient to achieve cost-effective low CO outlet concentrations.

The practical use of Pt/ceria catalysts for automotive fuel processors may therefore be limited by their high cost. In addition, a recently published report points out problems with catalyst stability under realistic conditions (59). Pt/zirconia catalysts have received some attention as sulfur-tolerant WGS catalysts (60, 61). However, their lower activity compared with that of Pt/ceria makes them even less cost effective. Gold catalysts have been shown to be excellent low-temperature CO oxidation catalysts and recently have received more attention for the WGS reaction (62–65). Catalytic activities can be high, and the catalysts are reported to be stable at temperatures below 300°C. However, gold catalysts lack stability toward higher temperatures, and activity is very sensitive to the preparative procedure; even with use of identical procedures, results are not always reproducible (65).

It is clear that an ideal catalyst for the WGS needs to be developed, especially for mobile applications. Indeed, Cu-Zn still dictates the performance standard for

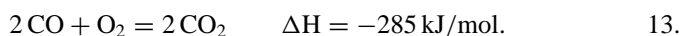
fuel cell reformers, even though its pyrophoricity is prohibitive for its use. Higher activity is always desired, as well as the tolerance to flooding and sulfur. In that respect, a precious metal catalyst has obvious advantages but often cannot compete with the price of a base metal system. A three- to fourfold increase in activity would be needed to achieve that advantage.

## Preferential Oxidation of CO

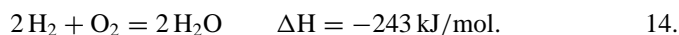
The exit concentration of CO from the WGS reactor is from 0.1 to 1.0% depending on operating conditions. It is essential to remove CO from the stream because it poisons the Pt anode of the PEM fuel cell (66). Whereas some manufacturers have a specification of 50 ppmvol of CO (and rely on an air bleed to the anode to further reduce CO in situ), others have an objective to reduce the CO to <10 ppmvol. The most effective mechanism for CO removal for fuel cell quality H<sub>2</sub> is selective oxidation. Because of the high ratio of H<sub>2</sub> to CO (>>100:1) in the reformat, the catalyst needs to be highly selective. The process to achieve this is called selective oxidation or preferential oxidation (PROX).

The objective of the PROX reaction is high CO conversion to CO<sub>2</sub> without excessive hydrogen oxidation (to water), i.e., to decrease the CO to less than 10 ppm.

$$1000 \text{ ppmvol} < \text{CO} < 5000 \text{ ppmvol},$$



$$400,000 \text{ ppmvol} < \text{H}_2 < 700,000 \text{ ppmvol},$$



Beginning as early as the 1960s preferential oxidation was used to remove CO from H<sub>2</sub> prior to ammonia synthesis (67–70). For example, Selectoxo<sup>TM</sup>, a particulate catalyst composed of an Fe-promoted Pt on alumina particulate (usually a tablet), reduces CO to the parts per million level from a hydrogen-rich stream (70).

Several factors must be considered in addition to the degree of CO conversion; the first factor is CO selectivity, which relates to the amount of air needed to react with CO. As the injected air increases, hydrogen loss, nitrogen dilution, and the heat generated through the exothermic oxidation of both H<sub>2</sub> and CO all increase. The temperature increase can lead to promotion of reverse WGS (Reaction 12) and methanation of CO (Reaction 5) and CO<sub>2</sub> (Reaction 8).

Second, the PROX catalyst must also work within the engineering constraints of the reactor. For example, the upstream WGS catalyst runs at >200°C, and the downstream PEM cell runs at 80°C. The PROX system may consist of two or more stages, depending on the inlet CO concentration and the amount of heat to be dissipated between stages. The sizing of the catalyst is also a critical parameter. It is understood that the catalyst needs adequate activity to handle the CO in the reformat at maximum flow. However, the reformer will, for the most part, run at reduced load. Therefore, it must function at varying flow. This is referred to as turndown. It is less widely known that, at low-space velocity, a Pt-based PROX

catalyst will produce CO by the reverse WGS reaction, in part because of the long residence time and the consumption of oxygen prior to the catalyst outlet.

## PROX Catalysts

The bulk of PROX catalyst formulations include a precious metal component, mostly Pt (71–73). The catalyst-mediated oxidation of CO is a multistep process, commonly obeying Langmuir-Hinshelwood kinetics for a single-site-competitive mechanism between CO and O<sub>2</sub>. In the first step, CO is chemisorbed on a surface site (e.g., Pt). At the same time, an oxygen molecule has to be adsorbed on a neighboring surface Pt site. The O–O bond cleaves and the oxygen atoms react with the surface-activated CO molecule to form CO<sub>2</sub>. An optimum range of O<sub>2</sub>/CO ratio is required in order to obtain the proper balance of adsorbed CO and adsorbed O<sub>2</sub> on adjacent sites. However, pure precious metals may lack the selectivity that is required for PROX. This is certainly the case for Pd, which has a strong affinity for hydrogen chemisorption.

Fe has been used to promote Pt (74, 75). The precious metal serves as the site for CO adsorption, whereas the Fe oxide promoter binds and dissociates the O<sub>2</sub> molecule, resulting in a noncompetitive, dual-site mechanism.

## ALTERNATIVES TO Pt FOR PROX

The literature has numerous citations of Ru as a catalyst for selective CO oxidation (68, 76). Two drawbacks exist with using Ru in this application. First, its recommended operating temperature is 140–200°C (77), well above the operating temperature of the PEM fuel cell (80°C); thus significant post-PROX cooling would be required. Second, Ru is an active methanation catalyst for both CO and CO<sub>2</sub>. In a recent patent application, it was recommended that the Ru be promoted with an alkali metal at a ratio of 1:7 (alkali:Ru), which lowers the operating temperature to about 100°C. Using a stream with 0.5% CO, a reference Ru catalyst had 250 ppm CO slip, whereas under the same conditions, Li- and K-promoted catalysts lowered CO to 69 and 22 ppm, respectively. In any case, the temperature must be controlled in a narrow range to avoid runaway methanation of the CO<sub>2</sub> in the process gas. A CO-selective Rh/alumina methanation catalyst has also been discussed (78).

The literature cites several other oxidation catalysts that have shown selectivity in the presence of hydrogen (79–82). These include Au, Pt, Pt/Ru, Ru, Rh, and Cu as the active metals, dispersed on various supports. Oh & Sinkevitch (79) compared the activities of alumina-supported precious metal PROX catalysts. Much of the published work with PROX catalysts has given unrealistic results because the experiments were performed in the absence of steam, an important reformat component. However, the work by Avgouropoulis et al. (83) has been highly informative because the experiments were performed with both CO<sub>2</sub> and steam present. Under these conditions, a highly active Au/alumina catalyst was deactivated fairly rapidly, whereas both Pt/alumina and Cu-CeO<sub>2</sub> had stable reactivity.

The fuel cell industry will benefit from a highly active PROX catalyst that does not exhibit reverse WGS activity or methanation of CO or CO<sub>2</sub>. This would permit deep removal of CO from a stream with >0.5% CO using a single PROX stage.

The use of precious metals for PROX is more expensive than base metals. However, the nearly complete recovery of the Pt in catalyst refining offsets the cost of the precious metal.

## PROX Catalyst Supports Particulates

A particulate, i.e., tablet, sphere, extrudate, powder, is the simplest form for a PROX catalyst. The catalyst can be prepared by impregnation and/or precipitation. Because the particle size of the metallic crystallites, as well as the chemical state of the metal, is crucial for catalytic activity, postdeposition treatment conditions (oxidative versus reductive temperature) are critical. During the PROX reaction, heat is released. The PROX bed can be passively cooled through radiant heat loss or actively cooled using a heat exchanger placed within the bed. Particulates including Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>, and Fe<sub>2</sub>O<sub>3</sub> are candidates for stationary applications but are unsuitable for use in mobile, e.g., automotive, sources where mechanical stability versus attrition needs to be optimized. Furthermore, the particulate bed introduces a pressure drop within the reactor, which may be acceptable for stationary installations but not for automotive use.

## Monoliths

The monolith approach is known for achieving high geometric surface area with little backpressure, and the catalyst layer, referred to as the washcoat, has little attrition in use. Monoliths can be ceramic or metal and have parallel channels, foams, or other structures. Because of the poor thermal conductivity of the ceramic monolithic support, which is normally cordierite, the monolith PROX catalyst operates adiabatically. There is a positive temperature gradient moving down the catalyst as the reaction moves toward completion. In this case, passive cooling is not useful. To control temperature, which is critical for maintaining selectivity and limiting side reactions such as reverse WGS and methanation, the PROX process can be divided between more than one monolith, with active cooling between stages. In multistaged designs, the injection of air can be distributed among the stages to optimize conditions for each stage (84, 85).

## Coated Heat Exchangers

A variation on the monolith approach is catalyzing the surface of a heat exchanger. Similar to a monolith, the heat exchanger has low backpressure. At the same time, the device is actively cooled, thereby maintaining the reaction in a desired range. The drawback of this device is primarily cost. Although adhesion of the catalyst to the metal surface is a concern, it is no longer an obstacle on the basis of experience gained in producing automotive exhaust catalysts with metal monolith substrates.



## PROX Design Considerations

The performance of the PROX catalyst in an ATR stream (having a representative dry gas composition of 50% H<sub>2</sub>, 20% CO<sub>2</sub>, 0.5% CO, balance N<sub>2</sub>) is determined by the interaction of the following parameters: (a) O<sub>2</sub>/CO ratio, (b) space velocity, and (c) process temperature. The influence of these parameters has been summarized by Shore & Farrauto (86).

PROX catalysts that operate at elevated temperatures (~200°C) could be designed to work nearly close-coupled to the WGS reactor. Eliminating or downsizing a heat exchanger would reduce system cost.

## Eliminating PROX

The whole issue of CO poisoning of the Pt fuel cell electrodes could be sidestepped through redesign of the fuel cell stack. Nafion membranes operate at about 80°C, and it is necessary to keep them hydrated. Research in other membranes may yield a design that could operate at higher temperature. For example, polybenzylimide membranes (1) operate at 180°C. No PROX catalyst is needed because at this temperature the fuel cell electrodes can tolerate a high CO concentration. At the elevated temperature, CO adsorption on the Pt electrodes is greatly reduced, and the PROX catalyst could become superfluous.

## Anode Tail Gas

The reformat from a fuel cell reformer typically produces >40–80% H<sub>2</sub> (dry gas). The anode electrode operates with ~80–85% H<sub>2</sub> utilization, and the balance of the unconverted H<sub>2</sub> must be oxidized so that its heat can be recovered. The heat of combustion can then be used to preheat the incoming feed water to make steam, thus improving the overall thermal efficiency of the system.

Catalytic or noncatalytic burners are generally used to oxidize and/or combust the remaining H<sub>2</sub> and any CH<sub>4</sub> that may be present. Generally, to oxidize H<sub>2</sub>, supported precious catalysts, especially supported Pt and Pd on alumina catalysts, are effective for this application. For a catalytic oxidizer, a radiant heater (87) was described in detail for stationary and mobile applications.

Whereas H<sub>2</sub> is easy to combust, it is very difficult to completely oxidize any CH<sub>4</sub> that may be present. For a catalytic system, supported Pd was used to combust methane, and PdO was found to be more active than the metallic Pd (88–90). Hicks et. al. (89) reported that the extent of oxidation of Pd was increased with decreasing particle size and also with increasing number of crystal imperfections, and that the PdO dispersed on alumina was much less active than the oxide dispersed over the surface of the palladium crystallites. Farrauto et al. (88) reported that the type of support for Pd has a significant effect on the decomposition temperature of PdO. For example, the decomposition temperatures for PdO/Al<sub>2</sub>O<sub>3</sub>, PdO/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, and PdO/La<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts were found to be 810, 900, and 912°C, respectively. Therefore, it

is possible to maintain PdO during the reaction by the proper choice of supports (91).

## **FUEL PROCESSOR CONSIDERATIONS: EFFECT OF MATERIALS ON GENERAL OPERATION OF A FUEL PROCESSOR**

Although the criteria for improved catalyst activity for each chemical step in fuel processing may appear straightforward, additional factors should be considered when the catalysts are installed and used in the final application: i.e., a highly integrated fuel processing reactor. Such reactors add complexity to the performance requirements of the catalyst through their high degree of integration of unit operations, their potential for exposing catalysts to poisons from the feed streams and the materials of construction, and any degradation products. Catalysts for fuel processing applications need to have broad operating latitudes and robustness as well as high activity.

### **Fuel Processor Designs**

A review of the research and patent literature shows two broad categories of fuel processing reformers being developed in industry and academia: the catalytic fuel processor and the membrane fuel processor. In the first case, designers have used catalysts to perform the relevant chemistry and thus reform hydrocarbons that can deliver hydrogen to the fuel cell. In the second case, developers have taken advantage of both membrane separations and catalyzed chemical reactions to deliver high purity hydrogen gas to an electrode stack.

### **Catalytic Fuel Processors**

Regardless of the category, many published fuel processor designs incorporate high degrees of interdependency among their unit operations. For example, in Hydrogen Burner Technology (92), the inlet air and fuel streams are preheated by absorbing the energy through heat exchange with the product gases of the reforming section. In Plug Power's World Patent (93), the steam generator used to feed the WGS reactor is claimed to be an electric heating unit, or a hydrogen or a natural gas burner with a heat exchanger. Little's U. S. Patent (94) discloses a highly integrated fuel processing reformer in which partial oxidation and steam reforming are performed within the central core of a cylindrical reactor that exchanges heat with the high- and low-temperature shift catalysts and desulfurization agents in the annular region. UOP has a pair of patents describing highly integrated fuel processing reformers (95, 96). One compact UOP design has a gas inlet in the central core that diverts axial flow through a partial oxidation catalyst bed to radial flow through consecutive high-temperature WGS, low-temperature WGS, and then preferential oxidation catalyst beds.

The high interdependency of the unit operations can lead to additional deactivation modes not anticipated by the individual unit operation. For example, contaminants from dusting or degradation of an improperly formulated WGS particulate catalyst can be carried downstream masking the PROX catalyst. If the reforming catalysts are prone to coke formation, this coke can be carried in the gas stream to mask downstream catalysts such as the high- or low-temperature WGS catalysts.

## Poisons and Contamination

Some sources of other poisons are more readily anticipated and need to be considered when developing a catalyst for practical use. A variety of sulfur species are expected in most common sources of hydrocarbon fuels. Water used in the fuel processor may be of widely varying quality and may carry contaminants such as halides or alkali ions. The air used by the fuel processor also needs to be considered for sources of contaminants such as particulates; even wind-borne sea-spray near seaside locations can cause difficulties.

Other contaminants can come from the materials of construction. Fuel processor designers and manufacturers must pay particular attention to all materials that contact gas streams. Catalysts can be poisoned by degradation products of gaskets, sealants, adhesives, insulation, tubing, connectors, reactor walls, and valve greases.

Not only do catalysts need to be optimized for activity in their intended operating window, but the catalysts must also demonstrate robustness and be able to maintain their steady-state performance levels after significant operation deviations caused by start-ups, shutdowns, or operational upsets. The operational window experienced during start-up and shutdown of a fuel processor may be critical for maintaining the life of the catalyst. During a shutdown, when the fuel processor is hot, and also during a start-up, when the processor is cold and perhaps no steam is yet available, care must be taken to avoid the coking regime in the reforming section. At the same time during start-ups and shutdowns, explosive mixtures of air and fuel or hydrogen-rich reformat are also to be avoided. The WGS catalyst developers must not only be sensitive to optimized activity in the temperature window of interest. They must also be sensitive to how the catalyst activity is maintained after exposure to oxygen or condensing water in a cooling, pelletized WGS reactor bed, for example.

Upsets in fuel processor operations related to an insufficient or excess supply of air, fuel, or water can occur and result in high- or low-operating temperatures. Although it is up to the fuel processor designers to engineer the safe handling and rapid response to such excursions, it is the responsibility of the catalyst developers to insure that their catalysts can withstand occasional process deviations without significantly reducing catalyst lifetime.

## Duty Cycle

During operation, a load-following fuel cell will experience multiple power levels as power demands vary. The dynamic responses of the catalyst and reactor are

important. In the instance of fuel cells for transportation applications, the dynamic response of the system is critical and monolithic catalysts are envisioned in such reformers. Even in a residential application where some pelletized fuel processing catalyst beds are used, the dynamics of the power demand still place a certain restriction on the rapid response of the system. The fuel cell system must be able to increase power output relatively quickly. This issue of “turndown ratio” places pressure on catalyst developers to provide catalysts with broader operating windows to widen operating latitude for the fuel processor design engineers.

The challenge for developing catalysts for fuel processing applications is balancing the need for high activity and long lifetimes with the practical demands of providing broad operating latitudes and robustness. For example, imagine the duty cycle for a fuel cell-powered home no longer connected to the grid. The response time for power must be rapid when the home occupants awake from sleep and lights, heat, and appliances are suddenly needed for the morning activities (97). For the Japanese market, it is expected that all homes will be grid parallel (connected to the grid). This will allow a base load fuel cell system with spikes managed by the grid.

## **HYDROGEN-SELECTIVE MEMBRANE: WHAT CAN IT OFFER TO A FUEL PROCESSING SYSTEM?**

The operational characteristics of PEM fuel cell dictate that a high-purity hydrogen with a maximum admissible CO level of 5–10 ppm must be produced by a miniature fuel processing plant integrated into a fuel cell electricity generator. The required high purity of hydrogen in the reformat (a mixture of H<sub>2</sub>, CO, CO<sub>2</sub>, N<sub>2</sub>, and steam produced by ATR and WGS processes) can be achieved by different means—either by running a catalytic PROX reaction, which preferentially oxidizes CO rather than H<sub>2</sub>, or by using gas separation techniques, e.g., pressure swing adsorption (PSA) or membrane separation. Several technical features make hydrogen-selective membranes a potentially attractive part of the fuel processing systems. An ideal membrane can produce very pure hydrogen; it can offer a steady-state operation, as opposed to transient adsorption-desorption cycles inherent in the PSA technology. In addition, the membrane incorporated into a reactor can stimulate the above-mentioned equilibrium conversions by shifting equilibrium of hydrogen-producing reactions involved in the fuel processing cycle, i.e., steam reforming and/or WGS reactions owing to a continuous withdrawal of hydrogen from the reaction zone.

These promising features have attracted the attention of many involved in development of fuel processing systems. Technical feasibility of hydrogen separation membranes in such applications has already been demonstrated and analyzed in several publications; however, a potential role of the membranes as components of the fuel processing systems is dependent on the cost issues rather than on entirely technical ones.

To be suitable for the fuel cell application, the hydrogen separation membrane should possess the following properties:

- selective permeation of hydrogen,
- high permeation rate at low partial pressure gradient,
- long-term stability in the reaction environment,
- the membrane and related equipment (gas separation modules, membrane reactors, etc.) must have relatively low cost.

## MEMBRANE MATERIALS AND COST CONSIDERATIONS

Dense Pd-based membranes have so far received most attention in application to hydrogen generation via hydrocarbon fuel processing. Typically employed as composite structures (e.g., a thin selective Pd layer over porous nonselective support, which provides adequate mechanical properties to the membrane), these membranes can offer outstanding separation selectivity. Thus Mardilovich & Ma (98) report on the porous stainless steel-supported Pd membrane with a H<sub>2</sub>/N<sub>2</sub> selectivity up to 5000. The membrane with a ~20- $\mu$ m-thick Pd-selective layer allows the H<sub>2</sub> flux up to 4 m<sup>3</sup>/(m<sup>2</sup> × h) at 350°C and pressure gradient of 1 atm. By being incorporated into the fuel processing system (e.g., integrated into the WGS reactor), the membrane with such permselectivity can potentially eliminate the PROX process. Equally important is the potential of running the WGS reaction at higher temperatures, where the intrinsic catalytic activity is higher but conversion is limited by the thermodynamic equilibrium. The membrane, which can selectively remove hydrogen (the product of WGS reaction) from the reaction zone, opens a possibility to decrease the amount of the WGS catalyst to be used in the fuel reformer by performing the reaction at higher temperatures.

These features seem to be so important that hydrogen separation membranes for fuel cell applications are currently being considered in a number of patents (99–114). In spite of significant challenges mainly associated with the development of technologies of membrane manufacturing, the work on hydrogen separation membranes continues.

Despite excellent selectivity toward hydrogen, Pd-based membranes may not find an immediate wide application in the fuel processors owing to their high cost. Thus assuming, as suggested in the literature, that 15 liters of H<sub>2</sub> per min are needed to generate 1 kW of electricity, we find that at the current price of ~\$30/g the cost of Pd needed for the above-described membrane of 20- $\mu$ m thickness is ~\$650/kW.

The only realistic way to reduce the cost of Pd-based membranes is to decrease the thickness of the selective layer without compromising the membrane permselectivity. One should bear in mind that the decrease in thickness leads to a quadratic cost improvement; thus a 10- $\mu$ m-thick Pd layer would have double the permeability and half the amount of the metal, i.e., equal flux at one fourth

the cost, which is still above \$160/kW. It can be assessed that the selective layers as thin as several micrometers are required in order for the Pd-based membranes to become economically viable in a future market of the fuel cell generators.

Alternative (non-palladium) types of membranes capable of separating hydrogen from the reformat gas mixtures under the reaction conditions are relatively scarce. Until now, significant efforts in making zeolitic membranes did not result in a reliable technology capable of manufacturing a H-selective membrane. On the other hand, composite carbon molecular sieve-based membranes, e.g., those developed by Shiflet & Foley (107), may represent an interesting alternative to the zeolitic ones. However, these membranes cannot perform the hydrogen purification function owing to a limited separation selectivity. Most likely they can be used only to shift equilibrium owing to a preferential removal of hydrogen relative to other components of the reformat. The engineering and economical viability of such an approach needs to be carefully analyzed. Despite a potentially lower cost compared with that of the Pd-based membranes because of a significantly lower separation selectivity ( $H_2/N_2 \approx 20$ ), the carbon molecular sieve membranes will likely invoke a more complicated system for separation of the permeate.

Regardless of the membrane type, for fuel cell applications there is one common limitation of membrane performance, i.e., relatively low upstream pressure. Thus in the residential fuel cell generators where the hydrocarbon feedstock is pipeline natural gas, the upstream pressure in the membrane device will be essentially close to atmospheric. Because the driving force for transport across the membrane is the partial pressure difference, one should think of an efficient way to sweep the permeate out of the downstream side. With the existing tight cost targets, the use of a traditionally applied sweep gas or vacuum may become a significant economic hurdle for the use of a membrane separation stage.

## MEMBRANE-BASED FUEL PROCESSORS

In membrane-based fuel processors, one finds the same high degree of process integration as in the catalytic-only processors. The designs differ mainly in the fact that high pressures are required for membrane operations and in the placement and integration of the membrane unit operation within the fuel cell system. With a few exceptions (108, 109) claiming  $CO_2$ -selective and CO-selective membranes, respectively, most of the fuel processors described in the literature employ membranes that perform selective or preferential permeation of hydrogen. According to the above-cited patent applications, a  $CO_2$ -selective layer of the Exxon's membrane (108) is composed of a hydrophilic polymer (e.g., polyvinyl alcohol, polyvinylpyrrolidone, polyethyleneoxide, polyacrylamide, polyvinylacetate) and an ammonium halide salt. Nedstack's (109) CO-selective membrane consists of a porous polymeric or inorganic membrane support impregnated with a solution of active salts (e.g.,  $PdCl_2$ ,  $RuCl_2$ ,  $CuCl_2$ ,  $LiCl$ ) that is able to transport the CO-containing compound.

IdaTech's U.S. Patent (111, 112) uses tube-in-a-tube exchangers and Pd-alloy membranes to put their combustor, reformer, hydrogen supply, and polishing reactors and lines in direct contact with each other. Pressures in their methanol/water reformers were quoted to be between 6 and 20 atm. A similar pressure range is specified in the Ford Global Technology U.S. Patent (110) in which metallic or ceramic hydrogen-specific membranes are used in hydrogen purification steps downstream from a reforming reaction.

The design in NGK Insulators' U.S. Patent (113) places the hydrogen-separating membrane, either Pd or Pd-Ag, inside the steam reforming chamber. In SK Corporations' patent (114), the concept of placing a hydrogen separation membrane within the reforming reactor is also discussed in detail. Their design is based on a highly integrated set of stacked alternating cells of reforming catalysts and hydrogen-selective membrane separators.

In its U.S. patent application (103), Toyota discusses nearly 30 different designs for fuel cell systems using fuel processors that include hydrogen-selective membranes of undisclosed composition. Their various designs highlight the complexity, interdependence, and flexibility in design among the various chemical unit operations of reforming, hydrogen separation, exhaust gas combustion, and fuel cell electrolysis.

## CONCLUSIONS

The PEM fuel cell system will likely be commercialized for stationary applications in the 5–10 kW range in the next three to four years, with mass production occurring shortly thereafter. It will be fueled by natural gas reforming because an infrastructure already exists in many homes and buildings throughout the world. The anticipated physical size is about that of a refrigerator, which can be conveniently installed in a basement. The major issue will be cost and reliability. Targets of \$500/kW will be cost effective. The reformer and especially the catalysts represent a significant cost issue so materials that can insure reliable operation over the expected duty cycles will be needed. The required properties of these catalysts can be understood only after long-term aging in real fuel processors are conducted. Such studies are currently underway.

Transportation applications will be far more difficult to achieve simply because of constraints in weight, size, start-up, response to transient operations, and cost reduction required to compete with the internal combustion engine. Cost must be decreased by a factor of 50–100 so the fuel cell system can be bought for \$35–50/kW for a 50 kW vehicle. There is also a need to define a useable liquid fuel for which an infrastructure exists. The projection that production-ready cars, cost competitive with the internal combustion engine, will be at least 10 years away is quite bullish, but given the commitment by so many automobile makers and other related companies, breakthroughs will come fast and furious.

The car companies envision the long-term solution will be a centralized service station that provides high-pressure H<sub>2</sub> to be stored on board as a hydride or in

a suitable high-pressure storage tank. As these technologies are advancing, the interim solution is an on-board fuel processor that operates on liquid fuel. Whatever scenario is selected, catalysts will play a key role.

The one certainty is that there will be an enormous amount of creative research and development for catalysts, adsorbents, and catalytic engineering necessary to commercialize fuel cell technology.

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