

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

Mohammad A Islam (Grad Student)
Shamsuddin Ilias (PI)*
Department of Mechanical and Chemical Engineering
North Carolina A&T State University, Greensboro, NC 27411

Abstract

Electroless plating is a popular technique for deposition of thin-film on metal or ceramic substrates. For hydrogen separation, thin film Pd and Pd/Ag composite membranes are being fabricated using electroless plating process. In conventional electroless plating, oxidation-reduction reactions between Pd-complex and hydrazine (reducing agent) results in evolution of ammonia and nitrogen in the form of gas bubbles. These gas bubbles when adhered to the substrate surface and in the pores, hinder uniform Pd-film deposition. This is major weakness of the conventional electroless plating bath recipe. Stirring or rotation of substrate during plating may lessen the problem but can not provide satisfactory resolution. Incorporation of suitable surface active agents with favorable structures into plating bath appears to be promising remedy of surface from growing gas bubbles within the plating substrate vicinity. The effects of surfactants on electroless plating bath stability and rate of deposition of palladium on micro-porous catalytic substrates were investigated. The surface morphology and compositional microstructures were examined using SEM (Scanning Electron Microscopy) coupled with in-situ EDS (Energy Dispersive Spectroscopy). The rate of palladium deposition was measured by the weight gain as a function of time. The surfactants studied included Trion X-100 (non-ionic surfactants), dodecyltrimethylammonium bromide (DTAB) (cationic surfactant) and sodium dodecylbenzenesulfonate (SDBS) (anionic surfactant). The surfactant molecules play an important role into the plating process by removing tiny gas bubbles through adsorption at the gas-liquid interface. It was observed that addition of non-ionic surfactant increased the palladium deposition rate by about 10% (at least) with improved surface morphology and microstructure. The membranes were tested and evaluated for H₂-permselectivity. The new membrane in tubular configuration was as membrane-reactor separator for simultaneous production and separation of hydrogen from steam reforming of methane by equilibrium shift.

Introduction

Conventional plating technique involves complex oxidation reduction between palladium complexes (e.g palladium chloride, Tetra-amine palladium nitrate, palladium acetate and palladium nitrate etc) and reducing agents (e.g Hydrazine, Sodium hypo-phosphite etc). Among many of the plating baths, palladium-hydrazine bath is the most widely applied in order to coat pure palladium film on the substrates. One of the problems of the electroless-hydrazine bath is evolution of nitrogen and ammonia and grow into bubbles form on the plating frontier. Rotating or the object being plated or controlled stirring of the solution may lessen the problems but not satisfactorily resolve completely. As a result, a considerable voids on the surface looses homogeneity and uniformity of deposition. Incorporation of suitable surface active agents reduces the possibility of nitrogen and ammonia molecule to grow into bubbles in larger form to prevent homogeneous deposition. Surfactants molecules play an important role in removal of nitrogen and ammonia molecules at gas-liquid interface. Many of the water soluble surfactants having moderately lower HLB values shows strong capability of removing nitrogen and ammonia from the solutions. accepted to explain aggregated surfactant-surface role. Application of various amphiphilic surfactants provides a convenient and a stable means of achieving surface smoothness by reducing considerable bubble coalescences. An appropriate and controlled amount of surfactant modifies the surface reactivity and adhesivity incorporating an immediate temporary bonding with palladium and substrate surface at the solid liquid interface.¹¹

In this work, we examined the surfactant's role on stabilized palladium bath in defect free palladium deposition. Deposited surface in presence of additives were characterized by EDS (energy dispersive Spectroscopy) and SEM (Scanning Electron Microscopy). The membranes were evaluated for hydrogen perm-selectivity. We also used the membrane as membrane-reactor separator for simultaneous production and separation of hydrogen from steam-reforming of methane.

Patent

[1] S. Ilias, and M.A. Islam, "Methods of Preparing Thin Films by Electroless Plating," US Patent Pending, Application No. 61052798 (May 2008).

* Corresponding address: ilias@ncat.edu

Materials and Methods

Various commercially available surfactant such as Trion X-100, Tergitol NP-9, dodecylbenzenesulfonic acid sodium salt, dodecyltrimethylammonium bromide were obtained from Sigma-Aldrich and used as received. Tergitol NP-9 and Trion X-100 were chosen as nonionic surfactant, dodecylbenzenesulfonic acid sodium salt (cationic) and dodecyltrimethylammonium bromide (anionic) were used to investigate the effect of ionic surfactants. Ammonium hydroxide (14.1N), Hydrazine (35 w %) and EDTA sodium salt were obtained respectively from Arcos and Fluka Chemicals respectively. Carbontetra-chloride and reagent grade ethanol were supplied by Fischer Scientific. Deionized water was supplied by Milli-Q purification system (Millipore). Substrate surface was 0.5 nm porous stainless steel membrane with 1 inch OD and 0.04 inch thickness. Average pore diameter were obtained from the manufacturer supplied product information. This support was obtained from Motts Corporation.

Results and Discussion

In the absence of suitable nucleating surface, reduction of palladium, via the reaction of hydrazine with palladium complex results inhomogeneous nucleation. SEM images of the deposited Palladium show that the morphology consist of large and non uniform agglomerates (Fig 1a), formed from fusing of spherical features (Fig 1b) which range in particle size 10 to 20 μ m agglomerates.

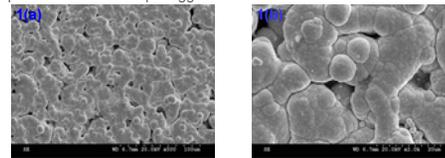


Figure 1: SEM images of Pd grown in absence of surfactant

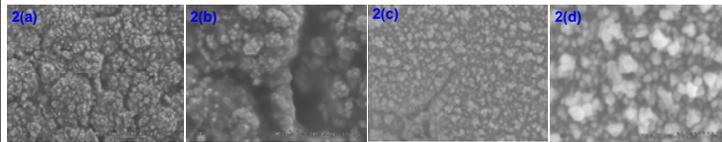


Figure 2: Electroless plating observed after 20 minutes of deposition cycle showing initial dendritic growth (a) and (b) Pd deposition microstructure; (c) and (d) Ag deposition microstructure

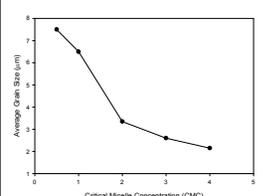


Figure 3: Average grain Size (μ m) of Pd deposited in 20 minutes of plating

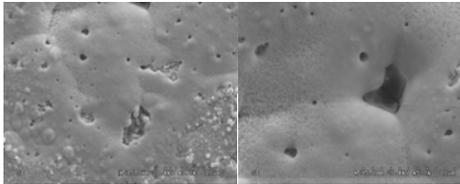


Figure 4: Surfactant activated Ag deposition showing agglomerated grain growth throughout the surface

Figure 5 shows the SEM images of surface morphologies in presence of different surfactants. In most cases of the deposition, intra-agglomerate porosities were evident and surfaces remain mostly open. The deposition in terms of surface morphology was found in presence of DTAB.

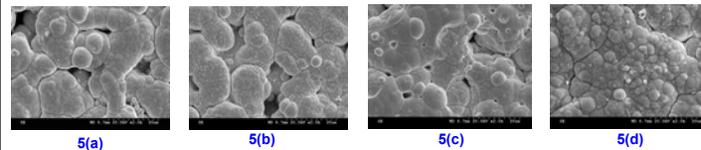


Figure 5. SEM images Palladium surface morphology (a) no surfactant; (b) SDBS -anionic; (c) Triton X-100 - nonionic; and (d) DTAB - cationic.

ACKNOWLEDGMENTS

- This research was sponsored by the Pittsburgh Energy Technology Center, U.S. Department of Energy, under Award No. DE-FG26-05NT42492. Dr. Arun Bose, NETL, Pittsburgh, is the DOE Project Officer.
- Analytical support from the Center for Advanced Materials and Smart Structures (CAMSS) of North Carolina A&T State University is gratefully acknowledged with special thanks to Drs. Jag Sankar, D. Kumar and Zhigang Xu.

Permeability Studies

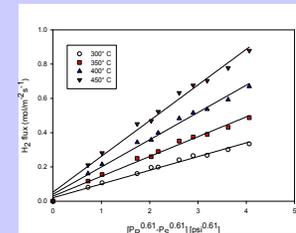


Figure 7: Hydrogen flux data for pd-PSS membrane with 7.68 μ m film fabricated in presence of DTAB

The membrane activation energy was found 16.877 kJ/mol, which is in good agreement with membrane thinner than 10 μ m

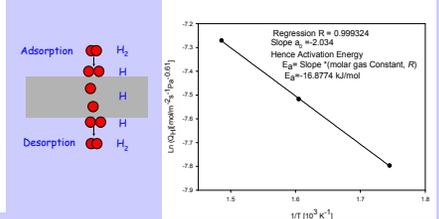


Figure 8: Arrhenius plot of H₂-permeability for the same composite membrane

Membrane Reactor – Steam Reforming of Methanol

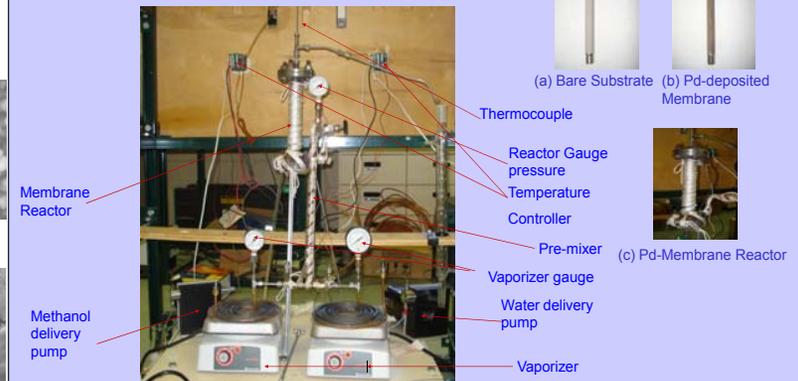


Figure 9: Membrane-Reactor Set-up Used in Methanol Reforming for Simultaneous Production and Separation of Hydrogen by Equilibrium Shift.

Table 1: Comparison of methanol conversion as a function of catalyst loading at S/M = 2.0, P_r = 2.0 bar

Catalyst Loading (Kg s/mol)	Model Prediction (% Methanol conversion)		Experimental Results (This Work)
	Membrane Reactor	Non-Membrane Reactor	
2	73.74	35.78	74.6
4	88.48	50.80	85.3
6	95.32	60.56	92.6
8	98.31	67.75	93.6

Commercial Catalyst (BASF K3-110)
Composition: CuO 40 wt%,
ZnO 40 wt%, Al₂O₃ 20 wt%
Nitrogen BET area: 102 ± 4 m²/gm
Pore volume: 0.35 ml/gm

CONCLUSIONS

- The results clearly explained that the rate of deposition and morphology of surface could be modified by varying the choice and concentration of suitable surfactants.
- Pd-Grain size can be manipulated and controlled by suitable selection of surfactants.
- The agglomerate structure clearly depends on the charge of surfactant (retention/collapse of micelles under Pd-deposition), the critical micelles concentration and possibly the ionic interaction of surfactant and Pd-bath solution.
- We successfully utilized the DTAB surfactant to tailor Pd-grain size in order to fabricate robust film.
- Pd-stainless steel membrane fabricated by the surfactant induced electroless plating has high perm-selectivity for hydrogen
- The new Pd-stainless membrane in tubular configuration was used membrane-reactor-separator to steam reforming of methane.
- The membrane reactor performed very well in terms of methanol conversion when compared with conventional tubular packed-bed reactor.