Title: **Development of Pd-Ag Composite Membrane for Separation of Hydrogen at Elevated Temperature**

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OBJECTIVES

The purpose of this project is to develop hydrogen-selective *Pd-Ag* composite membrane in microporous substrate for use in production and separation of hydrogen at elevated temperature. The objectives of this research are to:

1. Fabricate H_2-selective *Pd-Ag* composite membrane in planar and tubular configurations on microporous porous stainless steel substrate by electroless deposition process.
2. Study the H_2-permeation characteristics of *Pd-Ag* composite membranes using pure hydrogen and mixed gases. Evaluate the membranes for long term integrity and stability under thermal cycling for *Pd-Ag* film adhesion and H_2-permeation properties.
3. Using tubular *Pd-Ag* composite membrane, design and fabricate shell-and-tube structured membrane reactor and conduct steam reforming of methanol experiments to study the equilibrium shifts and permeation characteristics.
4. Validate the performance of the membrane-reactor using our previously developed membrane-reactor model for steam reforming of methanol.

ACCOMPLISHMENT TO DATE

Electroless Plating Bath Setup

An electroless plating bath with digital continuous monitoring of temperature is installed in a Fisher Scientific constant temperature water bath under a fume hood with following design features.

- Temperature of the Fisher bath can be controlled up to 90 °C with a safety factor ± 0.24 °C.
- Continuous solution temperature, P^H is able to measure ACUMET AP 061 pH digital meter which has an electrode equipped with K-type thermocouple.
- Individual deposition rate of palladium/silver is possible to obtain by taking difference of dry and deposited samples using Mettler Toledo AT 201 micro-balance which can measure within fine range up to 0.01 mg (10 μg).
- MasterFlex osmotic solution drive with flow control 500 ml/min to 4 liter/min.

In this work, bi-layered or multi-layered palladium silver growth or continuous Pd-Ag nuclei growth is being determined by XRD or EDS analysis. XRD and EDS analysis would be useful to calculate bulk composition of the samples and also to estimate the amount of Pd-Ag deposited with varying plating time. For composite membrane characterization, SEM, EDX and XRD works are being performed at the Center for Advanced Material and Smart Structure (CAMSS). We also studied the effects of surfactants on electroless plating bath stability and rate of deposition of palladium on micro-porous catalytic substrates were investigated. Also to better understand the role of EDTA in bath stability, we studied the Pd^{+2}/EDTA coordination kinetics in typical electroless plating bath conditions.

Permeability Measurement Set-up

To measure the gas permeability through Pd-membranes, we assembled and tested a computer controlled permeability measurement set-up with gas sampling connecting to a gas chromatograph (GC). The set-up will also be used for membrane-reactor study for steam reforming of methanol.

We have conducted permeability measurements of hydrogen through Pd-membranes that we fabricated in the lab. This work is in progress.

Modeling of Steam Reforming of Methanol

In this work, a packed-bed catalytic membrane reactor's performance is simulated based on simultaneous hydrogen generation and separation during steam-methanol reforming. A Pd-thin film on microprous stainless tubular support deposited by electroless deposition process is used as an H_2-selective membrane. The membrane reactor is configured in a shell and tube design where the reaction takes place in the tube side and hydrogen separation occurs radially in the shell side. A 2-D steady state membrane reactor-separator model was considered for the reactive reforming processes with effective radial concentration gradients due to hydrogen permeation across the membrane cylindrical surface. Coupled finite difference equations were formulated based on reaction thermodynamics of different chemical species. Results of the reactor simulation were highlighted based on reactor size, catalytic properties, inlet and outlet fluid flow parameters, operating conditions, space velocity and molar ratio. From parametric study, it was observed membrane reactor provided considerably higher conversion compared to non membrane packed bed reactor. This is attributed to continuous separation of one of the products (hydrogen) as reaction proceeds, which shifts the thermodynamic equilibrium rightward.

List of Published Journal articles, Completed Presentations and Student Receiving Supports from the Grant:

Presentations/Proceedings:

1. Islam, M.A., Basti, M.M., and Ilias, S., "Synthesis of Pd-Membranes: Pd^{+2}/EDTA Coordination Kinetics in Typical Electroless Plating Bath Conditions," Abstract and Preprint submitted to FUEL Division, ACS 2007 Annual Meeting, August 19-23, Boston, Massachusetts.
2. Akanda, M.H., Islam, M.A., and Ilias, S., "Modeling of Steam-Methanol Reforming in a Pd-based Membrane Reactor," Accepted for presentation at the 2007 NAMS Annual Meeting, June 12-16, 2007, Orlando, Florida.

3. Islam, M.A., and Ilias, S., "Modeling of Steam-Methanol Reforming in a Pd-based Membrane Reactor," Accepted for presentation at the 2007 NAMS Annual Meeting, June 12-16, 2007, Orlando, Florida.
4. Islam, M.A., and Ilias, S., "Effect of Surfactants in Fabrication of Palladium Thin-film Composite Membrane by Electroless Plating Method," Accepted for presentation at the 2007 NAMS Annual Meeting, June 12-16, 2007, Orlando, Florida.
5. Islam, M.A., and Ilias, S., "Modeling of Permeability Enhancement in Presence of Dislocations in α-phase Palladium-Hydrogen Equilibria," Presented at the 9th International Congress on Inorganic Membranes (ICIM9), June 25-29, 2006, Lillehammer, Norway.
6. Islam, M.A., and Ilias, S., "Modeling of Hydrogen Permeability in Presence of Dislocations in α-Phase Palladium-Hydrogen Equilibria," Paper #466, Proc. CHEMCON 2006, December 27-30, 2006, Bharuch, India.

Students Receiving/Received Supports:

M. A. Islam (Ph.D. candidate in Energy & Environmental Study)
M.H. Akanda (MS candidate in Chemical Engineering)