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PREPARATION AND CHARACTERIZATION OF COMPOSITE MEMBRANE FOR HIGH TEMPERATURE GAS SEPARATION

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Preparation and Characterization of Composite Membrane for High Temperature Gas Separation

CONTRACT INFORMATION

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OBJECTIVES

To develop a new class of permselective inorganic membranes, we have identified electroless plating as potential a route to deposit a thin metal film on porous substrate. Electroless plating is a controlled autocatalytic deposition of a continuous film on the surface of a substrate by the interaction of a metal salt and a chemical reducing agent. This method can give thin films of metals, alloys and composites on both conducting and nonconducting surfaces. The objective of this project is to develop thin film palladium membranes for separation of hydrogen in high temperature applications. We plan to use electroless plating to deposit thin palladium films on microporous ceramic and silver substrates and then characterize the membrane in terms of permeability and selectivity for gas separation. To accomplish the research objective, the project requires three tasks:

i. Development of a Process for Composite Membrane Fabrication

The work will involve the selection of methods for thin metal/metal-alloy film deposition on inorganic and ceramic microporous substrates. To assure reproducible film, optimization of the electroless deposition will be required. This step will involve determination of the optimum configuration of the plating bath, which consists of studying the effect of parameters like pH, temperatures, concentrations, type of reducing agent and sensitizing solution on the rate of deposition of the film.

ii. Characterization of Composite Membrane

The work for this task will start with the fabrication of composite membranes. The membranes will be characterized by surface measurements and by evaluation of the physical properties of the composite (film composition by EDAX, film thickness by SEM). The measurements will also include hydrogen gas permeability, steady state diffusion and the effect of thermal cycling.

iii. Development of Theoretical Model For Hydrogen Gas Separation

The work for this task will be to find or develop a suitable model to describe the permeation of hydrogen gas through a thin palladium film on a porous support. Models developed in the literature deal only with the permeation of gases through a metal membrane. These models may or may not be applicable to composite membranes. The applicability of the model will depend on the role of the porous support in permeation of gases. It is well known that the permeability of gases through porous ceramics increases at higher temperatures. However, the behavior of hydrogen permeation through a palladium film is much more complex process. It is believed that the hydrogen molecule dissociates to hydrogen atoms on one side of the membrane, diffuses through the film and reassociates on the other side. A theoretical model will be developed to facilitate prediction and interpretation of data obtained in the permeation experiments. Permeation through the porous substrate will be analyzed in terms of Knudsen and binary gas diffusion as well as surface diffusion. In case of Pd/substrate composites, a model will be developed that accounts for the kinetics of hydrogen diffusion.

BACKGROUND INFORMATION

The development of high temperature membranes to recover hydrogen is a topic of considerable scientific interest. Since coal gasification and several high-temperature industrial processes generate hydrogen as a byproduct, the recovery of hydrogen is of significant commercial importance. Recently, there has been increased interest in developing inorganic and composite membranes for in-situ separation of product hydrogen to achieve equilibrium shift in a catalytic reactor [1]. However, the productivity of these membrane reactors is severely limited by the poor permeability of currently available membranes. Commercially available non-porous membranes are either thick film or thick walled tubes. Since permeability is inversely proportional to film thickness, a thick film membrane acts as a poor perm-separator. Thus, the major challenge lies in developing a permselective thin film, without compromising the integrity of the film. The availability of such a membrane for high temperature applications could open new areas of research in membrane reactor technology and gas separation. The success of membranes in these applications will largely depend on the availability of membranes with acceptable permselectivity and thermal stability. The polymeric membranes currently available are not suitable for high temperature applications (>180 °C) because of their thermal instability. In addition, inorganic membranes (mostly ceramic), although thermally stable, are also unsatisfactory as they lack permselectivity because of their porous nature.

To develop a new class of permselective inorganic membranes, we have identified electroless plating as a potential route to deposit a thin metal film on microporous substrate. Electroless plating is a controlled autocatalytic deposition of continuous film on the surface of a substrate by the interaction of a metal salt and a chemical reducing agent. This method can give thin films of metals, alloys and composites on both conducting and nonconducting surfaces. In this research, we are using electroless plating to deposit thin palladium films on microporous ceramic and silver substrates.

PROJECT DESCRIPTION

Electroless Plating of Ceramic Substrate

Microporous ceramic alumina membranes (6 cm diameter, open porosity 10-15%, average pore size 5 μm from Alfa/Johnson Mathey) were coated with a thin palladium film by electroless plating. Electroless plating is explained by a combination of the cathodic deposition of metal and the anodic oxidation of reductant at the immersion potential. Palladium deposition occurs as the result of the following simultaneous reactions:

Anodic Reaction:

$$N_2H_4 + 4OH^{-1} \rightarrow N_2 + 4H_2O + 4e^-$$

Cathodic Reaction:

$$2Pd[NH_3]_4^{2+} + 4e^- \rightarrow 2Pd^0 + 8NH_3$$

Autocatalytic Reaction:

$$2Pd[NH_3]_4^{2+} + N_2H_4 + 4OH^{-1} \rightarrow 2Pd^0 + N_2 + 4H_2O + 8NH_3$$

Electroless plating is a three step process involving pretreatment of the substrate, sensitization and activation of the substrate surface, and electroless plating. Typical electroless plating bath compositions given in Table 1. In electroless plating, pretreatment of the substrate is essential in order to deposit metals effectively. One of the common procedures is the two-step immersion sequence using an acidic stannous chloride solution followed by an acidic palladium salt solution. The first bath is referred to as the sensitizer (tin chloride solution), while the second bath is referred as the activator (palladium salt solution). The net result of the sequence is the formation of finely-divided palladium nuclei which initiate the autocatalytic plating process. The formation of the palladium metal nuclei is believed to be due to a redox reaction taking place between the adsorbed or absorbed stannous ions on the surface and the palladium ions in the activation solution. The sensitization and activation step can be described by the following reaction:

$$Sn^{2+} + Pd^{2+} \rightarrow Sn^{4+} + Pd^0$$

The sensitization process controls whether the final metallic film is uniform. The composition of the sensitization and activation solutions is given in Table 2.

Membrane Characterization

The membranes will be characterized by measurements and evaluation of physical properties of the composite (film composition by EDAX, film thickness by SEM and a weight gain method).
The measurements will also include permeability and steady state diffusion, and the effect of thermal cycling. A steady-state counter diffusion method, using gas chromatographic analysis, will be used to evaluate the permeability and selectivity of the composite palladium membrane for hydrogen separation. Composite membranes will be characterized by conducting permeability experiments with hydrogen, argon, nitrogen and carbon dioxide. The

membrane characterization work is now in progress.

Model for Hydrogen Permeation

The permeation of hydrogen through a palladium film is a complex process. The process begins with sorption of hydrogen molecules on the film surface and ends with hydrogen desorption from the ceramic substrate. It is believed that the hydrogen molecule dissociates into hydrogen atoms on one side of the film , diffuses through the film and reassociates on the other side [3]. Hydrogen permeation through palladium is thought to be taking place by the following mechanism:

> *Sorption on the surface → Formation of hydrogen atoms → Diffusion of hydrogen atoms through the lattice → Formation of hydrogen molecules at the other surface → Desorption.*

The reaction kinetics of formation of hydrogen atoms from molecules and the reverse reaction are assumed to be very fast. The permeability can be considered as product of solubility and diffusivity. For isothermal, isobaric and plug flow conditions, the permeation rate of hydrogen can be given by [4]:

$$J_H = \frac{\overline{P}_H}{h}\left(p_1^n - p_2^n\right)$$

where J_H is the hydrogen flux, p_1 and p_2 are partial pressures of hydrogen on high and low pressure sides of the permeability cell. $\overline{P}_H$ is the hydrogen permeability at a given temperature and h is the thickness of the palladium film.

If diffusion through the bulk metal is the rate limiting step and hydrogen atoms form an ideal solution in the metal, then Sievert'law hydrogen solubility dependence holds and n is equal to 0.5. The hydrogen flux (J_H) is inversely proportional to the palladium film thickness (h) when the bulk diffusion is the rate limiting step. A value of n greater than 0.5 may result from several factors. For example, when the surface processes influence the permeation rate or when Sievert's law is not followed, a value of n greater than 0.5 may result. Leakage of hydrogen through defects in the metal film or through membrane seals may also increase the value of n.

With increasing temperature, the permeability coefficient increases and usually follows an Arrhenius type equation [5]:

$$\overline{P}_H = A_H \exp\left(-\frac{E}{RT}\right)$$

where A_H is the pre-exponential factor in the Arrhenius relationship for hydrogen permeability and E is the apparent activation energy of composite palladium-ceramic membrane. Here, it is assumed that the n in the hydrogen flux equation is essentially independent of temperature.

The above transport model will be used to facilitate the prediction and interpretation of data obtained in the permeability measurement experiments.

RESULTS

This is a three-year research grant. Currently we are at the first year of the project. Although we have started only recently, several key results have been obtained, including the following:

- Developed a three step procedure for electroless deposition of palladium on ceramic substrate. The three steps are: (i) preparation of the substrate; (ii) sensitization and activation of substrate; and (iii) electroless plating. Now, we are in a position to coat palladium thin-films on ceramic substrates by electroless deposition. Palladium (Pd) plating rate on a ceramic substrate at room temperature is shown in Figure 1.

- Designed and assembled a diffusion cell to measure diffusivity and permeability of hydrogen at high temperature and pressure.

FUTURE WORK

During next two and half years, we will work on the following tasks:

- Design and build an experimental system to measure the permeability and diffusivity of hydrogen gas through palladium plated composite membrane. Also develop a method to measure the gas species composition by chromatographic method.
- Using SEM and EDAX, characterize composite ceramic-palladium membrane for film thickness and film composition.
- Evaluate the fabricated membrane for permeability and selectivity for hydrogen in presence of other gases, such as argon, nitrogen and carbon dioxide.
- Extend this work to investigate the silver-palladium composite membrane for separation of hydrogen.

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Table 1: Typical Composition of Electroless Plating Bath.

Components/Variables	Concentration
$PdCl_2$	5.4 g/l
Ammonium hydroxide (28 percent)	390 ml/l
EDTA	40 g/l
Hydrazine (1 molar soluition)	10 ml/l
pH	11
Temperature	25 °C

Table 2: Composition of Senistization and Activation Solutions.

Sensitization Soluition	Concentration
$SnCl_2$	1 g/l
HCl	0.2 N
Activation Solution	
$PdCl_2$	0.9 g/l
HCl	0.2 N

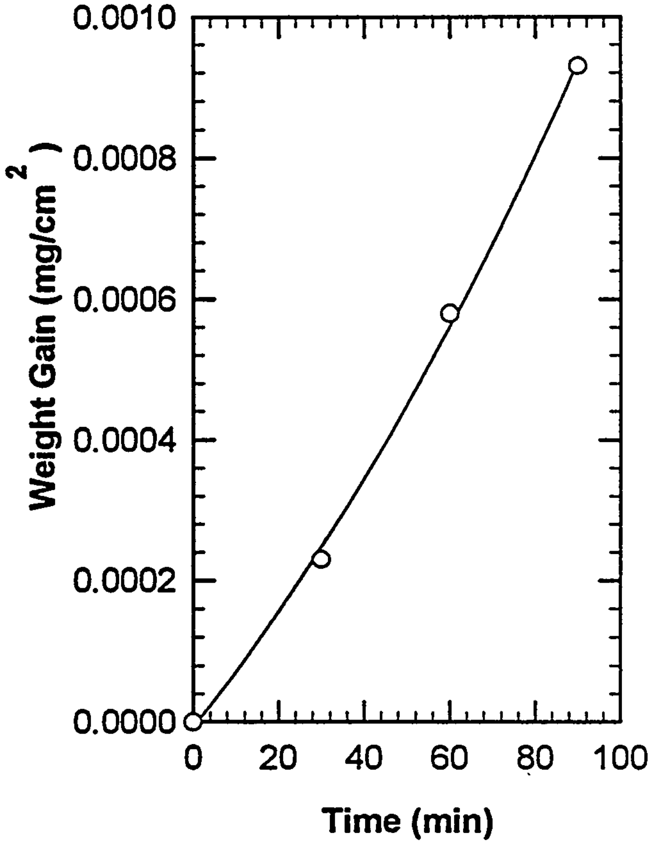

Figure 1: Palladium plating rate on ceramic substrate by electroless deposition at room temperature. Ceramic substrate is 6.0 cm in diameter, 7 mm thick, 10-15 % open porosity and 5 μm pore size.