DOE/MC/26040--T9

DE92 017666

NOVEL HYDROGEN SEPARATION DEVICE DEVELOPMENT FOR COAL GASIFICATION SYSTEM APPLICATIONS

DOE CONTRACT NO. DE-AC21-89MC26040

TOPICAL REPORT TASK 1

December, 1991

Prepared For:

UNITED STATES DEPARTMENT OF ENERGY
Morgantown Energy Technology Center
3610 Collins Ferry Road
Morgantown, WV 26507-0880

By:

ENERGY RESEARCH CENTER
3 Great Pasture Road
Danbury, CT 06813

Ashok Kush, Program Manager

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

PUBLISHED BY: *Dec*

7/28/92

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

LIST OF CONTRIBUTORS

Mohammad Farooque

Jennifer Fruchtman

Marge Gaylord

Ashok Kush

Joy MacDonald

Thomas Rostrup-Nielsen

EXECUTIVE SUMMARY

This report summarizes all results obtained under Task 1, Operation and Parameter Testing using Subscale Cells. Stable EHSD operation was demonstrated with the 4,400 hour life test of an EHSD. It was found that N_2 , CO_2 and CH_4 behave as equivalent inerts; EHSD performance is not affected by the balance of feed gas containing these components. High H_2 purity, >99%, is one of the main features of the EHSD. This product purity level is not sacrificed by increased H_2 recovery. CO , however, does adversely affect EHSD performance and therefore feed stream pretreatment is recommended. Concentrations up to 10 ppm H_2S and NH_3 were added to the feed gas stream to determine their effect on EHSD performance. These impurities did not affect EHSD performance.

LIST OF FIGURES

<u>TITLE</u>	<u>PAGE</u>
Figure 1. Schematic of an Electrochemical Separation Device	2
Figure 2. Schematic of Bulk Separation of Hydrogen From Coal Gasifier Streams	3
Figure 3. CFC System Concept	5
Figure 4. EHSD Performance With Various Diluents	7
Figure 5. EHSD Product Purity	7
Figure 6. Effect of CO Feed Content On EHSD Energy Demand	8
Figure 7. Estimated Performance for EHSD	9
Figure 8. EHSD Performance at Various Pressures	9
Figure 9. Effect of Temperature on EHSD Performance	10
Figure 10. Stable Long-Term EHSD Performance Demonstrated	11
Figure 11. EHSD Performance Using H ₂ S Containing Feed	12
Figure 12. EHSD Performance at Various H ₂ Flux Using H ₂ S/CO Containing Feed	13
Figure 13. EHSD Performance With NH ₃ Containing Feed	14

LIST OF TABLES

<u>TITLE</u>	<u>PAGE</u>
Table I. EHSD Design Parameters and Evaluation Ranges	6
Table 2. Comparison of EHSD Performance Using H ₂ S Containing Feed	12

OBJECTIVE

The objective of this program is to develop an electrochemical hydrogen separation device for cost-effective hydrogen recovery from coal derived gases. The potential applications are high purity hydrogen recovery from oxygen and air blown gasifiers as well as hydrogen-lean streams such as carbonate fuel cell anode exhaust.

In the present program, the effect of design and operating parameters (i.e., pressure, temperature, H_2 recovery and electrochemical catalyst loading) on EHSD performance were characterized in single subscale cells (25 cm^2 active area) and used to develop a mathematical model. Scale-up, full size (1000 cm^2) multi-cell stack operation and product purity were also demonstrated.

TECHNICAL BACKGROUND

The EHSD is an electrochemical hydrogen device based on the uniquely reversible nature of hydrogen oxidation-reduction reactions in electrochemical systems. The design is an offshoot of phosphoric acid fuel cell development. EHSD operating principle and hardware concept are shown in Figure 1.

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

Although any proton transfer electrolyte can be used, the phosphoric acid based system offers a unique

advantage because of its operating temperature of $\sim 200^\circ\text{C}$, which closely matches the gas exiting the water-shift reactor ($\sim 250^\circ\text{C}$).

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). The residual CO has a very minor effect on the operation of the EHSD.

FIGURE 1. SCHEMATIC OF AN ELECTRO-CHEMICAL SEPARATION DEVICE:

The Highly Reversible Hydrogen Oxidation-Reduction Reactions are Utilized for Efficient Hydrogen Separation Employing Cheap Carbon-Based PAFC Technology

Advanced coal gasification and gas separation technology offer an important pathway to the clean utilization of coal resources 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 coal gasification processes containing 20 to 60% H_2 is greatly needed.

Figure 2. SCHEMATIC OF BULK SEPARATION FROM COAL GASIFIER STREAMS

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

- Solvent systems based on selective absorption
- Pressure swing absorption 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 hydrogen-lean streams as encountered in coal gasification (20% hydrogen in air blown) systems. This presents

ENERGY RESEARCH CORPORATION

the need for novel concepts to efficiently achieve bulk separation of gases at moderate to high temperatures (100° to 700°C).

The electrochemical hydrogen separation device (EHSD), under development at ERC, has several attractive features as follows:

- The operating temperature (~200°C) is compatible with product gas from low temperature shift reactors.
- Atmospheric as well as elevated pressure can be used, and there is no pressure loss in the system; product H₂ is available at the feed stream pressure.
- Recovery of 90% H₂ from feed streams containing less than 10% hydrogen is feasible.
- The product H₂ purity is >99% (dry basis) and is virtually independent of H₂ concentration in the feed gas.
- Continuous operation. The process requires no equipment regeneration.
- Low energy cost: Depending upon the operating conditions, the energy requirement varies between 2 and 6 kWh/1000 SCF of recovered hydrogen.

Studies under DOE/METC contract DE-AC01-87MC23274 have indicated that by using the EHSD, 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 EHSD is increased from 54% to 60% based on the lower heating value of natural gas.

Figure 3. CARBONATE FUEL CELL SYSTEM CONCEPT: H₂ Recovery from CFC Anode Exhaust Improves Plant Efficiency

PROJECT DESCRIPTION

To accomplish the program objective, the work was broken down into three tasks. In Task 1, the effects of design and operating parameters on EHSD performance in single subscale (25 cm²) cells were evaluated. The parameters (temperature, pressure, membrane thickness, electrode Pt content, H₂ feed content, 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 involved the demonstration of scale-up, multi-cell operation and product quality. The cost of the EHSD system will be compared with a competing separation technology in

Table I. EHSD DESIGN PARAMETERS AND EVALUATION RANGES

PARAMETER	RANGE	UNIT
TEMPERATURE	190 200 220	$^{\circ}\text{C}$
PRESSURE	1 THROUGH 10	Atm
MEMBRANE THICKNESS	0.2 THROUGH 0.4	mm
ANODE Pt CONTENT	0.2 THROUGH 0.55	mg Pt/cm ²
CATHODE Pt CONTENT	0.2 THROUGH 0.55	mg Pt/cm ²
H ₂ FEED CONCENTRATION	5 10 30 60	mole %
FEED GAS IMPURITIES, (H ₂ S, NH ₃)	3 TO 10	ppm
CURRENT DENSITY	UP TO 400	mA/cm ²
HYDROGEN RECOVERY	UP TO 90	%

Task 3.

RESULTS

It was previously established that EHSD performance is not affected by the balance of the feed gas, whether CH₄, N₂, or CO₂ (Figure 4). This is an important feature of the EHSD because, unlike other separation devices, EHSD product hydrogen purity and recovery are independent of the relative concentrations of other major components in the feed gas. The EHSD can be used with air or oxygen blown gasifier exhaust (with a typical dry composition range of 30-60% H₂, 1-45% N₂, 24-35% CO₂, 1-4% CH₄), as well as methane producing gasifiers (with an approximate dry composition of 26% H₂, 18% N₂, 29% CO₂, 27% CH₄). It was also verified that the EHSD is capable of recovering 90% H₂ with a purity of greater than 99%

from low hydrogen concentration streams such as carbonate fuel cell anode exhaust. This product purity increases with rate of recovery which signifies that high product hydrogen purity is not sacrificed by high hydrogen recovery (Figure 5).

Several EHSD design parameters were investigated. It was determined that lowering the electrode platinum content

Figure 4. EHSD PERFORMANCE WITH VARIOUS DILUENTS: 80% Recovery is Feasible with Dilute H₂ Containing Streams; CH₄, CO₂, and N₂ Behave as Equivalent Inerts.

Figure 5a. PRODUCT PURITY vs. H₂ RECOVERY **Figure 5b. PRODUCT PURITY vs. FLUX**
High H₂ Purity is Not Sacrificed by Increased H₂ Flux

from 0.5 to 0.26 mg Pt/cm² did not affect EHSD energy requirement. This results in a reduction of EHSD capital cost. The EHSD membrane produces a resistive power demand which increases proportionally with membrane thickness. It was established that the membrane remains effective at a thickness in the range of 0.2-0.3 mm and therefore reduces the resistive energy demand.

Figure 6. EFFECT OF CO FEED CONTENT ON EHSD POWER DEMAND
CO Feed Content and H₂ Recovery Increase Power Demand

EHSD performance is affected by the presence of CO in the feed stream and is dependant on H₂ and CO content as well as the H₂ recovery (Figure 6). This effect is greater with low H₂ concentrations which indicates that pretreatment to reduce CO content in the feed gas is beneficial to the EHSD system.

A mathematical model was developed to predict EHSD power consumption for gases containing as low as 5% hydrogen. This model fits well with experimental data as shown in Figure 7. A well-developed model is an essential tool for plant design calculations and economic analysis.

Figure 7. ESTIMATED PERFORMANCE FOR EHSD
 The Mathematical Model is in Good Agreement with EHSD
 Experimental Results in a Range of H₂ Concentrations

Figure 8. EHSD PERFORMANCE AT VARIOUS PRESSURES
 EHSD Performance is Not Affected by Pressure

EHSD performance at various pressures was evaluated using several feed streams. Increasing operating pressure above atmospheric may reduce the electrical resistance of the EHSD and therefore show an

Figure 9. EFFECT OF TEMPERATURE ON EHSD PERFORMANCE

Increasing the Operating Temperature Decreases EHSD Power Requirement

initial decrease in required energy (Figure 8). Varying the pressure above one atmosphere does not affect the EHSD energy demand.

The effect of temperature on EHSD energy consumption was established. As expected, the power demand decreases as operating temperature increases (Figure 9). This is an important attribute of the EHSD system because it operates at temperatures

closely matching that of the gas exiting the water gas shift reactor and also adds versatility to the EHSD operating system.

Figure 10. STABLE LONG-TERM PERFORMANCE DEMONSTRATED
 EHSD Performance Stability Demonstrated at Increased H_2 Flux and Recovery

Long-term stable EHSD operation has been demonstrated. A subscale EHSD cell has operated for over 4,400 hours on a variety of feeds and at stringent operating conditions (Figure 10). The energy requirement remained stable throughout its operating life.

Studies were also conducted using feed streams containing trace quantities of NH_3 and H_2S . Research conducted on PAFC operating conditions has established that the presence of even small quantities of H_2S or NH_3 may adversely affect fuel cell

performance. As trace quantities of these components may be present in coal gasifier product streams, a study was undertaken to determine what effect they may have on EHSD performance.

The sulfur tolerance of the EHSD was investigated with subscale (25 cm²) cell tests. A variety of feed compositions containing up to 10 ppm H₂S were studied and the results indicate that EHSD performance is not

Table 2. Comparison of EHSD Performance Using H₂S Containing Feed

Feed Composition	10 ppm H ₂ S Bal H ₂	Neat H ₂
Energy Required, mV	66	67

affected by low levels of H₂S. The EHSD energy requirement using neat hydrogen and a 10 ppm H₂S/hydrogen feed are compared in Table 2. There is no change in EHSD performance due to the addition of the H₂S. Short term stability tests show that the energy requirement of a dilute H₂ stream containing 3.5 ppm H₂S is comparative to the EHSD energy requirement when using a dilute H₂S-free feed streams as shown in Figure 11.

Figure 11. EHSD PERFORMANCE USING H₂S CONTAINING FEEDS
H₂S Does Not Affect EHSD Performance

Figure 12. EHSD PERFORMANCE AT VARIOUS H₂ FLUX USING H₂S/CO CONTAINING FEED

The EHSD energy requirement with a feed containing H₂S and CO was also studied and it was verified that there was no increase in energy requirement due to the H₂S/CO containing feed; the addition of the H₂S did not increase the energy requirement. A comparison of the energy requirement at various H₂ flux using a 32% H₂/0.2% CO and 2 ppm H₂S feed stream with a H₂S-free 32% H₂/0.2% CO feed is shown in Figure 12.

The presence of H₂S in the feed stream will affect the purity of the product hydrogen stream. Equal concentrations of H₂S were detected in both the product hydrogen and the waste gas streams. This is due to the high solubility of the H₂S in the electrolyte.

The effect of ammonia in EHSD feed gas on the energy requirement was also investigated. PAFC studies have shown that there is a performance loss due to the presence of ammonia. It is thought that this performance loss is due to a reaction with NH_4^+ and phosphoric acid at the oxidant electrode. At EHSD operating conditions, there is no oxidant supplied and therefore no performance loss is predicted. This was substantiated in subscale cell tests using a variety of NH_3 containing feeds. Two feed gases were tested, one containing 2.6 ppm $\text{NH}_3/23\%$ H_2 and the other a

Figure 13. EHSD PERFORMANCE WITH AMMONIA CONTAINING FEED
There is No Change in Performance Due to the Presence of NH_3

straight hydrogen stream with 10 ppm NH_3 . As shown in Figure 13, the EHSD performance did not change due to the addition of NH_3 . Stable performance was observed in the short term stability tests conducted with the different NH_3 concentration feed gases.

performance. As trace quantities of these components may be present in coal gasifier product streams, a study was undertaken to determine what effect they may have on EHSD performance.

The sulfur tolerance of the EHSD was investigated with subscale (25 cm²) cell tests. A variety of feed compositions containing up to 10 ppm H₂S were studied and the results indicate that EHSD performance is not

Table 2. Comparison of EHSD Performance Using H₂S Containing Feed

Feed Composition	10 ppm H ₂ S Bal H ₂	Neat H ₂
Energy Required, mV	66	67

affected by low levels of H₂S. The EHSD energy requirement using neat hydrogen and a 10 ppm H₂S/hydrogen feed are compared in Table 2. There is no change in

EHSD performance due to the addition of the H₂S. Short term stability tests show

that the energy requirement of a dilute H₂ stream containing 3.5 ppm H₂S is comparative to the EHSD energy requirement when using a dilute H₂S-free feed streams as shown in Figure 11.

Figure 11. EHSD PERFORMANCE USING H₂S CONTAINING FEEDS
H₂S Does Not Affect EHSD Performance

END

DATE
FILMED
9/08/92