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*Nano*structured Membranes for Catalysis

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Porous films in the form of *nano*structured membranes are of interest in several electrochemical systems, as for use as electrodes in polymer exchange membrane and solid-oxide fuel cells. Over the past decade, solid-oxide fuel cells produced by sputter deposition as thin film layered structures [1,2] have progressed from a one milliamp output at 300 ºC to demonstration as *micro*fuel cell devices [3] capable of providing an output power at 600 ºC of several hundred milliwatts per square centimeter. More recently, sputter-deposited porous membranes have generated interest for use in *micro*fuel cells as electrodes [3,4] (Fig. 1) and as catalysts to reform hydrocarbons as methanol.

*Nano*structured membranes for catalytic functions, in particular, require optimization of a three-dimensional structure to provide functional materials with an ideal surface area to volume ratio. The *nano*structured membrane can potentially yield a much greater ratio than found in materials as produced by either conventional or nonconventional powder processing [1] or as produced by using photolithographic patterning and etching [2]. Recently, through the development of a physical vapor deposition method [4], metallic membranes have been produced with continuous open porosity at the *nano*scale. The experimental parameters needed to control the porous *nano*structure are found to be tractable and generic for many metals including gold, silver, nickel, and aluminum.

In general, Thornton and others have shown that a transition in structural morphology through four zones of growth occurs with increasing substrate temperature and sputter gas pressure. The primary effect of increased temperature is an enhancement of surface and bulk diffusion. First, Zone 1 has a structure consisting of tapered crystallites separated by voids. A transition Zone T follows that has a structure consisting of densely packed fibrous grains and a smooth surface. Zone 2 then features continuous columns from the substrate to a surface characterized by crystalline facets. Lastly, Zone 3 evolves as the recrystallized grain structure.

To stabilize the open porosity of a nanostructured membrane, a new zone of growth is observed as a variant of Zones T and 2.[4] A three-dimensional polycrystalline deposit with continuous open porosity is produced under the following general condition. A moderate, sputter gas pressure and an elevated substrate temperature about half the absolute melting point yields a *nano*structured metal with continuous open porosity. The moderate sputter gas pressure creates a range of incident angles for deposition and the elevated temperature promotes a faceted crystalline growth.

A recent result for depositing porous *nano*structured copper (Fig. 2) provides the basis for synthesizing copper alloys that are of interest for use as catalytic materials. Specifically, copper-zinc-oxide is a known oxide compound widely used for the direct reformation of hydrocarbon fuels at low temperatures. A porous *nano*structure is found in a several-micron thick copper-zinc-oxide coating, sputter deposited from a copper-zinc alloy target using a partial pressure of oxygen, as shown in a scanning electron microscopy (SEM) image (Fig. 3). The analysis of an energy dispersive spectrometry (EDS) scan that corresponds with this coating reveals the composition to be Cu-19%Zn-14%O. In summary, sputter deposition is a method used to prepare *nano*structured membranes with open continuous porosity. Examples are shown in applications as electrode and as catalytic membranes for energy conversion *micro*devices.

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1. A.F. Jankowski, *ECS Proc. 97-24 (1997) 107*.
2. A.F. Jankowski, R.T. Graff, J.P. Hayes, and J.D. Morse, *ECS Proc. 99-19 (1999) 932*.
3. A.F. Jankowski, J.P. Hayes, R.T. Graff, and J.D. Morse, *MRS Symp. Proc. 730 (2002) 93.*
4. A.F. Jankowski and J.P. Hayes, *J. Vac. Sci. Technol. A 21 (2003) 422*.

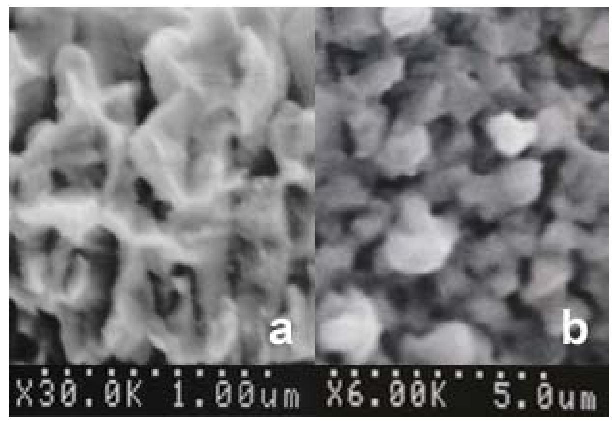

Fig. 1. SEM images of porous electrodes of (a) Ni, viewed in cross-section, and (b) Ag, in plan view, that were deposited at high temperature and sputter gas pressure.

Fig. 2. SEM image of a porous, *nano*structured Cu membrane viewed in cross-section that was sputter deposited at high temperature and gas pressure.

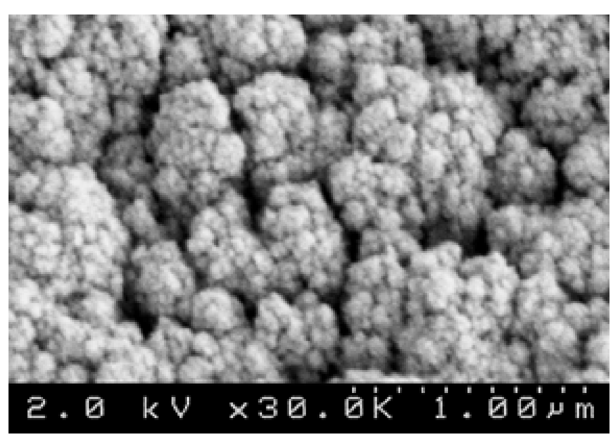

Fig. 3. SEM image of a Cu-Zn-O porous membrane, in plan view, that was reactively sputter deposited for use in catalytic hydrocarbon reformation.