I. Introduction

In partnership with the Department of Energy (DOE), Eltron Research & Development Inc. has developed a process technology that separates hydrogen from a mixed gas feed stream. This technology has been developed with a number of applications in mind such as dehydrogenation reactions, carbon sequestration, chemical production, and power & hydrogen co-production.

The two key advantages of Eltron’s dense metal membrane are that it is 10x cheaper than palladium membranes and has 10x better performance.

Additional characteristics make it viable for a variety of process applications. Such features include moderate temperature windows, wide pressure windows and catalyst tolerances to poisons.

Figure 1 shows the general concept for Eltron’s hydrogen separation membrane.

![General schematic of Eltron’s hydrogen separation membrane.](image)

Eltron’s hydrogen separation membrane is a dense metal alloy with two thin catalyst layers deposited on either side of the membrane. An oxidation or hydrogen dissociation catalyst is located on the high pressure feed side of the membrane. Once molecular hydrogen is dissociated, atomic hydrogen diffuses through the dense membrane. A reduction or hydrogen desorption catalyst is located on the low pressure sweep side of the membrane. The differential pressure across the membrane creates the hydrogen partial...
pressure force necessary to separate hydrogen. A wide variety of mixed gases containing hydrogen can be fed to the membrane. Eltron has tested feed streams containing mixtures of H\textsubscript{2}, CO\textsubscript{2}, CO, steam, He, N\textsubscript{2}, and H\textsubscript{2}S. The permeate or sweep side of the membrane can be operated with or without a sweep gas to produce a mixed gas or pure hydrogen depending on the application. Eltron has tested hydrogen separation membranes at temperatures ranging from 250 up to 450°C and differential pressures up to 1000 psig.

II. Applications

Eltron’s hydrogen membrane system can be utilized efficiently in a variety of industrial processes. These processes involve separation of hydrogen from feed streams produced from gasification, reforming, or petrochemical processes. Figure 2 shows a generalized flow diagram illustrating the concept for producing and separating H\textsubscript{2} from carbon containing feed stocks. In configurations A, B, and C syngas is produced by gasification of fossil or biomass fuels or by steam reforming of natural gas. In configurations B and C additional hydrogen is produced by reacting syngas with steam in a water-gas shift reactor. This reaction produces a feed stream of hydrogen and carbon dioxide with smaller amounts of steam and residual carbon monoxide. Finally, in configuration D a hydrocarbon feed stock is produced during petrochemical processing.

![Figure 2. Sources of hydrogen containing feed streams and use of Eltron’s membrane in various applications.](image-url)

Eltron’s membrane technology can be used in each of these different configurations. For example, in configuration A, Eltron’s membrane separates hydrogen from CO in a syngas feed stream. Potential applications include hydrogen removal to improve CO conversion in a WGS reactor, or CO purification. Alternatively, in configuration B, the syngas could be fed to an integrated membrane water-gas shift reactor to produce additional hydrogen.
and CO₂. As described below, Eltron’s membrane can be efficiently integrated with WGS catalyst for improved CO conversion by removing hydrogen as it is produced. In configuration C, Eltron’s membrane is placed after a WGS bed. Applications where a shifted feed stream is fed to the membrane include Integrated Gasification Combined Cycle-Carbon Capture & Storage (IGCC-CCS) power plants and synthesis of ammonia. Finally, in configuration D Eltron’s membrane is integrated with an alkane dehydrogenation catalyst. Removal of hydrogen by the membrane during dehydrogenation of an alkane feed stream would allow efficient production of light olefins such as propylene. Data relevant for each membrane configuration and application is included below.

Syngas Configuration

Syngas can be produced by multiple methods including steam methane reforming (SMR) of natural gas or gasification of coal, pet-coke, or biomass. Depending on the application it can be advantageous to remove hydrogen directly from a syngas feed stream. Eltron’s hydrogen membrane is capable of separating H₂ from syngas mixtures. Typically, hydrogen membranes such as Pd membranes are poisoned by carbon monoxide at low operating temperatures. Eltron has developed several catalyst compositions that show improved catalytic performance in the presence of high CO concentrations. For example, three different catalyst compositions were deposited onto Eltron’s hydrogen separation membrane and tested in syngas feed streams. Hydrogen flux results are plotted in Figure 3.

![Figure 3. H₂ flux at 340°C for Catalysts A, B, and C at different H₂:CO ratios.](image-url)
In a 3:1 H₂:CO feed stream Catalyst A had a H₂ flux of 43 mL/min/cm². In the same feed stream Catalysts B and C were poisoned less by the CO. Catalyst B had a flux rate of 58 mL/min/cm² and Catalyst C had the highest hydrogen flux of 65 mL/min/cm². Increasing the percentage of CO in the feed stream to 33 and then 50% caused a decrease in membrane performance for each catalyst; however, the observed flux rates are quite high when considering the amount of CO present in the feed stream.

### Integrated WGS Membrane Configuration

Eltron’s hydrogen separation membrane can be included in catalytic membrane reactors to shift equilibrium limited reactions to higher yields. In the water-gas shift reaction, steam is reacted with carbon monoxide to produce hydrogen and carbon dioxide as shown in Equation 1:

\[
CO + H_2O \leftrightarrow CO_2 + H_2
\]  

(1)

In configuration B, integration of a catalyst bed with a hydrogen membrane allows the membrane to remove hydrogen as it is produced by the catalytic reaction. This has the advantage of shifting the WGS reaction (Equation 1) to higher CO conversion. A hydrogen separation membrane can be integrated with a water-gas shift catalyst as shown in Figure 4.

**Figure 4.** Hydrogen membrane integrated with water-gas shift catalyst.
Eltron has demonstrated the efficiency benefits of integrating a water-gas shift catalyst bed with a high flux hydrogen membrane. Figure 5 shows CO conversion results for a membrane reactor tested under the following operating conditions: (i) 380°C; (ii) GHSV = 2000 h⁻¹; (iii) the feed stream consisted of 47.8 mol% H₂, 6.2 mol% CO₂, 7.8 mol% CO and 38.2 mol% steam, which corresponded to a steam-to-CO ratio of 4.9. When the hydrogen membrane was used to remove hydrogen as it was produced in the WGS reaction, a 96% CO conversion was achieved at the highest testing pressure. For comparison, the dashed line in Figure 3 indicates the theoretical CO conversion (81%) based upon thermodynamic equilibrium without H₂ removal.

![Graph of CO conversion vs. pressure for an integrated membrane WGS reactor operated at 380°C. The red dashed line indicates the theoretical CO conversion (81%) of the WGS reaction at thermodynamic equilibrium without H₂ removal.]

To put this performance data into perspective, it can be compared with that of a conventional WGS reactor. In order to achieve 96% CO conversion in a conventional WGS reactor, either a large amount of steam corresponding to an H₂O/CO ratio of 20 would be required at a temperature of 380°C, or an operating temperature below 260°C would be required when the same H₂O/CO ratio of 4.9 is used. The data in Figure 5 demonstrates that significantly less steam is needed to achieve a high CO conversion using an integrated HTM/WGS reactor, compared with a conventional high-temperature WGS reactor.
Shifted Syngas Configuration

Eltron’s hydrogen membrane in configuration C in Figure 2 would expose the membrane to a shifted syngas feed stream composed mostly of H\textsubscript{2} and CO\textsubscript{2}, but also some CO and steam. There are multiple advantages for applications utilizing Eltron’s hydrogen membrane in this feed stream:

- High hydrogen separation rates are possible since the water-gas shift mixture has a high hydrogen partial pressure.
- If the water-gas shift stream is fed to Eltron’s membrane at high pressures, then Eltron’s membrane keeps the retentate stream at high pressures. Since the retentate stream is composed mainly of CO\textsubscript{2} this configuration offers significant compression cost advantages for carbon sequestration as shown below.

a. IGCC-CCS

A general flow diagram for an IGCC-CCS co-production power plant is shown in Figure 6.

Figure 6. Generic flow diagram for separation of hydrogen and carbon dioxide in IGCC-CCS applications.
Gasified coal, after clean-up, is passed through a water-gas shift bed to maximize H\textsubscript{2} and CO\textsubscript{2} production. This feed stream is fed to Eltron’s hydrogen separation membrane. The 100% pure H\textsubscript{2} separated by Eltron’s membrane can be used for fuel cell or industrial uses, or fed to a hydrogen turbine for power production. One of the key advantages of Eltron’s membrane in IGCC-CCS applications is that the CO\textsubscript{2} is maintained at high pressures for efficient carbon capture and storage. Eltron has performed detailed modeling on this type of process and has demonstrated that the use of Eltron’s membrane in IGCC applications offers significant economic and thermal efficiency advantages. If carbon emissions are taxed this system offers even more advantages.

Figure 7 shows an example of data collected at Eltron under simulated IGCC conditions.

![Figure 7](image)

**Figure 7.** Plot of H\textsubscript{2} Flux in L/min and lbs/day vs. the difference in the square roots of the hydrogen partial pressure on each side of the membrane for a membrane tested under simulated IGCC-CCS conditions.

In this scale-up test two planar membranes were exposed to a feed stream composed of 41% H\textsubscript{2}, 3% CO, 17% CO\textsubscript{2}, 37% steam, and 2% He at 390°C. The pressure was increased to a differential pressure of 400 psig and a hydrogen flux of 5 L/min or 1.5 lbs H\textsubscript{2}/day was measured.
b. Ammonia Synthesis

A water-gas shift feed stream is also produced during synthesis of ammonia and ammonia derived products such as urea ammonium nitrate (UAN). In ammonia synthesis, as with IGCC, a water-gas shifted gas stream is produced by gasification or SMR followed by a water-gas shift catalyst. Traditionally a solvent based adsorbent is used to remove the CO$_2$ and a PSA system is used to purify the H$_2$ used in ammonia synthesis. Alternatively Eltron’s membrane could be used to separate the 100% pure H$_2$ needed for ammonia synthesis. In addition, the membrane allows the remaining CO$_2$ to be efficiently purified for further reaction with ammonia to produce UAN. A general flow diagram of this process is shown in Figure 8. Gas clean-up is not shown since the type and location of the gas clean-up will vary based on gasification or reforming.

![Figure 8. General flow diagram for separation of hydrogen and carbon dioxide in an ammonia and UAN synthesis application.](image-url)
Hydrocarbon Configuration

In another example of a membrane reactor, an alkane dehydrogenation catalyst could be integrated with Eltron’s hydrogen membrane, as shown in Figure 9.

Figure 9. Hydrogen membrane integrated with alkane dehydrogenation catalyst.

Catalytic cracking to produce ethylene and propylene is an energy intensive process. Using a catalytic process to produce olefins requires less energy and improves the selectivity of the dehydrogenation reaction. Integrating a dehydrogenation catalyst with a hydrogen membrane allows removing hydrogen as it is produced which shifts the equilibrium to higher olefin yields. The propane dehydrogenation reaction is shown in Equation 2:

\[ C_3H_8 \leftrightarrow C_3H_6 + H_2 \]  

(2)

Removing the hydrogen byproduct from propylene during this reaction will shift the reaction to higher percent conversion of propane to propylene.
**Sulfur Containing Feed Streams**

Many processes, including some of those discussed above, would likely contain some hydrogen sulfide (H$_2$S) in the feed stream depending on the type and location of gas clean-up utilized. H$_2$S concentrations greater than 20 ppm are typically found depending on the processes involved.

Pure palladium as a membrane or catalyst is not thermodynamically stable towards H$_2$S concentrations as low as 10 ppm in the temperature range of 320-440°C with ≤ 60% H$_2$ in the feed stream. Therefore, pure Pd hydrogen separation membranes cannot be used in any industrial hydrogen feed stream containing hydrogen sulfide concentrations greater than 10 ppm. Eltron has developed several catalyst alloy compositions that demonstrated improved resistance to H$_2$S up to 220 ppm in the feed stream. Figure 10 shows hydrogen permeability over time for Pd and three of Eltron’s catalyst alloys tested at 440°C in a feed stream containing 40% H$_2$, balance He, and 20 ppm H$_2$S.

![Figure 10](image.png)

**Figure 10.** Hydrogen permeability vs. time, one pure Pd membrane and three catalyst alloys. 100 micron membranes, 440°C, 40% H$_2$ feed & 20 ppm H$_2$S.

These tests were performed on 100 micron thick membranes. Figure 10 shows that exponential decay was observed for the Pd membrane. Eltron Catalyst D, E, and F, however, showed stable performance for 160 hours under these conditions. Catalyst E was also exposed to higher H$_2$S concentrations. Figure 11 shows Catalyst E tested at 440°C and 40% H$_2$ in the feed stream with three different H$_2$S concentrations: 20, 100, and 220 ppm. Figure 11 shows that high H$_2$S concentrations led to a slight decrease in permeability over 200 hours; however, for these high concentrations of H$_2$S the hydrogen permeability stability is very good.
Figure 11. Catalyst E tested at 440°C, 40% H₂ feed, three different H₂S concentrations.

Various Petrochemical Waste Gas Streams

Table 1 provides an additional list of gas streams in petrochemical processes with significant quantities of recoverable hydrogen for which the Eltron membrane system may be employed.

<table>
<thead>
<tr>
<th>Gas Feed</th>
<th>Hydrogen (% vol.)</th>
<th>Separated Gases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthesis Gas (SMR/ATR)</td>
<td>45 - 80</td>
<td>N₂, He, CO, CO₂, CH₄</td>
</tr>
<tr>
<td>Ethylene Cracker Offgas</td>
<td>70 – 85</td>
<td>CH₄, He, CO, C₂H₄</td>
</tr>
<tr>
<td>Styrene Monomer Offgas</td>
<td>90 – 95</td>
<td>CH₄, CO₂, C₃H₄, benzene, ethylbenzene</td>
</tr>
<tr>
<td>C3/C4 Dehydrogenation</td>
<td>90 - 95</td>
<td>CH₄, C₃, C₄</td>
</tr>
<tr>
<td>Chlor-alkali Offgas</td>
<td>99.5+</td>
<td>Cl, O₂, N₂</td>
</tr>
<tr>
<td>Ammonia Synthesis Purge</td>
<td>60 - 70</td>
<td>N₂, CH₄, Ar</td>
</tr>
<tr>
<td>Catalytic Reformer Offgas</td>
<td>70 – 85</td>
<td>CH₄, C₂ – C₁₀</td>
</tr>
<tr>
<td>Catalytic Cracker Purge</td>
<td>10 – 20</td>
<td>N₂, O₂, CH₄, CO, CO₂, H₂S, H₂O, C₂ - C₈</td>
</tr>
<tr>
<td>Hydrocracker Purge</td>
<td>75 – 85</td>
<td>CH₄, H₂S, H₂O, C₂ - C₆</td>
</tr>
<tr>
<td>Hydrotreater Purge</td>
<td>75 – 85</td>
<td>CH₄</td>
</tr>
<tr>
<td>MTBE Offgas</td>
<td>80 – 85</td>
<td>N₂, CO, CO₂, CH₄</td>
</tr>
<tr>
<td>Toluene HDA Purge</td>
<td>50 – 60</td>
<td>CH₄, C₂H₆</td>
</tr>
<tr>
<td>Coke Oven Gas</td>
<td>55 – 65</td>
<td>CH₄, CO, CO₂, N₂, Ar, O₂, C₂H₄</td>
</tr>
</tbody>
</table>

Source: Air Products
III. Eltron H₂ Membrane Testing Facilities

Eltron has extensive experience designing, constructing, and operating hydrogen membrane reactors. Eltron has in-house facilities to test hydrogen membranes under a wide variety of potential operating conditions to simulate the conditions expected in the processes outlined above. This allows us to demonstrate membrane performance in specific applications. Currently, Eltron has five reactors dedicated to membrane testing. The operating conditions for each of these reactors are summarized in Table 2.

Table 2. Operating ranges for Eltron’s hydrogen separation reactors.

<table>
<thead>
<tr>
<th>Feed Stream Composition</th>
<th>Reactor 1</th>
<th>Reactor 2</th>
<th>Scale-Up</th>
<th>HLT-A</th>
<th>HLT-B</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂ (SLPM)</td>
<td>5</td>
<td>2</td>
<td>30</td>
<td>2.2</td>
<td>2.2</td>
</tr>
<tr>
<td>He (SLPM)</td>
<td>2</td>
<td>2</td>
<td>2.8</td>
<td>0.035</td>
<td>0.035</td>
</tr>
<tr>
<td>CO₂ (SLPM)</td>
<td></td>
<td></td>
<td>5</td>
<td>0.95</td>
<td>0.95</td>
</tr>
<tr>
<td>CO (SLPM)</td>
<td></td>
<td></td>
<td>1.5</td>
<td>0.18</td>
<td>0.18</td>
</tr>
<tr>
<td>CH₄ (SLPM)</td>
<td></td>
<td></td>
<td>2</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>H₂O (g/hr)</td>
<td></td>
<td></td>
<td>1000</td>
<td>0.39</td>
<td>0.39</td>
</tr>
<tr>
<td>Max Feed Pressure (psig)</td>
<td>1000</td>
<td>800</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>Sweep Gas</td>
<td>Ar</td>
<td>Ar</td>
<td>N₂, H₂O</td>
<td>N₂, H₂O</td>
<td>N₂, H₂O</td>
</tr>
<tr>
<td>Max Sweep Pressure (psig)</td>
<td>700</td>
<td>250</td>
<td>500</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>Max Operating Temperature (°C)</td>
<td>500</td>
<td>500</td>
<td>500</td>
<td>450</td>
<td>450</td>
</tr>
</tbody>
</table>

Reactors 1 and 2 are Eltron’s high pressure screening reactors. These reactors are capable of high pressures on the feed and sweep sides of the membrane. The feed stream is composed of only hydrogen and helium at flow rates up to 5 SLPM.

The third reactor is Eltron’s scale-up reactor, shown in Figure 12.

![Figure 12. Left: furnace and containment vessel and right: control panel for Eltron's hydrogen membrane scale-up reactor.](image)

This reactor was designed for scale-up testing. The reactor is capable of testing multiple different membrane geometries including planar and tubular membranes as well as catalytic membrane reactors. The feed gas can be varied for testing different compositions of H₂, He, CO₂, CO, CH₄, and steam. Nitrogen and steam are available as sweep gases in this reactor, or the reactor can be operated without a sweep gas.
HLT-A and HLT-B are Eltron’s lifetime testing reactors, shown in Figure 13.

Figure 13. Eltron's hydrogen membrane lifetime testing skid.

These reactors were designed to allow testing hydrogen membranes under expected operating conditions continuously for up to 3000 hours. These reactors utilize low flow rates as shown in Table 1 to allow long-term testing. The reactor has the appropriate automated systems and safety features to allow unattended operation.

Eltron References & Links


http://video.energypolicytv.com/displaypage.php?vkey=b05d04e7bdcf237d12e6&channel=Sustainability

White Paper: Eltron’s Membrane employed for IGCC

Patent: Hydrogen Transport Membrane

Patent: Dense, Layered Membranes for Hydrogen Separation


Other References
http://www.fuelcellseminar.com/pdf/2006/Wednesday/3C/Approved%20Guro_David_0245_3C_683.pdf

This technology has been developed under partial funding from The Department of Energy.

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