

THE GEZRO PROCESS FOR OPEN-CYCLE HYDROGEN PRODUCTION

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Various scenarios using hydrogen as a general energy medium in the future have been proposed based upon its outstanding environmental compatibility, its ultimate derivation from an inexhaustible feedstock material (H_2O) and its high flexibility. At least until the next century, however, the overwhelming uses of hydrogen will be as a chemical feedstock, in chemical and metallurgical processing operations and the production of clean synthetic fuels. In particular, the conversion of coal into synthetic natural gas and liquefied synthetic fuels will require large amounts of hydrogen. Both present and projected demands for hydrogen require that new, higher efficiency and lower cost production methods be developed.

Currently the vast majority of hydrogen produced is made by open-cycle processes that consume natural gas, oil or other petroleum products as the feedstock material. The principal methods include steam reforming and partial oxidation both of which are followed by the shift reaction⁽¹⁾. Thermal efficiencies of such processes in terms of the combustion value of hydrogen produced compared to that of the input fossil fuels typically range from 50-80%. Only a small fraction of the hydrogen consumed presently is produced by water electrolysis in spite of the simplicity of the process, the product purity, and the good efficiency achievable in the electrolysis step itself by advanced methods (up to ~70-90%). This is due largely to the low overall efficiency (i.e., <35%) when electric generation and DC conversion steps from a base load thermal power plant are included. Much attention has recently been given to the closed cycle thermochemical decomposition of water in which heat at moderate temperatures (<1000°C) is used to carry out a series of reactions,⁽¹⁾ the net result of which is: $H_2O + H_2 + 1/2 O_2$. All other chemical intermediates in the process are recycled, ideally. Detailed analysis indicates that overall thermal efficiencies of 40-60% might be achieved. While numerous closed cycle processes have been theoretically proposed, none have yet been successfully operated in an integrated mode. Serious technical barriers, including corrosion, kinetics, system stability and design, combined with licensing uncertainties, the projected high cost of high temperature nuclear heat and process components shed serious questions on the viability of multi-step closed cycle processes for hydrogen generation, at least in this century. Thus it appears that open-cycle processes to make hydrogen will be very important for the foreseeable future.

The primary objective of this paper is to describe a new open cycle technique which will utilize coal or coal char from gasification to produce electrolytically pure hydrogen. The concept stems from our earlier high temperature fuel cell program, during which an electrolytic water dissociation cell using an oxygen ion conductive membrane was proposed⁽²⁾ and demonstrated⁽³⁾. By introducing a reducing gas at the cell anode, the voltage required to produce hydrogen from water is lowered. The new method is to use a ceramic membrane that is both an electron conductor as well as oxygen ion conductor. Thus the cell can operate in a "self-driven" mode, i.e., no

electrical driving force or electrodes are needed. Such a cell is shown schematically in Figure 1. Steam is passed over one side of the membrane while carbon monoxide is passed over the opposite side of the membrane. On the "cathode" side, the steam reacts at the surface with two electrons to yield hydrogen gas plus an oxygen ion, which is transported through the electrolyte to combine at the "anode" surface with carbon monoxide to form carbon dioxide plus two electrons. This process, operating without electrical input, has been named GEZRO. It should achieve overall thermal efficiencies, as defined earlier, of at least 60-70%.

The net reaction for the process is the well-known water gas shift reaction: $H_2O + CO = CO_2 + H_2$. Because the reactants are separated, the product hydrogen does not have to be purified with respect to CO or CO_2 . This has important implications to ammonia synthesis, for example, where CO impurity in the hydrogen acts as a catalyst poison. Also, the input carbon monoxide need not be pure. For this reason, GEZRO is particularly adaptable for integration into coal liquefaction or gasification technology. Figure 2 shows a possible cycle using gas obtained from coal which has been partially oxidized in air as the feed to GEZRO. Nitrogen from the air and coal contaminants such as sulfur also enter the GEZRO reactor; gas clean-up is accomplished subsequently at lower temperatures. On the steam side, a portion of the steam is reduced to hydrogen and the remainder is recycled. Heat exchangers, not shown in the diagram, would be used so that minimal heat input would be required. Figure 3 shows a cycle in which GEZRO is incorporated into a high BTU coal gasification scheme, such as HYGAS. In this cycle, hydrogen and steam from GEZRO are fed directly into the second stage gasifier (both hydrogen and steam are required to maintain proper heat balance in the gasifier) to react with coal and char and yield methane. The remaining char is partially burned in air to provide the input gas for GEZRO.

The GEZRO reactor can be considered as an electrochemical cell in which the cell voltage is zero (short circuit condition). For this case an effective average thermodynamic cell voltage, \bar{v} , may be defined by $\bar{v} = r\bar{j}$, where r is the electrolyte specific resistance, and \bar{j} is the average current density. Thus, r , which depends on the membrane material, and \bar{v} which is related to the driving force for the reaction (proportional to temperature and oxygen partial pressure differential) integrated over the reactor length, determine the output of the cell in terms of oxygen ions transported per unit area of membrane. For typical membrane compositions, it can be shown that by operating with countercurrent gas flows, it is theoretically possible at 800°C, to oxidize 80% of the CO to CO_2 while converting half of the input steam to hydrogen when the input steam flow rate is twice the input CO flow rate. In general, the process is expected to operate at between 700°C and 1000°C at any required pressure.

The critical problem in the development of a GEZRO reactor is the selection of a suitable membrane and our experimental program has centered in this area. Materials requirements include the following:

- (1) High oxygen ion conductivity,
- (2) High electronic conductivity,
- (3) Thermal stability,
- (4) Stability toward reactants and products,
- (5) Stability toward contaminants,
- (6) Mechanical stability and strength, and
- (7) Fabrication capability (thin and gas tight).

These properties are similar to those required by high temperature fuel cells, with the important exception that electronic conductivity, instead of being undesirable, is required. Indeed, the optimum condition for GEZRO is that the transport number for electrons (t_{e^-}) is equal to that for oxygen ions ($t_{O^{2-}}$), so that $t_{O^{2-}} = t_{e^-} = 0.5$. The severe operating environment, which includes corrosive and reactive gases (e.g., H_2S , SO_2 , COS) as well as a wide range of reducing conditions (10^{-20} atm $< P_{O_2} < 10^{-7}$ atm) at high temperatures, rules out many possible materials.

Because of its well-established use in experimental fuel cells, zirconia has been chosen as the initial candidate membrane base material. When certain oxide materials containing a cation in the +2 or +3 oxidation state are added to monoclinic ZrO_2 , the ZrO_2 is stabilized in a cubic fluorite crystal structure. The stabilization process leaves several percent oxygen ion vacancies in the structure and leads to significant ionic conduction. The ionic conductivity at a given temperature generally increases with the nature of the additive in the order $CaO < Y_2O_3 < Sc_2O_3$. The use of Y_2O_3 as a stabilizer appears attractive as a compromise between cost, long-term stability, reactivity toward sulfides, and reasonable conductivity. A maximum in the conductivity of the Y_2O_3 - ZrO_2 system occurs at about 7-8 m/o Y_2O_3 , at which point the purely ionic conductivity is about $0.1 \Omega^{-1} cm^{-1}$ at $1000^\circ C$. The addition of compatible transition metal oxides into the ionically conducting fluorite lattice is expected to introduce electronic conductivity, provided the additive goes into the structure and is not merely segregated along grain boundaries..

A program to synthesize and screen various three and four component ceramic compositions by means of microstructure analysis, electrical conductivity measurements, and transport number measurements, is in progress. Table I summarizes some of the compositions which have so far been successfully prepared and which have been sintered into dense, gas-tight shapes. The sintering conditions were found to be critical in achieving good materials properties. In general, sintering was carried out at temperatures between $1500^\circ C$ and $1900^\circ C$ in an atmosphere of either air or wet hydrogen; wet hydrogen atmospheres generally approximate the oxygen partial pressures used in the GEZRO process. Oxides of Mn, Zn, Ce, U, and Fe have been successfully added to yttria-stabilized zirconia to form pure single phase materials. Additive contents have ranged from 4.1 m/o to 13.4 m/o in compositions based on 7-8 m/o Y_2O_3 -stabilized zirconia. Other preparations involving 2-20 m/o of additive, and using other transition metals have been attempted or are in progress.

Electrical conductivity measurements have been completed on several of the above compounds using a two-probe AC technique. Platinum paste electrodes (Engelhard #6082) were applied to sintered bar samples which made pressure contact with platinum foil spacers in a sample holder constructed of alumina. Measurements were carried out as a function of temperature in the range between $500^\circ C$ and $1000^\circ C$ and as a function AC frequency in the range between 400 Hz and 50 kHz, in either pure nitrogen or carbon monoxide atmospheres. Figure 4 shows the results for selected compositions. In most cases, the plot of the logarithm of conductivity (σ) vs reciprocal temperature is linear. The most conductive and the lowest activation energy (0.47 ev) material yet measured is the 7 m/o Mn_2O_3 composition. Unfortunately, a severe decrease in the conductivity resulted within 70 minutes after carbon monoxide was introduced at high temperature. Post-run

examination revealed that reduction, probably to poorly conducting Mn^{+2} oxidation state, had occurred. Both ZnO and CeO_2 additives are more promising. As shown in Figure 4 the composition containing 8.1 m/o ZnO is somewhat more conductive than the 13.4 m/o ZnO material. Measurements for the 13.4 m/o ZnO composition in carbon monoxide revealed no significant deterioration in the conductivity even after several hours exposure. Similar results were obtained in the case of 8.1 m/o CeO_2 where measurements in both CO and N_2 are shown for comparison in Figure 4; in this case, the reducing atmosphere lowered the conductivity somewhat, but there was no change in activation energy. Finally, one four component system, containing 2.8 m/o UO_2 and 7.6 m/o Fe_3O_4 , was measured since earlier work had indicated this material to be a potential mixed conductor. Although this material has been prepared in the form of dense, gas tight discs, such preparations are not always repeatable. In addition, efforts to prepare tubular shapes by means of plasma spray techniques have not led to suitably dense material.

Measurement of transport numbers for oxygen ions and electrons for the above and other potential materials, is also underway. These measurements are being made by the emf-technique in which the voltage generated by differing known oxygen partial pressures on either side of a disc sample is measured and compared with the theoretical voltage obtained for pure oxygen ion conduction.

Table I

<u>Additive*</u>	<u>m/o</u>	<u>Sintering Temperature Time, Atmosphere to Produce Dense Sample</u>
ZnO	8.1	1510°, 5 hr., air
	13.4	1510°, 5 hr., air
	8.1	1700°, 5 hr., wet H_2
CeO_2	8.1	1510°, 5 hr., air
	8.1	1500°, 5 hr., wet H_2
	4.1	1510°, 5 hr., air
Mn_2O_3	7.0	1510°, 5 hr., air
UO_2/Fe_3O_4	2.8/7.6	1900°, 16-1/2 hr., wet H_2

References

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- (2) H.S. Spacil and C.S. Tedmon, Jr., *J. Electrochem. Soc.*, 116, 1618, (1969).
- (3) H.S. Spacil and C.S. Tedmon, Jr., *J. Electrochem. Soc.*, 116, 1627, (1969).

*All compositons based on 7-8 m/o Y_2O_3 -stabilized ZrO_2 .

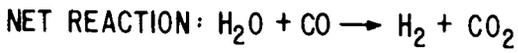
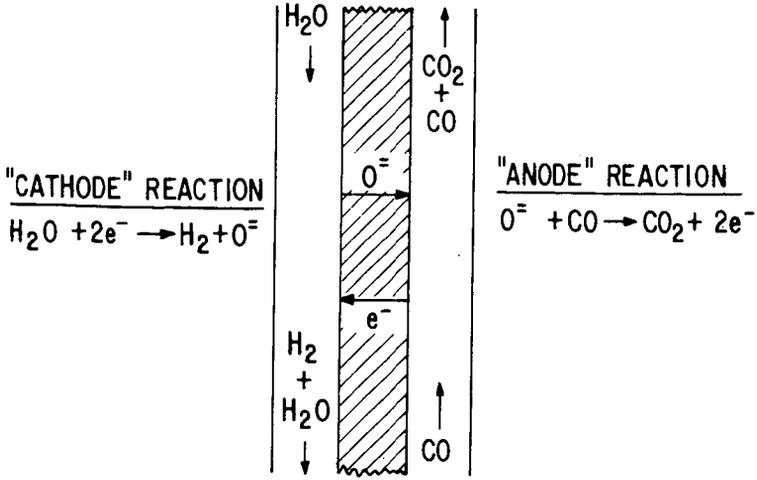


FIG. 1

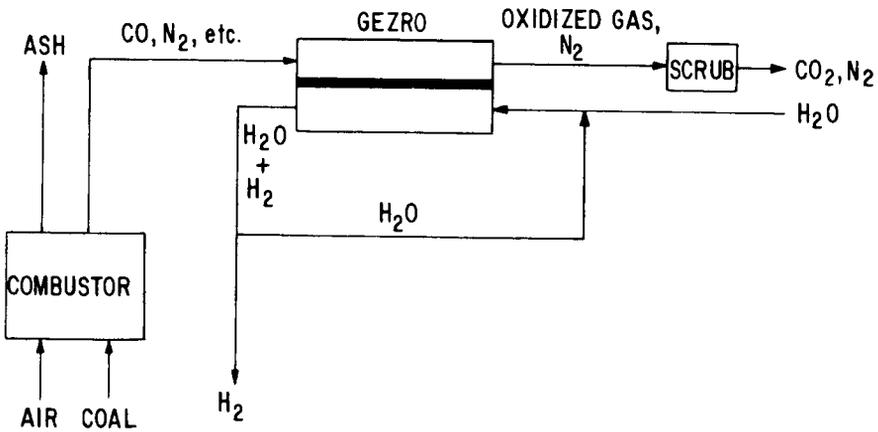


FIG. 2

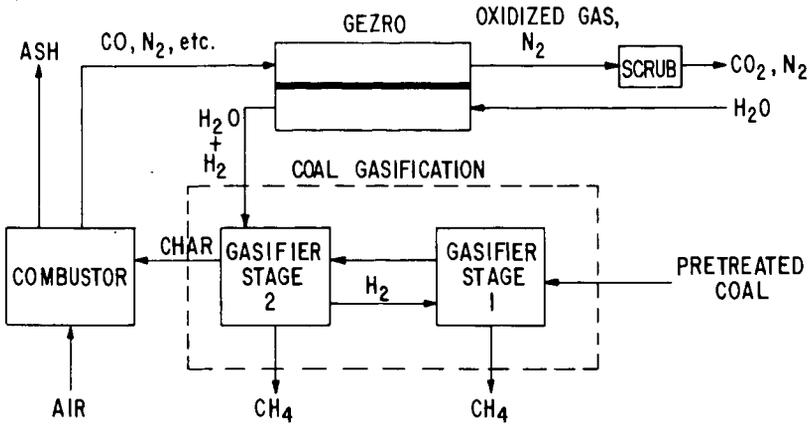


FIG. 3

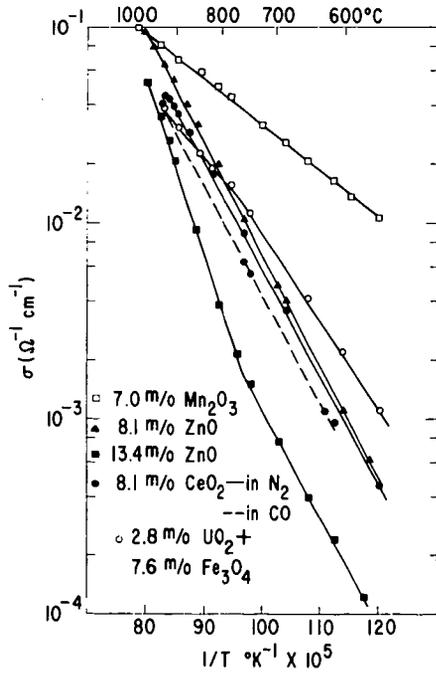


FIG. 4