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### Novel Electrochemical Hydrogen Separation Device Using Phosphoric Acid Membrane Cell

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NOVEL ELECTROCHEMICAL HYDROGEN SEPARATION DEVICE USING PHOSPHORIC ACID MEMBRANE CELL

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ABSTRACT

State-of-the-art hydrogen separation technologies operate at/or near ambient temperatures and are not considered very effective with gases containing low concentrations of hydrogen (such as coal-gas) and are susceptible to common impurities such as  $H_2S$ ,  $H_2O$ , and  $NH_3$ . Energy Research Corporation is developing an alternate, versatile process for hydrogen separation from any hydrogen-containing gas. This novel process involves oxidation of hydrogen at a gas diffusion anode to hydrogen ions, transportation of the ions under applied electrical field to a cathode, and reduction of the hydrogen ions at the cathode to hydrogen gas. The device offers many attractive features, including high hydrogen recovery (>90%), high product purity (>99%), tolerance to a variety of impurities, flexible product pressure, efficient operation with very dilute gases, negligible pressure loss, and wide operating pressure range including atmospheric. The feasibility of this electrochemical hydrogen separation device (EHSD) has been demonstrated at ERC using hydrogen concentrations as high as 75% (reformer product) and as low as 10% (process purge). The operating principle, design, and performance (current-potential relationship, product gas purity, effect of feed hydrogen concentration on hydrogen recovery and power requirements) of this process are presented in this paper.

INTRODUCTION

Application of the hydrogen separation device is for the separation of pure hydrogen from hydrogen containing streams such as reformed fuel, coal-gas, and various process purge streams. The recovered hydrogen can be used in chemical processes, many of which require greater than 95% purity hydrogen.

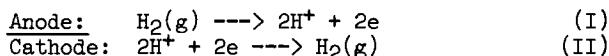
State-of-the-art hydrogen separation techniques available for this application include cryogenic processing, pressure-swing adsorption, and semipermeable membrane separation[1-9]. A metal hydride based separation process is also under development[10]. Each of these processes has advantages and limitations, as described in Table 1, and the process of choice depends very much on the specific application. These processes operate at/or near ambient temperature, and are not suitable for applications at temperatures above 100°C. In addition, none of these processes are considered very economical for recovering hydrogen from hydrogen-lean streams. A recent study conducted under DOE/METC Contract DE-AC21-85MC22130[11] has indicated that for 99.5% purity hydrogen recovery from coal-gas using an advanced semipermeable membrane, the separation efficiency is only 40% and the separation cost is \$1.55 per 1000 SCF of H<sub>2</sub>.

An EHSD, which is described by block diagram in Figure 1, is the subject of several U.S. patents[12-16], and offers many unique features. These include: high hydrogen recovery, high product purity, tolerance to feed gas impurities, continuous operation, low pressure drop, pressure flexible operation, flexible product pressure, low separation energy requirement and long service life. Thus, the EHSD system projects to more flexible operation and better performance characteristics than the state-of-the-art technologies.

Energy Research Corporation has successfully demonstrated the technical feasibility of the process. The theoretical basis, potential application, current status and planned activities of EHSD development are discussed next.

#### THEORETICAL BASIS FOR EHSD

The EHSD is an electrochemical hydrogen separation device based on the unique electrochemical characteristics of hydrogen, namely the highly reversible nature of its oxidation-reduction reactions. The principle and the hardware concept are illustrated in Figure 2. The reactions through which hydrogen separation occur are:



Hydrogen from a gas mixture is oxidized to H<sup>+</sup> ion and transported through a cation transport electrolyte membrane under an electric field and discharged as pure hydrogen on the cathode side.

Although any proton transfer electrolyte can be used for hydrogen separation, the phosphoric acid-based system offers some unique advantages for this application. The hydrogen-containing stream (especially coal-gas, reformer product

TABLE 1

MAJOR FEATURES OF CONVENTIONAL HYDROGEN RECOVERY ALTERNATIVES: Each Process Provides Advantages as well as Limitations and the Choice is Very Much Specific to the Application.

CONVENTIONAL HYDROGEN SEPARATION ALTERNATIVES	ADVANTAGES	DISADVANTAGES
CRYOGENIC - Condensation and Separation of Nonhydrogen Components.	High Recovery; High Purity (90-99%); Product Available Essentially at Feed Pressure.	Become Competitive Only When Hydrocarbons are Present.
PRESSURE-SWING ADSORPTION (PSA) - Uses a Cyclic Multiple Vessel System to Adsorb Everything but the H <sub>2</sub> .	Product Available Essentially at Feed Pressure; High Purity (99.9%); High Recovery (70 to 85%).	Feed Gas Must be at Pressure. Purge Gas is Vented at Atmospheric Pressure.
MEMBRANE SEPARATION - Uses the High Permeability of Hydrogen Relative to the Other Components to Recover Hydrogen.	Relatively High Product Purity (95 to 99%) and High Recovery (85%) with Right Feed Conditions.	High Feed Pressure Needed; High Feed Concentrations Desirable for High Recovery; Poor CO <sub>2</sub> and H <sub>2</sub> O Separation. H <sub>2</sub> /CO Separation Roughly 30:1; Large Product Side Pressure Drop.
METAL HYDRIDE - Uses a Cyclic Multiple Vessel System to Absorb Only the Hydrogen.	Potential for High Purity (99%) and High Recovery with Low H <sub>2</sub> Feed Concentration and Low Feed Pressure; High Separation Cost for Impurity Free Feed.	Common Impurities CO, O <sub>2</sub> , H <sub>2</sub> O Rapidly Poison the Metal Hydride Formers; High Pressure Limitations.

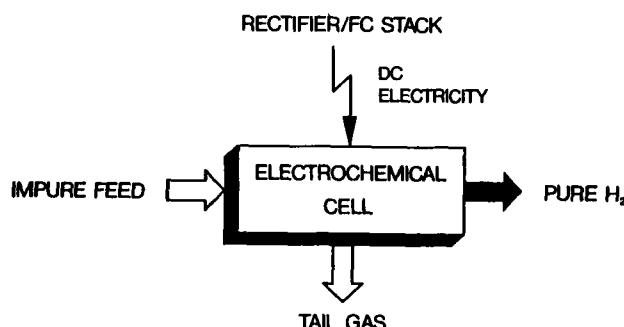


FIGURE 1:  
ELECTROCHEMICAL HYDROGEN SEPARATION SYSTEM

The EHSD Operates Efficiently on any Hydrogen-containing Feed-stock LD100s

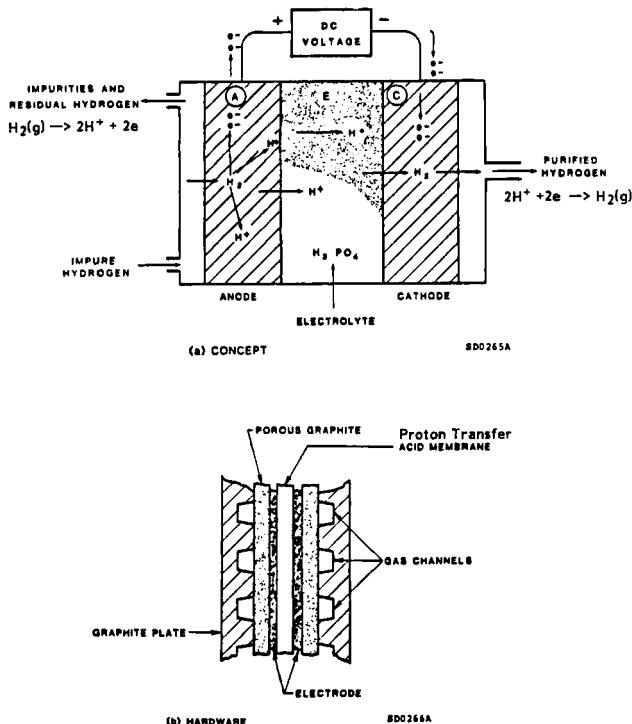


FIGURE 2. SCHEMATIC OF AN ELECTROCHEMICAL HYDROGEN SEPARATION DEVICE:

The Highly Reversible Hydrogen Oxidation-Reduction Reactions are Utilized for Efficient Hydrogen Separation Employing Low Cost Carbon-Based Cell Design Developed for PAFC

gases and fuel cell anode exhaust) may contain large concentrations of CO. For efficient hydrogen recovery, conversion of the major portion of this CO to hydrogen by the low temperature water-gas shift reaction is necessary. The phosphoric acid operating temperature of  $\sim 200^{\circ}\text{C}$  provides a close match with the desired shift temperature of 200 to  $250^{\circ}\text{C}$ . Thus the PAFC (Phosphoric Acid Fuel Cell) based EHSD system can also be more easily integrated in a coal-gasification system, requiring less cooling/reheating subsystems.

#### EHSD APPARATUS

The EHSD cell hardware is similar to the phosphoric acid fuel cell (PAFC), and is indeed an offshoot of the PAFC stack. The EHSD hardware, however, is less complex because of simpler

electrochemistry and reduced heat transfer requirements. The EHSD stack enjoys the following advantages over the PAFC: it has no cooling requirements; the Pt loading is drastically minimized; operation at more uniform temperatures is possible; it requires one less manifold; and there is no problem with materials degradation.

The EHSD electrodes are of the type used in acid fuel cells and are catalyzed with a small amount of metallic platinum (between 0.05 and 0.5 mg/cm<sup>2</sup>). Typically, such electrodes have a porosity of between 50 and 90%, the pores of the electrodes are partially filled with electrolyte to provide a three-phase interface for the anodic oxidation and cathodic reduction of hydrogen. The liquid-gas interface is stabilized by partial wetproofing of the electrodes with polytetrafluoroethylene (PTFE).

The amount of electrical energy needed for producing a given amount of purified hydrogen depends mainly on the electrical resistance of the device. A cell structure consisting of thin, large area components is required to reduce the electrical energy need. The cell design requirements to a large extent are similar to those of the phosphoric acid fuel cells. Therefore, the bipolar cell stack assembly developed for the PAFC can be adapted for this device. This construction can be seen in the cell cutaway drawing of Figure 3. The components constituting the device, namely plate, anode, electrolyte membrane, and cathode, are repeated to obtain a multicell module.

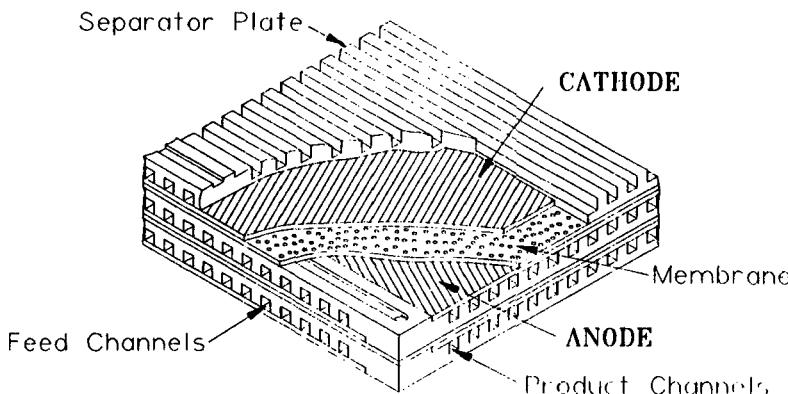
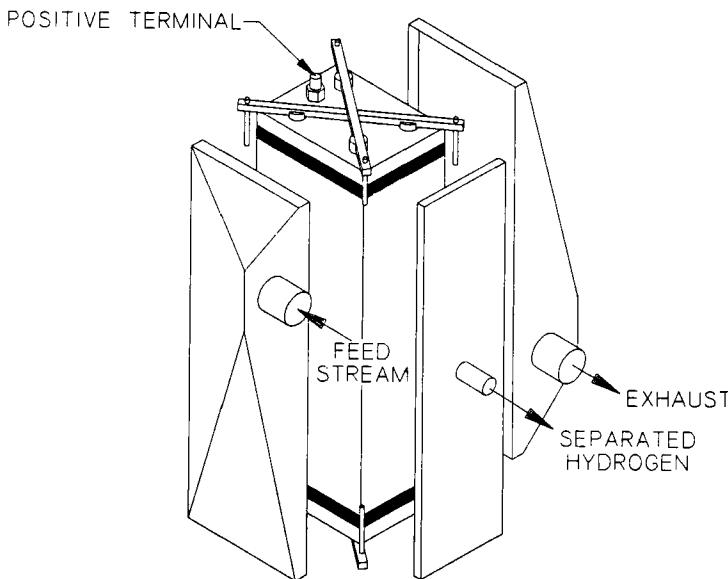


FIGURE 3. HARDWARE CONCEPT:

The EHSD Single Cells are Stacked in a Pile to Obtain a Multicell Module

To conveniently supply the feed stream and to collect product and tailgas streams from the multicell stack, a crossflow arrangement where reactant (feed stream) and product (separated hydrogen) flow at right angles can be employed. This arrangement is shown in the stack assembly drawing of Figure 4. The impure feed gas distribution is accomplished by the use of a manifold attached to one of the faces of the module. The gas which exits the anode and has been depleted of hydrogen is collected from the opposite manifold, and a third manifold is used to collect the product hydrogen.



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FIGURE 4

**EHSD STACK CONCEPT:**

Only One Manifold is Required of the Product Side

The bipolar cell stack is supported between rigid end plates and compressed by means of a crossbar-tie rod assembly to ensure intercell electrical contact. The direct current (DC) is applied through insulated terminals on the end compression plates.

**DIVERSE APPLICABILITY OF EHSD**

The most important applications of the EHSD relate to bulk hydrogen separation for use in chemical processes. In addition,

the device is a potential candidate for a variety of other applications. ERC has identified that, in addition to simple hydrogen recovery, the electrochemical hydrogen separation process brings in other potential system benefits in several process applications, making its use highly attractive. Some typical examples of these applications are discussed below.

Energy Research Corporation has shown that the efficiency of the natural gas-fueled Molten Carbonate Fuel Cell (MCFC) power plant can be improved, approximately 5 percentage points<sup>[17]</sup> by using an EHSD to reclaim hydrogen and CO<sub>2</sub> separately from the MCFC anode exhaust for recycle to the fuel cell. Application in a coal gasification MCFC plant is also being considered.

The EHSD can also be utilized to supply hydrogen for a hydrodesulfurizer in a fuel processing system, allowing the separated hydrogen to be withdrawn at a higher pressure than the feed. The reversible compression energy is supplied electrochemically. This feature enables recycling of the hydrogen to the hydrodesulfurizer without pressure booster equipment.

#### PHOSPHORIC ACID TYPE EHSD PERFORMANCE

Feasibility of the EHSD concept has been verified at ERC in bench scale single cells and short subscale stacks. The operating performance characteristics of a single cell (25-cm<sup>2</sup>) hydrogen separator are shown in Figure 5 for three different hydrogen input compositions simulating pure hydrogen, reformer products, and very lean hydrogen streams. A higher applied potential is required with lower H<sub>2</sub> feed concentrations to overcome concentration effects and diffusion losses. The EHSD performance with MCFC anode exhaust gas presented in Table 2 demonstrates that high current density operations (400 mA/cm<sup>2</sup>) with 90% recovery are achievable without incurring significant diffusion losses. These results signify that high hydrogen recovery and high current density operation with lean hydrogen gas stream is entirely feasible.

The current-voltage and energy consumption data for a 20-cell (328-cm<sup>2</sup>) hydrogen transfer device are shown in Figure 6. The single cell EHSD performance was essentially reproduced in this 20-cell stack, indicating that no performance loss is incurred in scaleup.

The effect of the fraction of hydrogen removed from the feed gas on the required potential in a bench-scale cell is given in Figure 7. The potential which must be applied remains essentially constant until well over 90% of the hydrogen in the feed stream is removed. Because of the high hydrogen ion transfer rate compared to the much slower diffusion of the unwanted gaseous components through the membrane, a high degree of product purity

TABLE 2. EHSD PERFORMANCE ON HYDROGEN-LEAN GAS:  
High Recovery and High Current Density Operations  
are Feasible for Hydrogen Recovery from a Hydrogen-  
Lean Gas

Pressure: 1 ATM  
Temperature: 190°C  
Anode Gas: MCFC Anode Exhaust Gas (13.4% H<sub>2</sub>,  
51% CO<sub>2</sub>, 0.1% CO, 35% H<sub>2</sub>O)  
H<sub>2</sub> Transfer: 90%

Current Density mA/cm <sup>2</sup>	Cell Voltage, mV		Measured Loss, mV	Theoretically Expected Loss
	Anode Gas Pure H <sub>2</sub>	Anode Gas Simulated MCFC Exhst		
	A	B		
160	48	113	65	63
200	60	123	63	67
240	73	140	67	71
280	81	155	74	75
320	95	170	75	81
360	109	186	77	88
400	119	208	89	96

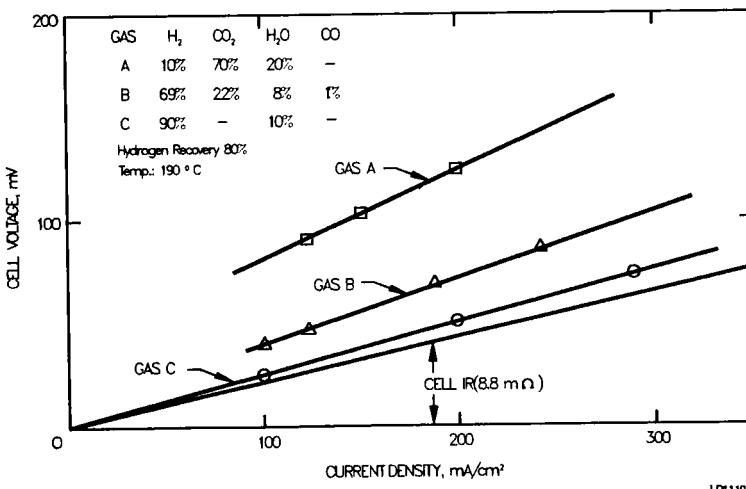


FIGURE 5. BENCH-SCALE HYDROGEN SEPARATOR CELL PERFORMANCE (25-cm<sup>2</sup>):  
Efficient Hydrogen Reclamation from Low Hydrogen Containing Gases is Entirely Feasible

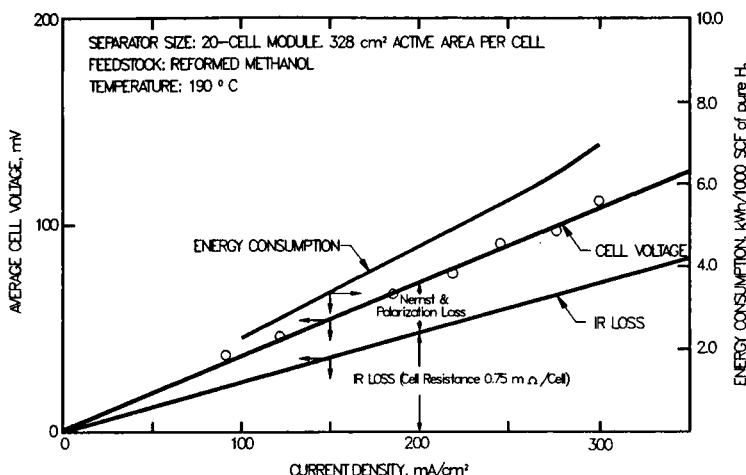


FIGURE 6. PERFORMANCE OF A 20-CELL EHSD MODULE:  
The Single Cell EHSD Performance was Reproduced  
in a 20-Cell Stack

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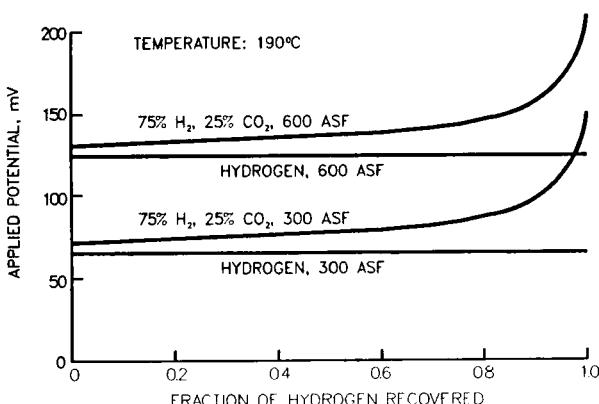


FIGURE 7. PRODUCT RECOVERY POTENTIAL:  
Up to 90% Hydrogen Recovery in EHSD is Achievable

LD1112

is achieved even in a single pass device. A multi-pass EHSD system can be employed to enhance the product purity further. Table 3 presents the results of gas chromatographic analysis of the product hydrogen obtained from a 25-cm<sup>2</sup> laboratory cell operating at 600 mA/cm<sup>2</sup>. These data show that product purity greater than 99% is available from a single pass system. The energy required for hydrogen separation is dependent on the feed gas composition, percent separation, and current density. Figure 8 shows the EHSD power consumption for 90% H<sub>2</sub> reclamation from a hydrogen-lean gas stream (MCFC anode exhaust) for different current density operations. Less than 4 kWh/lb-mole is required for recovery of 90% hydrogen from a stream containing only 13.4% H<sub>2</sub>.

TABLE 3. GAS COMPOSITION OF DIFFERENT STREAMS:  
EHSD Product Purity is Better than 99%

Gas	Feed Gas, %	Product, % (Dry Basis)
Hydrogen	69.4	99.81
Carbon Dioxide	23.1	0.19
Water	7.5	-
<b>TOTAL</b>	<b>100.0</b>	<b>100.0</b>

The EHSD system offers promise for an attractive device for pure hydrogen production from hydrogen-containing gases such as purge streams, coal-gas, and hydrocarbon reformed gas. The results presented here have demonstrated its technical feasibility and identified design parameters, as well as several attractive performance characteristics. Some limited multi-cell testing has been conducted and more is planned in the future. Preliminary economic estimates have projected the cost of 99% pure hydrogen recovery by EHSD from reformed fuel to be less than \$0.50/1000 ft<sup>3</sup>. Demonstration of endurance and a detailed economic evaluation of a potential use is planned in a DOE/METC sponsored program currently in place.

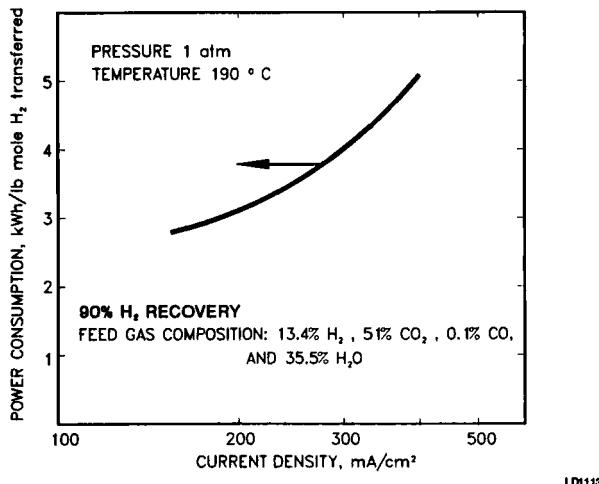


FIGURE 8. POWER CONSUMPTION (DILUTE STREAM):  
Less Than 4 kWh is Required for Reclaiming 1 lb-mole  
of Hydrogen from MCFC Anode Exhaust

#### ACKNOWLEDGEMENT

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