353a Development of Encapsulated Submicron Pd and Pd/Ag Alloy Hollow Fiber Membranes for a Membrane Fuel Processor

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Pd and Pd/Ag alloy membranes are synthesized and studied for more than a decade for their usage in hydrogen production in membrane reactors and hydrogen purification systems. Challenging issues facing the development of these devices are the permselectivity and stability of these membranes. Thin membranes (~2 µm thick) give a moderate flux of the order of ~0.1 mol/m^2s, but at the expense of selectivity towards H_2. Comparatively thick membranes (10-15 µm) gives high selectivity (>1000) but poor H_2 flux of the order of $10^{-2} mol/m^2s$. Another issue of paramount importance is the long term stability of Pd and Pd/Ag alloy membranes especially in a reaction environment. Pd and Pd/Ag alloy membranes of thickness ~10 µm are found to be more stable than thin membranes (~3 µm). Several attempts have been made by researchers to solve the above said issues and one among them was coating of Pd impregnated □-Al_2O_3 and subsequent deposition of Pd by electroless plating and is still in the developmental stage. We are developing a novel type of submicron thick Pd and Pd/Ag alloy hollow fiber composite membranes which is encapsulated between two □-Al_2O_3 layers. The hollow fiber supports used for Pd deposition are of 2mm OD and are made of symmetric □-Al_2O_3 having pore sizes of ~ 0.1 µm diameter. They are modified by a ~2 µm thick coating of □-Al_2O_3 layer on the outer surface by sol-gel coating. The pore sizes are reduced to the order of 5-10 nm. This layer is found to be critical for preparation of stable permselective membranes. Pre-plating of Pd is carried out on this □-Al_2O_3 layer by conventional sensitization and activation techniques. Electroless plating is carried out at a temperature of around 50-60^0 C to achieve a rate of deposition of the order of 5 µm/h. The rate of deposition and the thickness deposited on the hollow fiber is monitored online by a quartz crystal microbalance. The plating is stopped when the thickness is ~ 0.5 µm. Plated membranes are dried in an oven overnight at 120^0 C . A layer of ~2 µm thick □-Al_2O_3 is coated by slip casting over the submicron level Pd film and fired at 500^0 C. Hence the developed composite hollow fiber membrane has a Pd film encapsulated between two □-Al_2O_3 layers as shown in figure-1 below. The top □-Al_2O_3 serves to minimize the defect formation during thermal and pressure cyling of the submicron Pd film while giving a high enough permselectivity. The permeation studies show that the membrane has a separation factor(H_2/N_2) ~100 and a H_2 flux ~ 0.1 mol/m^2s for a temperature range of 300-500^0 C and at a transmembrane partial pressure difference of ~ 5 atm H_2. Similarly Pd/Ag alloy membranes are also developed by encapsulating submicron films between two □-Al_2O_3 layers. The procedure is similar except after a submicron level high temperature deposition of Pd, a thin layer corresponding to ~25 wt% Ag is deposited by electroless plating. The membrane is then alloyed in an atmosphere of H_2 at a temperature of 550^0 C for 10 -20 h. The resulting composite hollow fiber is again coated with ~2 µm thick of □-Al_2O_3 layer.Two variants of the Pd and /or Pd/Ag alloy encapsulated membranes are also developed to increase the selectivity of the membranes towards H_2. This is achieved by further modifying the above said Pd encapsulated membranes by one more electroless plating procedure conducted in a diffusion controlled mode. The idea was only to cover any defects in the submicron thick Pd film which is encapsulated. One variant is synthesized using a vacuum applied to the lumen of the membrane during electroless plating and another variant without vacuum. Plating times for both cases are an important factor to produce membranes of high permselectivity. For vacuum assisted electroless plating, the plating time is restricted to the induction time for nucleation. This prevents any deposition of Pd other than in the already existing encapsulated Pd film. The other variant was synthesized by electroless plating utilizing the capillary forces which will force the plating solution to the encapsulated Pd film. Plating time is kept very short in the order of induction time for nucleation. Diffusion time of Pd complex into the surface of the Pd film from the outside □-Al_2O_3 layer surface through the nanometer sized pores is of the order of 0.01s where as the induction time for nucleation is of the order of minutes (~10 minutes). This ensures more Pd deposition in the encapsulated film and helps to cover the defects. A high enough temperature ~ 60^0 C is maintained to ensure that the deposition of Pd is diffusion controlled. The performance of resulting membranes is tested by permeation studies. A detailed schematic of the various stages in the synthesis of encapsulated Pd membrane is shown in figure-2. Figure-2a shows a thin submicron layer (~ 0.3-0.5 µm) of Pd over γ-Al_2O_3 coating on α-Al_2O_3 support. The defects in this thin submicron membrane(Figure-2a) can vary from submicron to angstrom levels (10^{-7} to 10^{-10} m). During further conventional electroless plating Pd crystallites grow radially (Figure-2e) and hence the thickness over a defect free layer is usually greater than the thickness of Pd layer over the defect. In other words the thickness of Pd layer is not uniform and could be prone to defect formation where the Pd layer is thinner as shown in Figure-2e. During encapsulation using γ-Al_2O_3, the submicron level (10^{-7} to 10^{-8} m) pores are reduced to nanometer sized pores. During further electroless plating, Pd deposits preferentially on the defects as these are most likely to be the directly exposed surface to the plating solution. Hence, this helps to keep the thickness minimal while covering / removing the defects in the submicron level membrane and subsequently it provides a high selectivity with a reasonable flux of H_2. Separation factors are found to be higher (>100) than that of the parent Pd encapsulated membranes with the permeation fluxe of H_2 in the order of 0.1 mol/m^{2}s. The stability of the Pd encapsulated membranes and its variants are under testing and initial results are promising. The probability of defect formation in Pd membranes is a function of membrane surface area exposed. Encapsulation helps to reduce that exposed surface area. The permeation flux is not compromised due to the thinness of the membrane. Further long time stability under permeation and reaction conditions at 5 atm and temperatures greater than 300^0 C is still in progress and the results will be presented. Hence, the encapsulation helps to keep the membrane thin without early defect formation, while providing a high H_2 flux of the order of ~ 0.1 mol/m^2 s with separation factors >100. As the membrane thickness is ~ <1 µm and the number of electroless plating steps are not more than two, the usage of Pd is minimal and hence is less expensive to synthesize than conventionally electroless plated Pd membranes (~5-10 µm thick) of comparable permselectivity. We will describe the on going efforts in our laboratory to enhance the permselectivity of the encapsulated membranes and the efforts to integrate these membranes into a catalytic packed bed reactor.

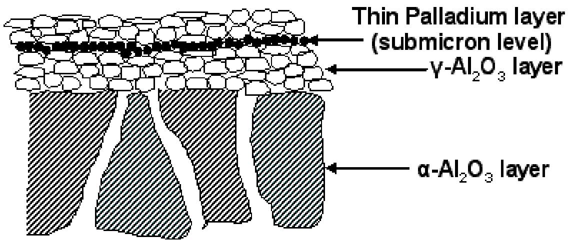

Figure - 1

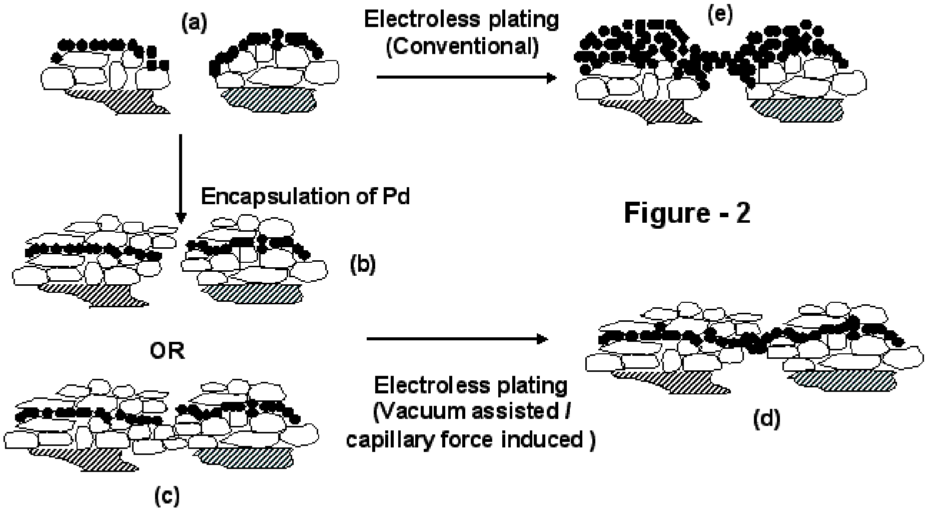

Figure - 2