II.D.3 High Permeability Ternary Palladium Alloy Membranes with Improved Sulfur and Halide Tolerance

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Objectives

- Utilize iterative modeling, rapid fabrication, and testing approaches to develop and demonstrate an ultra-thin durable ternary palladium (Pd)-alloy membrane with excellent resistance to sulfur and halogen attack.
- Use density functional theory (DFT) methods to predict hydrogen (H_2) flux through $Pd_{96}M_4$ for M = nickel (Ni), rhodium (Rh), platinum (Pt), niobium (Nb), tantalum (Ta), vanadium (V), magnesium (Mg), and yttrium (Y). Use same methods to predict H_2 flux $Pd_{74}Cu_{22}M_4$ for at least three of the same M.
- Screen initial set (≤ six) of ternary alloys by pure gas (H_2 and nitrogen [N_2]) permeation experiments.
- Fabricate a minimum of 20 membrane specimens with different copper (Cu) concentrations based on Georgia Tech hydrogen transport predictions for the two to three most promising ternary element additions.
- Complete four to five preliminary tests membrane samples at TDA and IdaTech with clean synthesis gas (syngas) and single impurity additions of hydrogen sulfide (H_2S) and carbonyl sulfide (COS).
- Produce a minimum of 5 ft^2 of optimized membrane material for use at the Colorado School of Mines (CSM) and TDA and for independent third party evaluation by IdaTech.
- Complete mixture permeation testing with H_2/carbon monoxide (CO) and H_2/H_2S binary mixtures with best three samples from the final optimization study.

Technical Barriers

This project addresses the following technical barriers from the Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- Hydrogen Embrittlement
- Poisoning of Surfaces
- Impurities in Hydrogen

Technical Targets

Year 1

- Use DFT methods to predict H_2 flux through $Pd_{96}M_4$ for M = Ni, Rh, Pt, Nb, Ta, V, Mg, and Y. Use the same methods to predict H_2 flux $Pd_{74}Cu_{22}M_4$ for at least three of the same M.
- Screen initial set (≤ six) of ternary alloys by pure gas (H_2 and N_2) permeation experiments.

Year 2

- Fabricate a minimum of 20 membrane specimens with different Cu concentrations based on Georgia Tech hydrogen transport predictions for the two to three most promising ternary element additions.
- Complete four to five preliminary tests of membrane samples at TDA and IdaTech with clean syngas and single impurity additions of H_2S and COS.

Year 3

- Produce a minimum of 5 ft^2 of optimized membrane material for use at CSM and TDA and for independent third-party evaluation by IdaTech.
- Complete mixture permeation testing with H_2/CO and H_2/H_2S binary mixtures with best three samples from the final optimization study.

Table 1 lists current test information for a number of membranes and compares it with U.S. Department of Energy (DOE) target values.

TABLE 1. Progress towards Meeting DOE Targets

Performance Criteria	2010 Target	2015 Target	SwRI® Membranes
Flux (scfh/ft^2)	200	300	210
Operating Temperature (°C)	300-600	250-500	200-500
Sulfur Tolerance (ppmv)	2	20	50
System Cost (\$/ft^2)	500	<250	
ΔP Operating Capability (psi)	400	800-1,000	5-150
Carbon Monoxide Tolerance	Yes	Yes	Yes
Hydrogen Purity (%)	99.5	99.99	99.97
Stability/Durability (years)	3	>5	
Permeate Pressure (psi)	N/A	N/A	

N/A - not applicable

Accomplishments

- Efficient and accurate DFT calculation methods were developed to tackle two key challenges:
  - A large number of sites must be sampled with DFT calculations.
  - A statistically valid model that extends DFT data to include all possible sites is needed.
- Tested seven ternary alloys for hydrogen permeation rates under pure gas experiments. Tests were conducted under a range of pressures (five to 150 pounds per square inch gauge [psig]) and temperatures (200°C to 500°C).
- Showed that the addition of four weight percent silver (Ag) to a Pd-Cu alloy membrane improves the permeability by 20 to 25 percent.
- Used computer modeling to predict unique alloy compositions that showed (theoretic) excellent hydrogen solubility and permeability. These compositions were validated through laboratory tests.
- Evaluated promising classes of ternary alloys as membranes under different concentrations of H_2S, hydrogen chloride (HCl), N_2, and other contaminants.
- Successfully tested issues with membrane mechanical strength using the membrane test assembly with 5-um thick foils.
- Achieved 33% higher hydrogen permeability at 400°C than that reported by CSM – due to a suspected difference in membrane conditioning.
- When the membrane assembly cooled and was transferred to the sulfur-poisoned furnace, the membrane failed when it had reached temperature and 100 psig syngas was applied.

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Introduction

A critical step in the transition to the hydrogen economy is the separation of hydrogen from coal gasification gases (syngas) or methane (CH_4). This is typically accomplished through membrane separation. Past research has shown that Pd alloys possess great potential as robust and economical membranes. However, the search for the optimal binary or ternary alloys is an involved and costly process due to the infinite number of alloy variations that could be prepared and tested. Recent modeling work at GeorgiaTech using DFT identified several promising ternary alloy compositions with improved hydrogen permeability. These promising ternary alloy compositions, along with various additives at different concentrations, may be tested via DFT calculations and used to guide experimental membrane development efforts.

Self-supporting, dense Pd alloy membranes have exhibited extremely high hydrogen permselectivity and the ability to produce high purity hydrogen feed streams needed for fuel cell applications. The combinations of binary and ternary alloys that can be produced with Pd are theoretically infinite. The use of DFT modeling is an economical and efficient approach to identify promising alloy combinations, which can then be fabricated and evaluated to determine optimum alloy combinations.

Approach

Southwest Research Institute® will lead this membrane advancement effort through the development of materials using advanced physical vapor deposition methods. This includes high power-pulsed magnetron sputtering and plasma-enhanced magnetron sputter deposition to produce thin (<5 micron) Pd alloy membranes. The unique feature of these techniques is the ability to rapidly produce uniform membranes of almost any alloy composition with areas up to 100 in^2.

CSM will perform initial screening of experimental membranes under controlled atmospheres to confirm that the targeted structures and compositions have been produced. Test results will be used to guide and refine DFT-based modeling and guide the vacuum deposition effort. When one or more promising classes of ternary alloys have been identified, TDA Research will evaluate these membranes under different concentrations of H_2S, HCl, N_2, and other contaminants for extended periods up to several hours. Synergistic effects, if any, may also be examined.

Results

DFT-based model predictions are in agreement with literature data for binary alloys indicating:

- Adding Ag or gold (Au) either increases or holds permeability constant relative to Pd.
- Adding Ni or Pt significantly diminishes permeability relative to pure Pd.

Figure 1 displays the DFT-based modeling results for temperature dependence of permeation rates for seven alloys with composition $Pd_{96}M_4$ (at%).

The influence of thickness on the pure hydrogen flux at 400°C and 32 psia hydrogen feed pressure is shown in Figure 2.

The effect of composition and temperature on hydrogen permeability for a number of PdCuAu ternary membranes is displayed in Figure 3.

Results of these studies indicate that:

- All ternary additives strongly enhance permeation relative to $Pd_{70}Cu_{30}$, but all except Ag cause slightly decrease in permeation relative to $Pd_{74}Cu_{26}$.
- More than 37 binary and ternary films have been fabricated with specific compositions to test hydrogen permeability and sulfur tolerance.
- Hydrogen transport appears to be bulk-diffusion limited for all membranes tested at temperatures above 573 K.

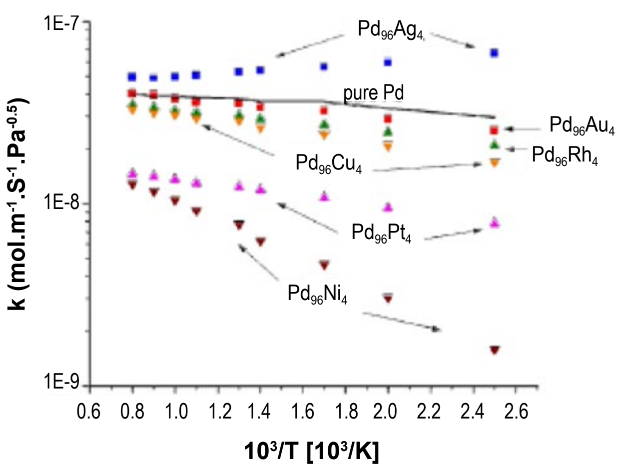

FIGURE 1. DFT-Based Modeling Results for Seven Alloys with Composition $Pd_{96}M_4$ (at%)

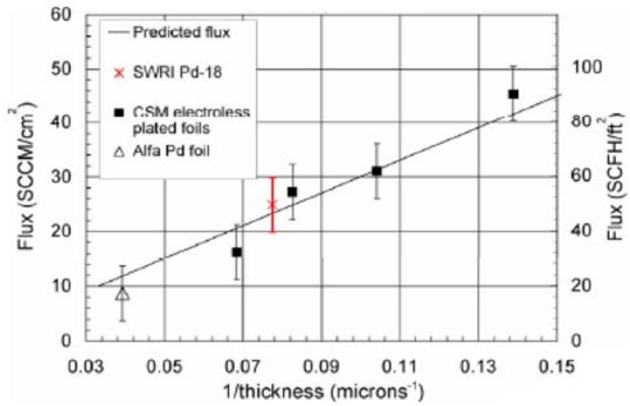

FIGURE 2. Hydrogen Flux as a Function of Thickness at 400°C, 5 cm $Hg^{0.5}$ Pressure Gradient

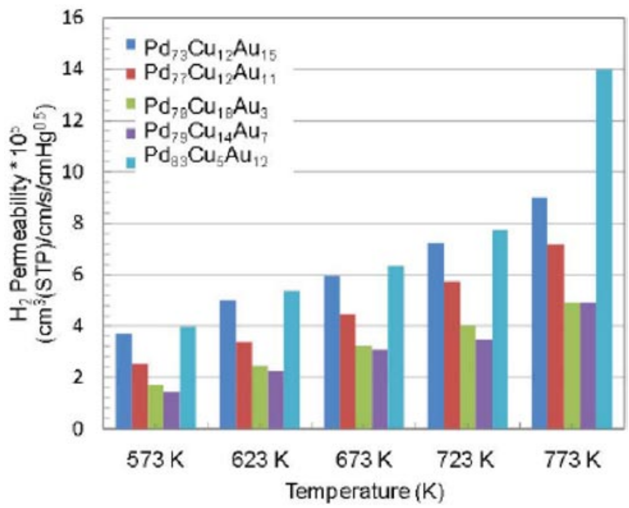

FIGURE 3. Hydrogen Permeability for Ternary Alloy Membranes

- PdCuAu has the highest permeability of the ternary alloys tested.
- Binary alloys of Pd with Cu, Ag, Au, and ruthenium (Ru) have comparable permeabilities to literature values.
- In ternary PdCuAu alloys studied, reducing Cu content and raising Au content improves permeability.

Conclusions and Future Directions

So far, more than five membranes have been tested under DOE specified test conditions.

Future work will:

- Produce a minimum of 5 ft^2 of optimized membrane material for use at CSM and TDA and for independent third party evaluation by IdaTech.

- Complete mixture permeation testing with using DOE specified mixtures with best three samples from the final optimization study.
- Continue model validation with pure hydrogen and test mixtures for ternary PdCuX combinations at different stoichiometry.
- Use the data obtained in Year 1 and Year 2 to optimize membrane form factor (composition, thickness, foot-print, etc.).