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Development of an Electrochemical Hydrogen Separator

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CONTRACT INFORMATION

Contract Number DE-AC21-89MC26040

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Period of Performance September 27, 1989 to October 26, 1992

Schedule and Milestones	FY 90	FY 91	FY 92	FY 93
	O D F A	J A O D F A	J A O D F A	J A O
Task				
1. Design and Operating Parameter Evaluation	-----			
2. Multicell Module Operation		-----		
3. Cost Evaluation and Comparison with Competing Systems			-----	

SCHEDULE MILESTONES

PROJECTED DATE

1. Submit Multicell Module Test Plan	6-30-90
2. Establish Model to Predict EHS Performance	2-28-91
3. Complete Long Term Single Cell Testing	11-29-91
4. Complete Design and Construction of Multicell Module	3-31-92
5. Complete Multicell Module Testing	9-15-92
6. Complete System Study and Cost Evaluation	9-28-92
7. Submit Final Project Report	10-26-92

OBJECTIVE

The objective of this program is to develop an electrochemical hydrogen separation device for cost-effective hydrogen recovery from various dilute hydrogen streams. Potential applications include high purity hydrogen recovery from oxygen and air blown gasifiers, as well as hydrogen-lean streams such as a carbonate fuel cell anode exhaust. Other potential applications include recovery of hydrogen used to mitigate corrosion in boiling water reactors (BWRs).

In the present program, the effect of design and operating parameters (e.g. pressure, temperature, and H_2 recovery on EHS performance have been characterized in single subscale cells (25 cm² active area) and presented as a mathematical model. Full size (1000 cm²) multi-cell-stack long term operation has also been demonstrated. Process conceptual design and economics for a potential application will be evaluated for the EHS and a competing technology.

BACKGROUND

The EHS is an electrochemical hydrogen separator based on the uniquely reversible nature of hydrogen oxidation-reduction reactions in electrochemical systems. The principle and the hardware concept are shown in Figure 1.

Hydrogen from the mixed gas stream is oxidized to H^+ ions, transported through a cation transport electrolyte membrane (matrix) under an applied electric field and discharged in a pure hydrogen state on the cathode. The cation transfer electrolyte membrane provides a barrier between the feed and product gases.

The EHS design is an offshoot of phosphoric acid fuel cell development. Although any proton transfer electrolyte can be used, the phosphoric acid based system offers a unique

Figure 1. Schematic of an Electrochemical Hydrogen Separator

The highly reversible hydrogen oxidation-reduction reactions are utilized for efficient hydrogen separation employing low cost carbon-based cell design developed for PAFC.

advantage because its operating temperature of $\sim 200^\circ\text{C}$ makes it tolerant to trace CO and also closely matches the water-shift reactor exit gas temperature ($\sim 250^\circ\text{C}$).

Hydrogen-containing streams in coal gasification systems have large carbon monoxide contents. For efficient hydrogen recovery, most of the CO must be converted to hydrogen by the low temperature water-shift reaction (Figure 2).

Advanced coal gasification and gas separation technologies offer an important pathway to the clean utilization of coal resources

Figure 2. Schematic of Bulk Separation from Coal Gasifier Streams
Hydrogen Separator Operates on Shift Converter Output

in the United States. Hydrogen is used today as a major chemical feed stock and is expected to play an ever-increasing role in the future. Thus, the separation technology for recovering hydrogen from the coal gasification product streams containing 20 to 60% H_2 is greatly needed.

Commercial and developmental separation processes known today can be grouped into the following process types:

- Solvent systems based on selective absorption

- Pressure swing adsorption in a packed sorbent bed
- Cryogenic methods
- Semipermeable membranes

These processes operate at moderate to low temperatures and require high pressures. None of these processes are considered very economical for the hydrogen-lean streams encountered in coal gasification (20% hydrogen in air blown) systems. This presents the need for novel concepts to efficiently achieve bulk separation of gases at moderate to high temperatures (100° to 700°C).

The electrochemical hydrogen separator (EHS), under development at ERC, has several attractive features:

- The operating temperature (~ 150°-200°C) is higher than those associated with the currently available devices and is compatible with the low temperature shift reactors.
- The EHS can operate at atmospheric as well as elevated pressures and the product H_2 is available at the feed stream pressure.
- High hydrogen recovery factor: 90% H_2 recovery from feed streams containing less than 10% hydrogen is feasible.
- High hydrogen purity: The product H_2 purity is >99% (dry basis) and is virtually independent of H_2 concentration in the feed gas.
- The process is continuous.
- Low energy cost: Depending upon the operating conditions, the energy requirement varies between 2 to 6 kWh/1000 SCF of recovered hydrogen.

Studies under DOE/METC contract DE-AC01-87MC23274 have indicated that by using the EHS, unreacted hydrogen from the carbonate fuel cell anode exhaust can be economically recovered and recycled as shown in Figure 3. The projected energy efficiency of a carbonate fuel cell power plant containing an EHS is 60% based on the higher heating value of coal.

Figure 3. Carbonate Fuel Cell System Concept

H₂ recovery from anode exhaust improves plant efficiency

PROJECT DESCRIPTION

In order to accomplish the program objective, the work has been broken down into three tasks. In Task 1, the effects of design and operating parameters on EHS performance in single subscale (25 cm²) cells were evaluated. The parameters (temperature, pressure, matrix thickness, anode Pt content, cathode Pt content, H₂ feed concentrations, feed gas impurities, current density, and hydrogen recovery) and their ranges are presented in Table 1. A mathematical

performance model was developed for design calculations. Task 2 involves the demonstration of scale-up, multi-cell operation, endurance, and product quality. The cost of the EHS hydrogen separation process will be compared with a competing separation technology in Task 3.

RESULTS

1. The feasibility of recovering 80% H₂ (>99% pure) from lean hydrogen streams containing as low as 5% hydrogen (dry basis) has been established (Figure 4). This implies that very low H₂ concentration streams such as carbonate fuel cell anode exhaust can be used to recover pure H₂.

2. It has also been established that with the EHS no distinction exists between N₂, CH₄, and CO₂ with regards to bulk separation of H₂ (Figure 4). Unlike other separation devices, the EHS plant design will be independent of the relative concentrations of CH₄, N₂ and CO₂, and the EHS can be used for air/oxygen blown gasifiers as well as methane producing gasifiers. This is a very important advantage of the EHS.

3. Over 99% pure H₂ can be recovered from streams containing as low as 5% H₂, and product H₂ purity increases with higher rate of recovery (Figure 5). This indicates that product H₂ purity does not have to be sacrificed to achieve high H₂ recovery.

4. The previous mathematical model, which was successfully verified with feed streams containing greater than 70% H₂, has been extended to predict EHS power consumption for gases containing as low as 5% H₂ (without contaminants), as shown in Figures 6 and 7.

5. The effect on EHS performance of dilute fuels (20% H₂) containing various concentrations of CO (0.1, 0.3 and 0.5%) has been investigated.

**Table 1. EHS Design Parameters and Ranges Evaluated
in Subscale-Cell Tests (Task 1)**

PARAMETER	RANGE	UNIT
Temperature	190 200 225	°C
Pressure	1 through 10	atm
Matrix Thickness	0.2 through 0.4	mm
Anode Pt Content	0.2 through 0.55	mg/cm ²
Cathode Pt Content	0.2 through 0.55	mg/cm ²
H ₂ Feed Concentration	5 10 30 60	mole %
Feed Gas Impurities	H ₂ S, NH ₃	ppm level
Current Density	Up to 400	mA/cm ²
Hydrogen Recovery	Up to 90	%

Figure 4. EHS Performance with Various Diluents
80% recovery is feasible with very dilute H₂ containing streams; CH₄, CO₂, and N₂ behave as equivalent inerts the EHS

Figure 5. Hydrogen Recovered From Dilute Feed Gas
Purity Improves With Increasing Specific Recovery Rate

Figure 6. Estimated vs. Experimental Power Consumption in EHS
Good Agreement for Dilute H₂ Streams

The power demand is dependent upon H₂ and CO content in the feed gas as well as on H₂ recovery (Figure 8). The effect of CO is greater with low concentrations of H₂, which indicates that pretreatment to reduce CO content in the feed gas is beneficial to the EHS system. The experimental results have not yet been incorporated into the mathematical model.

6. Feed streams containing up to 10 ppm NH₃ or H₂S were found to have no effect on EHS power requirement. Even with feed streams containing CO, low levels of H₂S did not increase the EHS power requirement. However, when H₂S is present in the feed stream low levels of H₂S were found in the pure H₂ product stream.

7. Increased operating temperature decreases the power requirement of the EHS (Figure 9). This is an important attribute because it adds versatility to the EHS system.

Figure 7. The Effect of H₂ Feed Concentration and H₂ Recovery on EHS Power Demand
The EHS is Operable with a Range of H₂ Fuel Concentrations

8. Operating at increased pressure does not affect the EHS power requirement (Figure 10). In fact, there is an initial decrease in power requirement at increased pressure due to a lower electrical resistance.

9. Long-term stability of the EHS has been demonstrated. A subscale-cell was operated for over 4,400 hours using a variety of feed streams and hydrogen recovery rates (Figure 11).

10. Scale-up and stability of the EHS has been demonstrated with the 10-cell EHS module. The module was constructed by stacking 1.1 ft² EHS cells (Figure 12). Performance has remained stable after 1400 hour of operation (Figure 13).

Figure 8. Effect of CO on EHS Performance
Increased CO Concentration Substantially Increases EHS Power Consumption

Figure 9. Temperature Effect on EHS Performance
Increasing the Operating Temperature Decreases the EHS Power Requirement

Figure 10. Pressure Effect on EHS Performance
The EHS is Operable at Various Pressures Without Affecting Power Consumption

Figure 11. Stable Long Term EHS Subscale Performance Demonstrated
EHS Performance Stability Demonstrated at
at Increased H_2 Flux and Utilization

Figure 12. 10-Cell EHS Module
The Multicell Test Module Was
Constructed with 1.1 ft² Cells

Figure 13. 10-Cell EHS Module Test
Multicell Module Test Verifies Scaleup Capability

CONCLUSIONS

Ability to separate hydrogen by the EHS process has been demonstrated for a wide range of conditions. Scale-up capability has been verified by construction and successful operation of a multicell EHS stack.

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