Ultra Pure Hydrogen for Fuel Cell Operation

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The first practical fuel cells to be developed used pure oxygen and hydrogen. It has proven to be quite feasible to adopt certain of these cells to use air at the oxygen electrode, that is, the cathode.[1] An intensive effort is underway to develop cells which can use a more convenient fuel at the anode.[2] However, it appears unlikely that such cells will be available for practical application in the near future.

One alternate approach is to separate a conversion function from the cell and modify the anode to use an impure hydrogen-rich gas. It is relatively simple, for example, to dissociate ammonia[3] and it would appear to be easier to modify the anode to handle the resulting 75% hydrogen in nitrogen mixture than it was to modify the cathode to handle the 21% oxygen in nitrogen mixture which is air. Residual fuel gas from the anode can then be burned to supply the energy requirements of the dissociation reaction. This method of operation has recently been described by ASEA.[4]

Producing a hydrogen-rich gas from hydrocarbons (or from oxygenated hydrocarbon derivatives such as alcohols) requires appreciably more elaborate conversion equipment and the product gas stream will contain a variety of impurities. Methane, carbon monoxide, carbon dioxide, nitrogen and water vapor may all be in the hydrogen-rich stream. The presence of these impurities introduces a large number of problems with respect to the development of anodes and to the design of the fuel cell battery system. The conditions for efficient operation of gas diffusion electrodes with gases containing inerts have been developed by Baucke and Winsel.[5] In the case of gases containing potential catalyst poisons, however, it may well be much more desirable to combine hydrogen purification with the fuel conversion function so that only pure hydrogen need enter the cell.

The production of hydrogen for fuel cell applications has been explored for a considerable time. A number of reports prepared recently indicate the difficulties which arise in scaling down conventional processes for manufacturing hydrogen.[6,7,8] Conventional processing schemes are as shown in Figure 1.

- The primary reaction may be steam reforming or partial combustion or a combination of the two. In any event it involves a high temperature endothermic reaction to which heat energy must be supplied.

- Carbon monoxide removal is generally accomplished by the catalysed water gas shift reaction wherein carbon monoxide reacts with water vapor to form carbon dioxide plus hydrogen. Recent advances in catalyst composition permit this reaction to proceed at commercially operable rates at moderate temperatures.[9,10] The advantage is that the equilibrium is sufficiently favorable so as to require only a single stage of shift reaction in a plant producing about 99% purity hydrogen. Formerly several stages with intermediate carbon dioxide removal were required. While the shift reaction is exothermic the temperature level is such that the heat is not generally usefully recoverable.

- Carbon dioxide removal is done at near ambient temperatures by scrubbing the gas with suitable regenerable basic reagents. A variety of reagents and processes are available.[11,12,13]

- Final purification is often accomplished by catalytically hydrogenating the residual oxides of carbon to the much less objectionable impurity methane, followed by drying the product hydrogen stream. Alternately cold box processing, generally involving a liquid nitrogen wash, can be used.

It is evident that scaling down conventional equipment without significantly altering the process steps cannot result in any appreciable reduction of equipment components in small hydrogen generators for fuel cell use.

The Engelhard Hydrogen Process provides a new improved approach for solving these problems by combining three basic concepts:

- a hydrogen producing reaction

- the removal of pure product hydrogen

- the utilization of the residue as fuel to supply the energy requirements of the process.

This makes it possible to design and construct compact hydrogen generators. The process is schematically indicated in Figure 2.

The dissociation of ammonia is a suitable hydrogen producing reaction. An earlier paper[14] describes the design, construction and performance of a miniature generator delivering 4 SCFH of hydrogen to serve a 200 watt fuel cell. This unit was developed for the Electronics Research and Development Laboratories of the United States Army.

Hydrogen generators based on hydrocarbons are of much greater general interest. Engelhard is currently engaged in constructing a number of liquid hydrocarbon fueled hydrogen generators having hydrogen output capacities in the range of 4 to 600 SCFH.

Steam reforming of hydrocarbons lends itself well to the Engelhard Hydrogen Process because the energy required for the process is liberated outside of the reaction zone rather than within it as in the case of partial combustion. Thus the residual fuel gas can be used to operate the process.

While various hydrogen removal methods may be considered, diffusion through a material permeable only to hydrogen accomplishes the objectives in one simple step and can be readily adapted for use in small hydrogen generators such as we are discussing here. Palladium and palladium alloys are well known for their ability to diffuse hydrogen. Several reviews of the hydrogen permeation process have recently been presented.[15,16,17] The process is unique in that it supplies the purest grade of hydrogen available: ultra-pure hydrogen containing no impurities measurable by presently available techniques. Use of ultra-pure hydrogen greatly simplifies fuel cell battery design. With no impurities contamination of the electrolyte does not occur, nor do inert gases accummulate. The requirement of venting such gases which would complicate the mechanical design of a fuel cell battery can be eliminated with ultra-pure hydrogen.

The Engelhard Hydrogen Process is a highly efficient way of producing hydrogen. This becomes particularly important if it is to be considered as a component of a fuel cell power source package. Now consider the energy balance of a hydrogen generator as shown in Figure 2, for the steam reforming version with liquid water and liquid hydrocarbon feed streams. In principle the energy content of the product hydrogen would be the same as the gross heating value of the hydrocarbon feed and the generator would have an energy conversion efficiency of 100%. For this the following conditions would have to be met: The product hydrogen and the flue gas leave the apparatus at the same temperature as the incoming streams. The water contained in the flue gas is discharged as a liquid. No radiation and convection heat losses occur. In practice these idealized conditions cannot be realized.

The temperatures of the output streams can be brought to relatively low levels by heat exchange, output hydrogen against incoming combustion air, flue gas against fuel and water feed streams. It is not feasible, however, to usefully recover the latent heat of the water vapor in the flue gas, and this may represent a sizeable loss.

Radiation and convection losses depend upon the size and arrangement of the apparatus, and vary from very small relative to the gross heating value of the fuel fed, in large generators, to as much as 20% in very miniaturized generators.

The energy loss represented by any excess water fed as a liquid but discharged as a vapor in the flue gas is one reason for operating at the lowest possible molal water to carbon ratios. Another reason is to reduce the water vapor content of the reformed gas stream and hence to increase the partial pressure of hydrogen in the diffusion zone. This reduces the amount of palladium alloy required and the overall size and weight of the apparatus. A third reason is that if the ratio is sufficiently low a combined hydrogen generator-fuel cell power source could operate with no external water supply if the fuel cell can be engineered so that the water produced from the hydrogen consumed is returned to the steam reforming hydrogen generator.

There is currently a great interest in developing improved catalysts for the steam reforming of normally liquid hydrocarbons.[18,19] Moreover, for universally useable hydrogen generator-fuel cell power sources a catalyst is required capable of steam reforming any type of currently available hydrocarbon fuel, in particular gasoline, jet fuel, and diesel fuel meeting present military specifications. Such catalysts do not appear to be available at the present.

In the Engelhard hydrogen generators now being built proprietary catalysts are being used which have demonstrated the ability to steam reform a wide variety of hydrocarbon structures, i.e. paraffins, naphthenes, olefins, aromatics. Commercial fuels such as BTX raffinates (essentially C_6-C_9 paraffins), light naphthas, and jet fuels such as JP-4 have been steam reformed with these catalysts at molar water to carbon atom ratios of three or lower, with runs of over 1000 hours, provided the sulfur content was below 40 ppm. In tests with other commercial fuels having higher sulfur contents, excessively rapid catalyst deterioration was observed, which we have ascribed to sulfur poisoning.

The maximum sulfur content permitted by military specifications for JP-4 is 4000 parts per million;[20] we have found it interesting that batch after batch of JP-4, from at least one refiner, has consistently analysed under 50 ppm. We believe this reflects how overly liberal sulfur specifications are in this day of modern refineries. Nowadays sulfur removal often occurs incidentally to other processing and is frequently done to protect the process equipment and catalysts used by the refiner. When and if direct conversion of hydrocarbons in fuel cells becomes a reality a sulfur problem is likely to arise there also. It would appear reasonable and desirable that any new fuel specifications be written with low sulfur limits.

Returning to the mechanical aspects, it must be remembered that although the Engelhard Hydrogen Unit is appreciably simpler

than other hydrogen manufacturing processes it still requires a number of components and controls. There are ways of designing certain very small generators to operate without any auxiliary electric power, but in general pumps and blowers and controllers are necessary, all of which require power.

One version is illustrated in a simplified schematic flow diagram, Figure 3. Fuel and water are metered to the system in fixed ratio by controlling the speeds of positive displacement pumps to supply adequate feed for the hydrogen demand at any instant. The feed stream is heated in a flue gas exchanger, it is then reformed and product hydrogen removed in the reactor/diffusor. The hydrogen stream is cooled against incoming combustion air, which is metered by a speed controlled positive displacement blower. The residual fuel gas from the reactor/diffusor passes through a high temperature back pressure control valve, on to the furnace burner where it is burned with the controlled combustion air. The flow rates of the fuel/water feed and the combustion air must be closely controlled to maintain high efficiency. Feed, air, and product hydrogen flows are not linearly related, which complicates the control system.

The interplay between generator size and weight, efficiency, and power requirement is complex. Optimization is particularly difficult and critical in generators for mobile fuel cell power systems. There is need for more efficient auxiliary equipment than now available. For example, in one 140 SCFH unit under construction, theoretical feed pump power is 2 watts, air blower power 50 watts, while actual available equipment requires 200 watts and 400 watts respectively.

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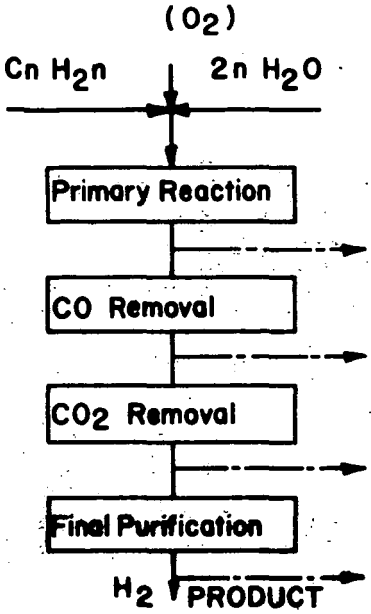
FIGURE 1
HYDROGEN MANUFACTURING PROCEDURES



MOLS

H_2	CO	CO_2	CH_4	H_2O	Σ
215	65	30	5	75	390
270	10	85	5	20	390
270	10	1	5	20	306
236	—	—	16	—	252

FIGURE 2
ENGELHARD HYDROGEN PROCESS

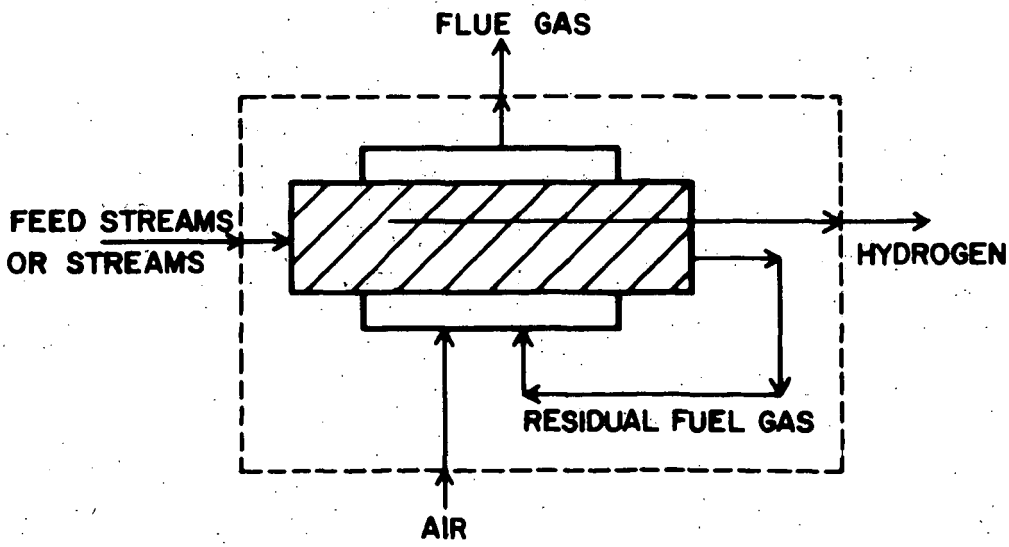
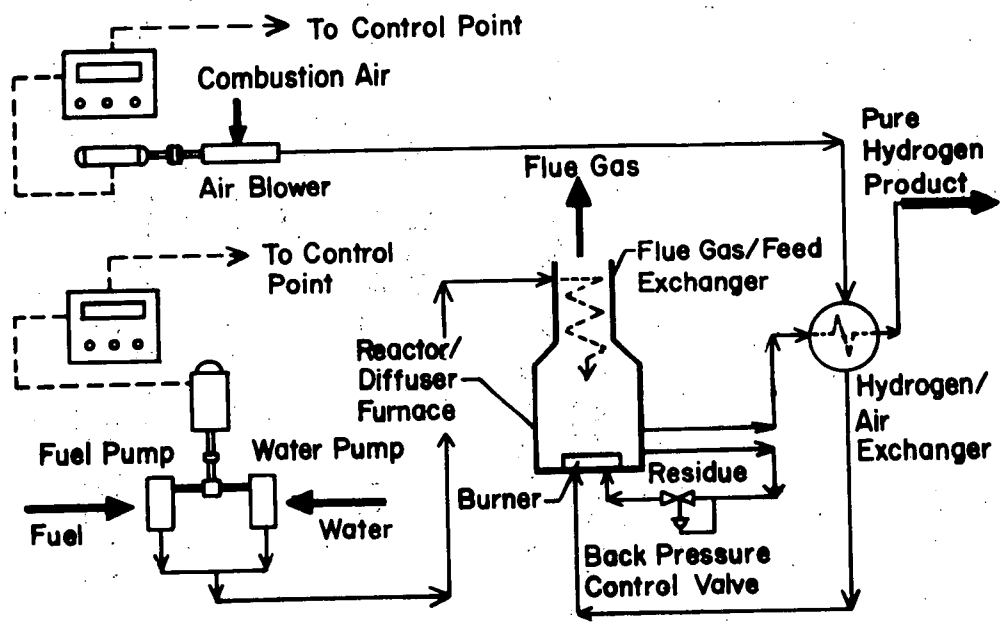



FIGURE 3
EHP SCHEMATIC FLOW DIAGRAM