PROJECT facts

Advanced Research

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U.S. Department of Energy
Office of Fossil Energy
National Energy Technology Laboratory

Palladium/Copper Alloy Composite Membranes for High Temperature Hydrogen Separation

CONTACTS

Robert R. Romanosky
Technology Manager
Advanced Research
National Energy Technology Laboratory
3610 Collins Ferry Road
P.O. Box 880
Morgantown, WV 26507-0880
304-285-4721
robert.romanosky@netl.doe.gov

Arun C. Bose
Project Manager
National Energy Technology Laboratory
626 Cochrans Mill Road
P.O. Box 10940
Pittsburgh, PA 15236-0940
412-386-4467
arun.bose@netl.doe.gov

J. Douglas Way
Colorado School of Mines
Chemical Engineering Department
1500 Illinois Street, AH 447
Golden, CO 80401-1887
303-273-3519
dway@mines.edu

Description

In a three-year project sponsored by the University Coal Research (UCR) Program for the U.S. Department of Energy, Office of Fossil Energy (DOE-FE), a team led by the Colorado School of Mines investigated the development of high productivity, sulfur tolerant composite metal membranes for hydrogen production. The development of palladium-copper alloy separation membranes holds great promise for advanced coal-based power and fuel production technology applications. Over the long term, hydrogen is anticipated to be the fuel of choice for both the power and transportation industries. For a hydrogen-based energy structure, fossil fuel-based technologies will be required to generate hydrogen for various uses including energy production and value-added commercial products. Simple, effective means are needed for separating hydrogen from fossil-based synthesis gas (syngas) streams. A robust, cost-effective palladium (Pd) alloy membrane that is highly selective for hydrogen (H_2) has the potential to change the chemical industry by replacing traditional reaction and separation procedures, thereby resulting in sizable savings in energy consumption and capital investment in equipment.

Various metallic and ceramic substances have been considered as candidates for membrane applications. Palladium and its copper (Cu) and gold (Au) alloys, as well as nickel (Ni), platinum (Pt), and other metals in Groups III-IV of the periodic table, all are permeable to hydrogen. Metal membranes made of palladium and its alloys are the most widely studied due to their high hydrogen permeability, their chemical compatibility with many gas streams containing hydrocarbons, their ability to handle a high volume and rate of flow (flux), and their theoretically infinite ability to separate any and all hydrogen (selectivity). Palladium alloys often possess higher hydrogen permeability than pure palladium. They also are unaffected by thermal cycling and have some resistance to sulfur (S) poisoning.

Objectives

Previous UCR research demonstrated that very thin (1 µm thick) Pd-Cu composite membranes can be fabricated that exhibit high H_2 flux and are also resistant to hydrogen sulfide (H_2S) degradation. At that time, several very interesting phenomena were observed, including the influence of surface structure on H_2 transport, and the inhibition of H_2 flux by H_2S in the presence of H_2S and CO_2.

PROJECT DURATION

Start Date
07/10/03

End Date
08/31/06

COST

Total Project Value
$200,000

DOE/Non-DOE Share
$200,000 / $0

ADDRESS

National Energy Technology Laboratory
1450 Queen Avenue SW
Albany, OR 97321-2198
541-967-5892

2175 University Avenue South
Suite 201
Fairbanks, AK 99709
907-452-2559

3610 Collins Ferry Road
P.O. Box 880
Morgantown, WV 26507-0880
304-285-4764

626 Cochrans Mill Road
P.O. Box 10940
Pittsburgh, PA 15236-0940
412-386-4687

One West Third Street,
Suite 1400
Tulsa, OK 74103-3519
918-699-2000

CUSTOMER SERVICE

1-800-553-7681

WEBSITE

www.netl.doe.gov

Based on earlier observations, the objectives of this project were to investigate the following:

- Identify factors important in membrane fabrication (particularly on metal supports), and fabricate composite membranes on tubular, porous, stainless steel substrates;
- Optimize the membrane crystal and surface structure and bulk alloy composition, with respect to minimizing the membrane thickness while maximizing hydrogen flux and selectivity;
- Investigate the effects of temperature, pressure, and gas composition on H_2 flux and membrane selectivity, particularly using mixtures representative of coal-derived syngas;
- Seek to understand what might cause the different separation factors observed during mixture measurements, especially the inhibition of H_2 flux in the presence of H_2S and carbon monoxide (CO); and
- Fabricate composite Pd alloy membranes that meet FE pure hydrogen flux targets

Accomplishments

This project contributed to the development of high productivity, sulfur tolerant composite metal membranes for hydrogen production and membrane reactors. Composite Pd and Pd alloy metal membranes with thin, dense films (1-7 µm) were prepared on porous stainless steel and ceramic supports, meeting or exceeding the FE year 2010 and 2015 pure hydrogen flux targets at a differential pressure of only 20 pounds per square inch gauge (psig). For example, a 2 µm pure Pd membrane on a Pall AccuSep® substrate achieved an ideal H_2/N_2 separation factor of over 6,000, with a pure hydrogen flux of 210 standard cubic feet per hour (SCFH)/ft_2 at 20 psig feed pressure.

Similar performance was achieved with a $Pd_{80}Au_{20}$ composite membrane on a similar stainless steel substrate. Extrapolating the pure hydrogen flux of this Pd-Au membrane to the FE target conditions (150 psi absolute (psia) feed pressure and 50 psia permeate pressure) gives a value of 508 SCFH/ft_2, which exceeds the 2015 target. At these thicknesses, it is the cost of the supporting substrate and not that of the Au or Cu that will dominate the large-scale module costs. A direct comparison of face-centered cubic phase Pd-Cu and Pd-Au alloys on identical supports demonstrated that a $Pd_{85}Au_{15}$ alloy membrane was not inhibited by CO, CO_2, or steam present in a water-gas shift feed mixture at 400 °C, had better resistance to sulfur than a $Pd_{94}Cu_6$ mixture, and had over twice the hydrogen permeance.

Additional Information

Way, J. Douglas, and Thoen, Paul M., Palladium/Copper Alloy Composite Membranes for High Temperature Hydrogen Separation: Final Technical Progress Report, DOE Grant DE-FG26-03NT41792 (Golden, CO: Colorado School of Mines, Reporting Period: September 1, 2003 to August 31, 2006).