Preparation of Nanostructured Membranes by Reactive Depositions from Supercritical Fluids

James J. Watkins, **Michael Tsapatsis** and **Dionisios G. Vlachos**

Department of Chemical Engineering, University of Massachusetts, Amherst, MA 01003

Introduction: The fabrication of structured materials for applications in optics, microelectronics, sensors, membranes, and catalysis often requires the deposition of metal or metal oxides onto or within supports or templates. Due to various fundamental constraints of deposition reactions in vapor and liquid media, current metallization techniques are typically impractical for supports with complex surface topographies when the size of the features drops below 100 nm or when the desired deposition must occur deep within a macro or mesoporous substrate. These constraints are relieved by a novel deposition technique developed in our laboratories.[1-5] The process, called Chemical Fluid Deposition (CFD), involves the reduction of organometallic compounds in supercritical carbon dioxide to yield high-purity deposits. The enabling advantages of CFD are derived from the physicochemical properties of the supercritical solvent, which lie intermediate to those of liquids and gases. Transport and reduction in solution offer low process temperatures, high reagent concentrations and eliminates precursor volatility requirements associated with vapor phase techniques. Moreover the absence of surface tension and low viscosity of supercritical fluid (SCF) solutions are ideally suited to the delivery of relatively high concentrations of organometallic precursor(s) within porous environments. In this report we describe the utility of CFD for the preparation of dense, nanostructured Pd membranes of prescribed thickness at controlled depths within Al_2O_3 supports using an opposed reactants geometry. Membrane position is predicted by a simple transport model. A detailed simulation is under development to describe membrane structure and evolution.

Pd Membranes: Dense palladium metal membranes have application in H_2 recovery and purification, and are vital for the further development of membrane reactors.[6] Due to the poor mechanical strength and low flux of thin Pd foils, supported palladium membranes are required. While Pd is the most promising candidate for dense metal membranes,[7] it is prone to H_2 embrittlement. This problem has traditionally been addressed by alloying Pd with various metals (Ag, Ni or Au).[7] It has also been suggested that Pd, tightly packed into the pores of a supporting matrix exhibits enhanced resistance towards embrittlement.[8,9] Finally, optimization of deposit microstructure can significantly impact flux: nanocrystalline palladium, exhibits enhanced hydrogen permeation, probably due to the large relative volume of grain boundaries.[10] The ideal deposition scheme would therefore produce continuous nanocrystalline Pd alloy films deep within a support. CFD can accomplish this objective.

Experimental: Dense palladium films are deposited within porous alumina substrates by Opposed Reactants Chemical Fluid Deposition (ORCFD). In this geometry, the metal precursor and reducing agents are introduced on opposite sides of the support (Figure 1).[5] The deposition chemistry is the H_2 reduction of the metal precursors, π-2-methylallyl (cyclopentadienyl)palladium (II) ($CpPd(\pi-C_4H_7)$) and palladium(II) hexafluoroacetyl-acetonate ($Pd(hfac)_2$). Metal alloys can be deposited using multiple precursors.[2] The α-alumina disks (2.1 cm diameter x 0.17 cm thick) exhibit a porosity of 0.5 and an average pore size of about 0.2 μm. High purity CO_2 (60 ^{0}C, 150 bar) was used as the solvent. The continuous ORG reactor system is shown in Figure 2. The reactor, precursor reservoir, syringe pumps, and plumbing were constructed of stainless steel. The substrate and PMP polymer barrier (used to mitigate the flux of H_2 through the support) divided the reactor into separate precursor and H_2 chambers. High-pressure syringe pumps (Isco 500D) delivered the supercritical fluid streams to their respective reaction chambers at controlled rates.

(1.) Blackburn, J. M.; Long, D. P.; Watkins, J. J., *Chem. Mater.*, 2000, 12, 2625-2631. (2.) Long, D. P.; Blackburn, J. M.; Lazorcik, J. L.; Watkins, J. J., in preparation, 2001. (3.) Long, D. P.; Blackburn, J. M.; Watkins, J. J., *Adv. Mater.*, 2000, 12, 913. (4.) Watkins, J. J.; McCarthy, T. J. U.S. 5,789,027,1998. (5.) Fernandes, N. E.; Fisher, S.C.; Poshusta, J. C.; Vlachos, D. G.; Tsapatsis, M.; Watkins. J .J. submitted to *Chem. of Mater.* 2000.

Results and Discussion: We fabricated Pd layers at controlled depths in porous alumina supports by varying the PMP barrier thickness and the H_2 and precursor concentrations. The membrane depths, as measured by optical microscopy of the cross section, ranged from about 80 to 600 µm beneath the precursor-side surface. A typical result is shown in figure 3. An electron probe microanalysis line scan (left) indicates the bright band in the optical micrograph (right) is a dense Pd film. Figure 4 shows the region of dense deposition in a typical membrane viewed by scanning electron microscopy. The Pd deposit completely fills the spaces between the sintered alumina particles. XRD analysis was performed on Pd films deposited near the surface and characteristic reflections for Pd were observed. From the Pd (111) peak, the grain size was estimated by Scherrer's method to be ~90Å. High resolution TEM analysis of individual Pd crystals deposited at low concentration under similar conditions is consistent with this result. Annealing palladium films deposited by CFD for 18 hr at 500°C under a He atmosphere produced an increase in primary grain size from 80-95 Å to 120-130 Å as measured by XRD. The N_2 flux through membranes annealed in this manner was 3.1 x 10^{-6} mol/(m^2 s), or about 60,000 times less than the flux through the bare support. The reduction of N_2 flux through the support indicates that the Pd films prepared by ORCFD were continuous and dense after annealing. Further investigations of H_2 permeation performance, selectivity and stability are underway.

Modeling Deposit Position and Structure: The membrane position and thickness can be predicted from a simple mass-transport limited model.[5,11] In the limit of an infinitely fast, irreversible reaction occurring in a porous substrate of thickness L, the reaction zone B (figure 1), becomes infinitesimally thin and the precise position of the reaction zone, Δx (as measured from the precursor side), is found by balancing the diffusive fluxes of reactants in regions A and C. Figure 5 presents a comparison between the predictions of the model and the actual depths measured using optical microscopy. Membranes made with Pd(hfac)$_2$, were deposited slightly deeper into the support than predicted by the model. This can be corrected by accounting for incomplete ligand hydrogenation.[5]

The prediction of deposit structure requires a full description of transport and chemistry of the reagents, pore structure evolution, nucleation, and growth processes. An overall multiscale framework is being developed to account for all of these phenomena. The continuum conservation equations of species are discretized using central finite differences in space and the resulting equations are integrated using LSODA, which automatically changes the integration scheme when stiffness is identified in the system of differential equations. Due to the multiple length scales encountered, molecular and mesoscopic models are explored at smaller scales for nucleation and growth. Various prototype reaction and nucleation schemes have been explored to delineate the controlling parameters. One such scheme is

$$H_2\ (f) + P\ (f) \longrightarrow I\ (f) \qquad \text{(homogeneous)} \qquad (1)$$
$$I\ (f) + I\ (f) \longrightarrow Pd\ (s) \qquad \text{(nucleation)} \qquad (2)$$
$$H_2\ (f) + P\ (f) \xrightarrow{\ Pd\ } Pd\ (s) \qquad \text{(growth)} \qquad (3)$$
$$I\ (f) \xrightarrow{\ Pd\ } Pd\ (s) \qquad \text{(growth)} \qquad (4)$$
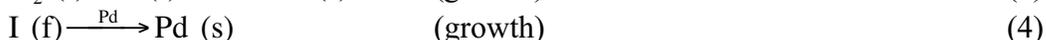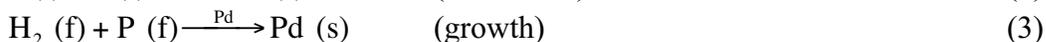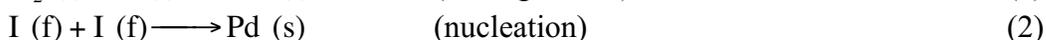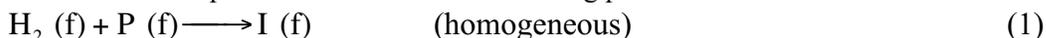
Here, I represents an intermediate species for nucleation and growth and P is the organometallic precursor. Simulations using the above generic scheme for high Thiele modulus successfully predicts the depth of the deposit from the surface of the substrate. The concentration of the intermediate increases until a critical concentration is reached, after which it is consumed by nucleation and growth via reactions 2 and 4. It has been found that the nucleation kinetics are critical in determining the thickness of the deposit and the ability to make nanocomposite materials, whereas the relative concentrations of H_2 and precursor determine the location of the deposit within the substrate.

(6.) Hsieh, H. P. *Inorganic Membranes for Separation and Reaction*; Elsevier: Amsterdam, 1996; Vol. 3. (7.) Shu, J., *Canad. J. Chem. Eng.* ,1991, 69, 1036-1060. (8.) Yan, S., *Ind. Eng. Chem. Res.,* 1994, 33, 616-622. (9.) Jun, C.-S., *J. Mem. Sci.*, 1999, 157, 107-115. (10.) Bryden, K. J., Ying, J. Y., *Mat.l Sci. Eng.*, 1995, A204, 140-145. (11.) Tsapatsis, M.; Gavalas, G. R., AIChE J. 1992, 38, 847-856.
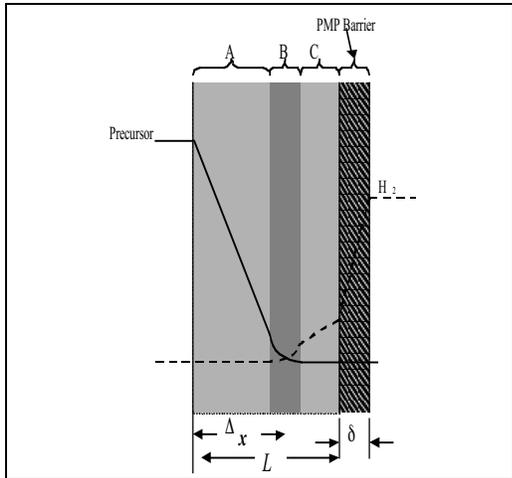
Figure 1. Deposition Zone for ORCF
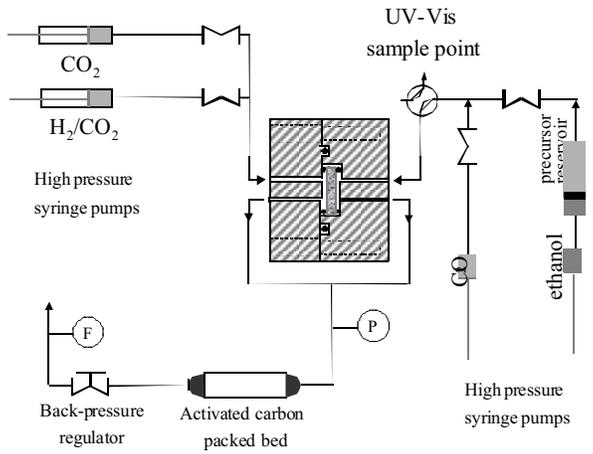

Figure 2. CFD Opposed Reactants Deposition System
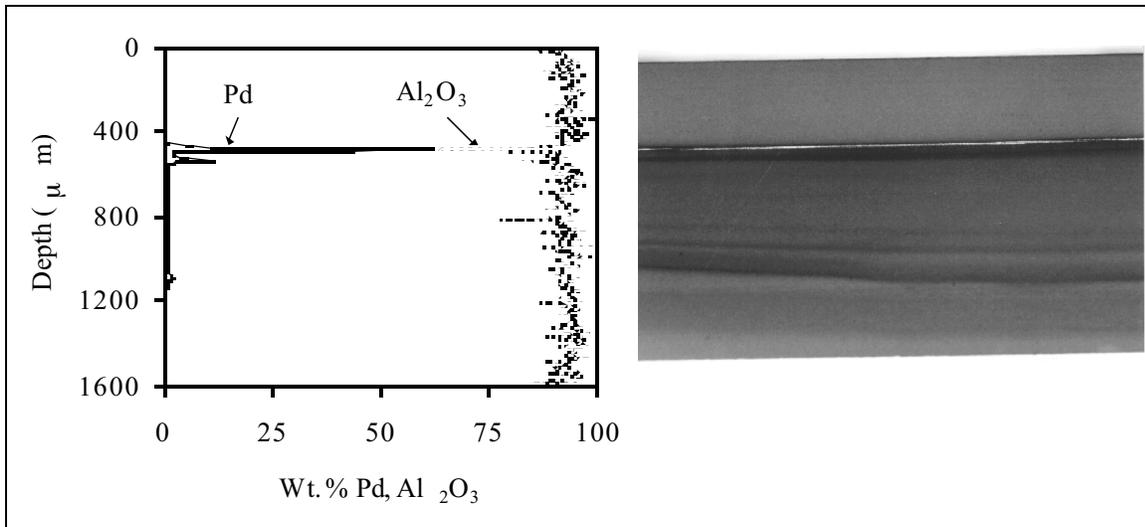
Figure 3. EPMA and Optical Microscopy Analysis of a thin Pd membrane deposited within an Al_2O_3 support.
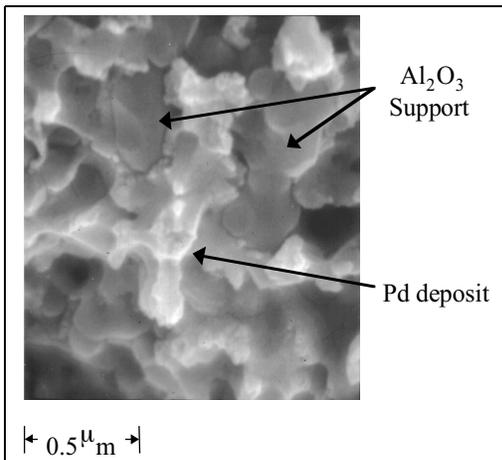


Figure 4. SEM micrograph of a Pd membrane.
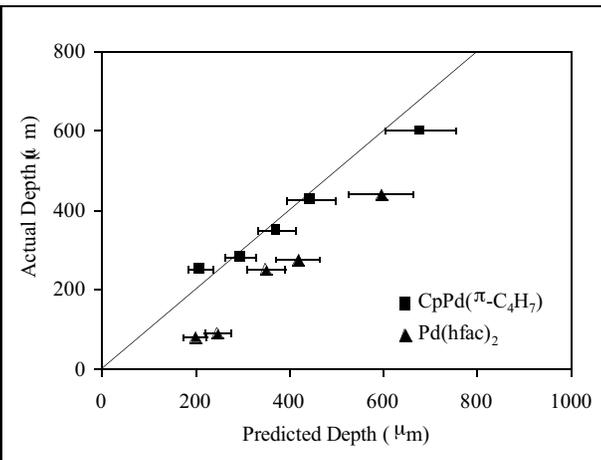
Figure 5. Parity plot comparing the actual depth of the Pd deposit to model predictions.