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

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ABSTRACT

The U.S. energy industry is undergoing a profound transformation driven by changes such as deregulation of power generation, increasingly more stringent environmental standards and regulations, global climate change concerns and other market forces. In recent years, there has been growing interest in Proton Exchange Membrane Fuel Cell (PEMFC) technologies for down-to-earth applications because of its high power density, high efficiency and almost zero emission to the environment. The major focus on PEMFC technology is to develop fuel cell system for transportatiion applications, which require development of low cost cell components and reliable, high-purity H2-fuel source. The PEMFC tecghnology is attractive because of its low operating tremperature and ease of start-up. The U.S. Military has a pressing need for lightweight, compact power supplies to support troops in the field and fuel cell-based power system is being evaluated as a major contender to fill the vacuum.

Reformed methanol, liquid and gaseous light hydrocarbons are expected to major fuel source in PEMFCs for terrestrial transportation application. The poisoning of the expensive electrocatalysts by CO in the reformed fuel is a major concern. Crossover of methanol in direct methanol PEMFC is also problematic. Catalytic cracking of ammonia to hydrogen is a serious contender for fuel source. Whether it is reforming methanol, methane and liquid hydrocarbons as a source for hydrogen or cracking of ammonia for hydrogen for fuel cells, separtion of hydrogen at elevated temperature is a major technical issue. In this context, membrane-based technology as fuel process appears very attractive.

We propose to develop an inorganic metal-metal composite membrane to study reforming of liquid hydrocarbons and methanol by equilibrium shift in membrane-reactor configuration, viewed as fuel processor. Based on our current understanding and experience in the Pd-ceramic composite membrane, we propose to further develop this membrane to Pd and Ad-Ag alloy membrane on microporous stainless steel support to provide structural reliability from distortion due to thermal cycling and hydrogen embrittlement. Because of the metal-metal composite structure, we believe that the associated end-seal problem in the Pd-ceramic composite membrane in planar and tubular configurations would not be an issue.

Our proposed research if successful will have several technological advatages over other conventional hydrogen purification methods which include: (a) Reforming reaction is not limited by thermodynamic equilibrium, as soon as hydrogen is formed, hydrogen is tranported selectively across the membrane, (b) Reforming and separation is carrried out in a single unit, thereby eliminating the need of hydrogen separation and recovery units, and (c) The membrane-

reactor-separator (fuel processor) is modular and compact in size and will lead to significant cost and energy savings.

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:

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) from interdisciplinary research center (IRC) of North Carolina A&T State University.

Optimization of the plating bath is in progress. Due to large number of experiments and inconvenience of having supplies and custom made equipments from different companies make difficult to complete this task in time. At least, 36 designed experiments have to be performed to optimize bath operating conditions. Statistical and theoretical analysis shows three parameters such as temperature, osmotic pressure and pH are critical for any constant composition electroless bath. It is theoretically predicted that variation of temperature, pressure and osmotic pressure at three levels require 27 statistically significant experiments. At each level, it requires at least 9 sub-run at different plating time to understand plating kinetics. It accounts about 243 experimental runs for proper optimization of the electroless plating bath.

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

Presentation:

Islam, M.A., and Ilias, S., "Modeling of Permeability Enhancement in Presence of Dislocations in α-phase Palladium-Hydrogen Equilibria," accepted for presentation at 9^{th} International Congress on Inorganic Membranes (ICIM9), June 25-29, 2006, Lillehammer, Norway.

Students Receiving/Received Supports:

M. A. Islam (Ph.D. candidate in Energy & Environmental Study)