—ABSTRACT—

Sulfur Thermochemical Processes with Inorganic Membranes to Produce Hydrogen

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Sulfur Thermochemical Processes with Inorganic Membranes to Produce Hydrogen

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Thermochemical cycles are potentially the most efficient method for the production of hydrogen (H_2). These cycles involve a series of chemical reactions where the net result is that high-temperature heat and water produce H_2 and oxygen (O_2). Thermochemical processes have potentially greater efficiency than electrolysis because conversion of heat to H_2 requires fewer steps than conversion of heat to electricity and electricity to H_2. Moreover, the capital costs for these processes may be lower because of the economics of scale associated with chemical processes. The source of heat can be a high-temperature nuclear reactor, solar, or ultimately a fusion energy system.

The first thermochemical cycles were developed in the 1960s and 1970s. With the return of low-cost oil and natural gas in the late 1970s, the research on these H_2 production technologies was substantially reduced. For several reasons, renewed interest now exists in these methods of H_2 production: (1) the growth in demand for H_2 to convert heavy oils and tar sands to gasoline, (2) the interest in a H_2 economy, and (3) concerns about greenhouse gases impacting the global climate. While the same basic thermochemical cycles of interest in the 1970s are being investigated today, major advances have occurred in chemical technologies. These technical advances have the potential to significantly improve process efficiency, performance, and economics. The leading candidates for H_2 production are the sulfur thermochemical processes. Inorganic separation membranes are being developed to improve these processes.

The two leading thermochemical processes for H_2 production are the sulfur–iodine process and the hybrid process. Both processes have the same high-temperature, highly endothermic (heat-absorbing) gas-phase reaction:

$$2H_2SO_4 \quad 2H_2O + 2SO_3 \quad 2SO_2 + 2H_2O + O_2 \quad (850EC) \tag{1}$$

The two thermochemical processes have different lower-temperature chemical reactions. The sulfur–iodine process has two other chemical reactions that when combined, (1) yield H_2 and O_2 from water and heat and (2) recycle all other chemical reagents.

$$I_2 + SO_2 + 2H_2O \quad 2HI + H_2SO_4 \quad (120EC) \tag{2}$$

$$2HI \quad I_2 + H_2 \quad (450EC) \tag{3}$$

The hybrid process (also known as the Westinghouse, GA-22, and Ispra Mark 11) has a single electrochemical step that completes the cycle.

$$SO_2(aq) + 2H_2O(l) \quad H_2SO_4(aq) + H_2(g) \quad \text{(Electrolysis: 80EC)} \tag{4}$$

In theory, the peak efficiencies could approach 70%; however, this requires the development of several new technologies. Inorganic membranes are being considered to address several limitations within these processes.

In each of these cycles, the high-temperature sulfur trioxide (SO_3) dissociation reaction (Equation 1; Table 1) is an equilibrium chemical reaction that requires a catalyst. High temperatures and low pressures drive the reaction towards completion. Studies have concluded that the required process temperatures at 1 to 10 bar need to be very high: -850ºC. After the high-temperature dissociation reaction, all the chemicals must be cooled to near room temperature, the SO_2 separated out and sent to the next chemical reaction, and the unreacted sulfuric acid (formed by recombination of SO_3 and H_2O at lower temperatures) reheated back to high temperatures. Unless the chemical reactions go almost to completion, the energy losses in separations and the heat exchangers to heat and cool all the unreacted reagents (H_2SO_4) result in an inefficient and uneconomical process.

TABLE I. Thermodynamic Equilibrium for H_2SO_4 Decomposition

		Equilibrium Fraction of Sulfur as		
Pressure (Bar)	**Temperature (EC)**	**% SO_2(g)**	**% SO_3(g)**	**% $H_2SO_{4(g)}$**
1	700	54	46	0.1
1	800	76	24	0.02
1	900	88	12	0.004
1	1000	94	6	0.001
10	700	31	67	1.7
10	800	53	46	0.4
10	900	72	28	0.1
10	1000	84	16	0.03
100	700	14	69	17
100	800	30	64	6
100	900	48	50	2
100	1000	64	35	1

A high-temperature inorganic membrane is being developed to separate SO_2, H_2O, and O_2 from the SO_3. If these reaction product gases are removed, the remaining SO_3 (with a catalyst and heat) will disassociate into its equilibrium concentrations. If the reaction gases can be selectively removed, the process can be driven to completion. The membrane operates with a higher pressure on one side and a lower pressure on the other side. This pressure difference (a few bar) drives the separation process. The membrane offers three potential uses. First, the membrane can be used to reduce the peak temperature of the SO_3 dissociation step by several hundred degrees to as low as 700EC, thus reducing the challenges of high-temperature materials. Second, the dissociation step can be operated at high pressure (-100 bar) rather than at low pressures, thus lowering capital costs. Third, some combination of lower temperatures and higher pressures can be used. Each of these options has the potential to increase efficiency and lower capital costs.

Oak Ridge National Laboratory has developed and fabricated a wide variety of inorganic membranes, several of which are now commercial products in large-scale use. Based on this historical experience, a development program to build membranes for this application has been initiated. A new test loop has been constructed to test membranes for this particular separation at required conditions (temperatures, pressures, corrosive gas environment). The operation of inorganic membranes is not fully understood. Consequently, several membranes from our inventories have been chosen and will be tested using O_2, SO_2, and SO_3 as a function of temperature. Based on the experimental results and theory, custom membranes for this specific application will be fabricated and tested. This is an iterative procedure. In parallel, studies have been initiated to understand the performance requirements for such membranes. The results of the initial experiments and the analysis are described in the full paper.