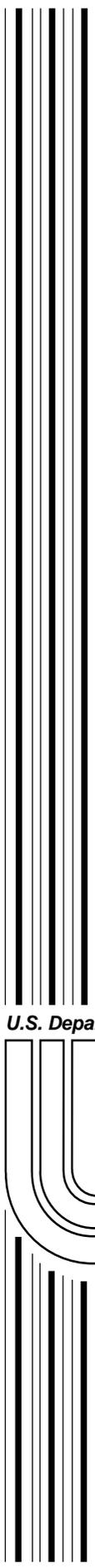


Characterization of Vapor Deposited *Nano* Structured Membranes

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Abstract

The vapor deposition methods of planar magnetron sputtering and electron-beam evaporation are used to synthesize materials with *nano* structured morphological features that have ultra-high surface areas with continuous open porosity at the *nano* scale. These *nano* structured membranes are used in a variety of fuel cells to provide electrode and catalytic functions. Specifically, stand alone and composite nickel electrodes for use in thin film solid-oxide, and molten carbonate fuel cells are formed by sputter deposition and electron beam evaporation, respectively. Also, a potentially high-performance catalyst material for the direct reformation of hydrocarbon fuels at low temperatures is deposited as a *nano* structure by the reactive sputtering of a copper-zinc alloy using a partial pressure of oxygen at an elevated substrate temperature.

Introduction

The use of vapor deposition technologies improves the performance and figure of small solid-oxide fuel cells.[1,2] The development of porous electrodes using micro electronic fabrication methods [3-6] enabled the development of MEMS-based [6-8] thin-film fuel cells. For example, a thin-film solid-oxide fuel cell was micro-fabricated with a porous nickel anode and a zirconia electrolyte.[7] Testing was conducted with air for the oxidant and a 2-6 cc·min⁻¹ flow of 4% H₂ for the fuel. A maximum power output of 145 mW·cm⁻² at 0.4 Volts was produced from a 2 mm sq test cell at 873 K.

The sputter deposition process can be used to create *nano* structured membranes that possess continuous open porosity. The deposition parameters needed to control the porous *nano* structure are found to be tractable for many materials. In general, structural morphologies found for conventionally sputtered coatings can range from porous columnar to dense polycrystalline. The transition in morphology through four zones of growth type occurs with increasing substrate temperature and sputter gas pressure. “Zone 1” has a structure consisting of tapered crystallites separated by voids. A transition “Zone T” has a structure consisting of densely packed fibrous grains and a smooth surface. “Zone 2” features continuous columns from the substrate to a surface characterized by crystalline facets. Lastly, “Zone 3” represents the re crystallized grain structure. The primary

effect of increased temperature is an enhancement of surface and bulk diffusion. The new growth zone found for the stabilization of a porous *nano* structure appears to be a variant of “Zones 1-2”. A three-dimensional polycrystalline deposit with continuous open porosity was produced under the general conditions of an increased working gas pressure and a substrate temperature approximately half the absolute melting point.

The objective to further integrate hydrocarbon reformation with the anode support structure of thin film fuel cells motivates the development of non-planar porous *nano* structures.[9,10] Porous *nano* structured membranes can be used to reform hydrocarbon fuels and to function as conductive electrodes. For catalytic functions, in particular, the control of a three-dimensional structure at the *nano* scale provides the possibility to produce materials with an ideal surface area to volume ratio.[9-11] In this paper, we report on the characterization of several *nano* structured membranes synthesized by magnetron sputtering and electron-beam evaporation. The structure of nickel is examined singularly and in a composite membrane. In addition, we examine the structure and composition of a low temperature catalyst that potentially avoids the coking problem associated with the direct reformation of methanol by nickel.

Sample Preparation

Magnetron sputter deposition is used to produce metals with continuous open porosity in three dimensions.[5] Planar magnetrons are operated in the dc mode using a working mixture gas of Ar_xO_{1-x} within a vacuum chamber that is cryogenically pumped to a base pressure of 10^{-6} Pa. Substrate wafers of silicon, sapphire, etc. are attached to a copper platen that is heated by a boron-nitride resistive element. A “Zone S” type, growth morphology is produced for substrate temperatures that are about half the melt point (to promote faceted growth) using a moderate, sputter gas pressure (to create a wide range of incident angles). Samples of nickel and copper-zinc-oxide were prepared for assessment as electrodes, and for catalytic fuel reformation in micro-fluidic fuel cell devices.[7,9].

Electron-beam evaporation is used to form the metal coating that is integral to a porous and conducting composite membrane for molten carbonate fuel cells.[11] A rod fed source is used in a cryogenically pumped

vacuum chamber. The substrate reverse is heated directly using a quartz lamp. The evaporative metal coating provides direct electrical contact to the insulating substrate that is a woven cloth of zirconia fibers.

Results and Analysis

The use of a moderate sputter gas pressure and an elevated substrate temperature yields a *nano* structured membrane characterized by open porosity. The moderate sputter gas pressure of 1.3 Pa creates a range of incident angles for deposition and the elevated temperature of 900-1000 K promotes a faceted crystalline growth in nickel. For this 10 μm thick nickel coating, the plan view and cross-section images (shown in Fig. 1) now reveal 200-400 nm size grains with a *nano* scale porosity that ranges in size from 10^1 to 10^2 nm. Preliminary Brenauer-Emmett-Teller (BET) measurements indicate an ultra-high surface area for this ~35% porous coating as determined by density analysis.

The catalytic performance of the confirmed, *nano* structured Ni membrane was assessed with regards to the conversion efficiency for the hydrocarbon fuel reformation reaction of $\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 3\text{H}_2$ as measured by analyzing gas product samples.[9,10] As part of an anode support structure, a 35-44% conversion efficiency is measured for 33 mg of the Ni coating in the flow through mode. For comparison, a 50 mg sample of a commercial-grade copper-zinc-oxide catalyst is found to steam reforms 70% of a $\sim 1 \text{ ml}\cdot\text{hr}^{-1}$ flow at 548 K, and 100 % of a $0.33 \text{ ml}\cdot\text{hr}^{-1}$ flow. Therefore, synthesizing Cu-Zn-O in the form of porous membrane would be ideal for use in micro fuel cell systems. This result is now seen for a “Zone S” type *nano* structure (shown in Fig. 1) in a reactively sputter deposited Cu-Zn-O coating. The plan view image reveals $<100 \text{ nm}$ size grains with a *nano* scale porosity that ranges in size from 10^1 to 10^2 nm. Quantification of the energy dispersive x-ray spectra (shown in Fig. 2) taken from the coating with a 15 KV electron beam using the ZAF correction for atomic number, absorption, and fluorescence yields a film composition of $\text{Cu}_{0.67}\text{Zn}_{0.19}\text{O}_{0.14}$.

The use of a flexible cloth composed of woven zirconia fibers along with a conducting nickel screen comprise the air electrode for molten carbon fuel cells.[11] To enhance the point contact between the zirconia cloth and the nickel screen, the surface of the zirconia cloth was metallized using an electron-beam deposition process. This coating process must not reduce the functional porosity of the cloth in order for the molten carbon

to flow through to its surface unimpeded during operation of the carbon cell. After the electron-beam deposition process, a *nano* structured composite membrane is revealed in the plan view images (shown in Fig. 3) of the nickel-coated cloth. At low magnification, the scanning electron microscopy images appear to have a porous weave at 10^1 μm to the zirconia cloth. At high magnification, the nickel coating appears to have a “Zone 1” type, porous *nano* structure with a <300 nm grain size that provides a high surface area for electrode contact.

In a test case of operation at 1073 K, particulate carbon produced from furnace oil pyrolysis was used as the fuel source and was discharged against two different nickel air cathodes in a molten carbonate fuel cell. One test assembly had the nickel coating and the other did not. The *LLNL composite membrane* consisted of the zirconia fabric coated on both sides with the *nano* structured nickel and used a coarse nickel sponge (with 80 pores- cm^{-1}) for the anode and cathode current collectors. The second test assembly used a proprietary commercial cathode and was conducted with an uncoated zirconia fabric. The cell potential and power density performance, as a function of current density, (shown in Fig. 4) was improved using the *LLNL composite membrane*. [11] The carbon fuel cell using the *LLNL composite membrane* yields >100 $\text{mW}\cdot\text{cm}^{-2}$ of power at current density levels above 150 $\text{mA}\cdot\text{cm}^{-2}$ whereas this performance was not achieved using the proprietary commercial cathode and zirconia fabric without the *nano* structured nickel coating.

Summary

The use of vapor deposition is demonstrated as a method to form *nano* structured membranes in fuel cells. Characterization of the vapor deposits reveals a *nano* structure to the grain and pore size. Examples are shown in application as potential, high performance electrodes and as catalytic membranes for use in thin film fuel cells that can utilize hydrocarbon fuels. Both metals (as Ni) and metal-oxides (as Cu-Zn-O) can be sputter deposited as *nano* structured membranes with a continuous open porosity, i.e. a sponge-like “Zone S” morphology. The matrix of the sputter deposited coatings is *nano* structured at a 10^2 - 10^3 nm grain size and the open porosity is *nano* scale at 10^1 - 10^2 nm. For electron-beam evaporative coatings, a “Zone 1” type morphology of loosely bound crystallites forms a *nano* structure that reduces the contact impedance between the insulating

membrane and the electrode mesh. The impact is the improved performance of carbon fuel cells using the *nano* structured composite membrane. This work was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

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Figures

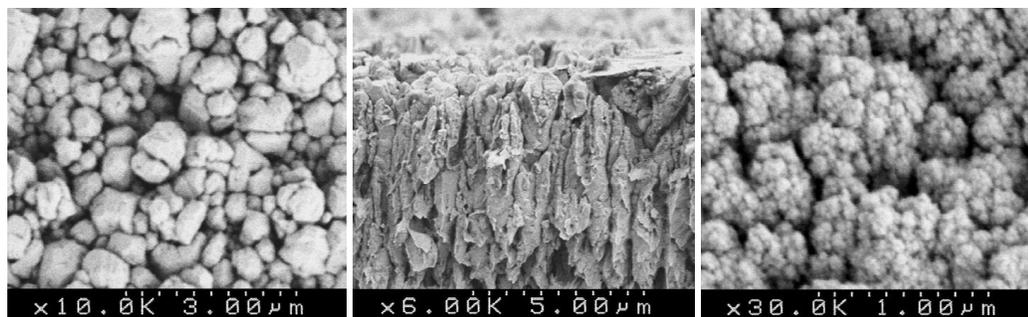


Fig. 1. Scanning electron microscope images of *nano* structured membranes of Ni viewed in plan view (left) and cross-section (center), and of Cu-Zn-O in plan view (right) that were each sputter deposited at an elevated temperature with a high, working gas pressure.

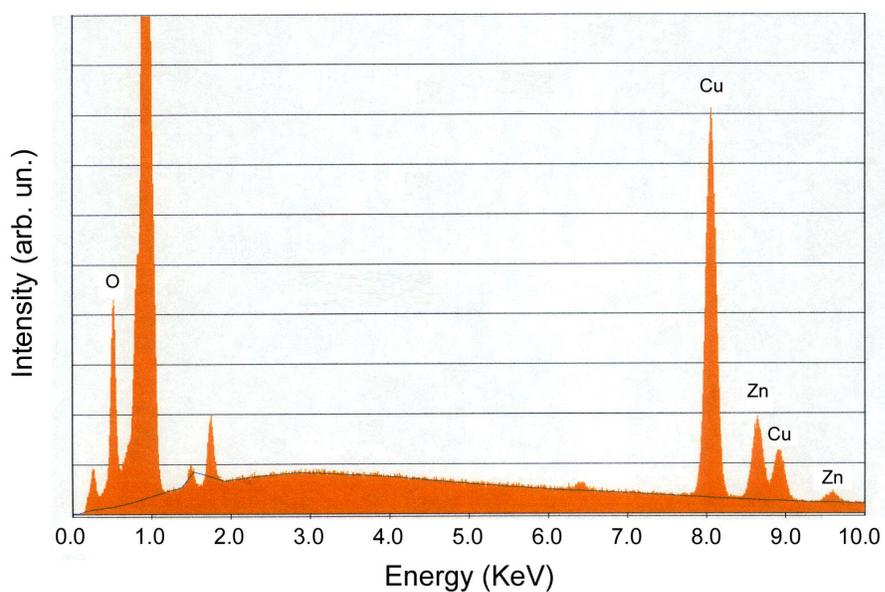


Fig. 2. The energy dispersive spectra of the Cu-Zn-O sputter deposited coating on silicon indicates the coating composition is 19 at.% Zn and 14 at.% O.

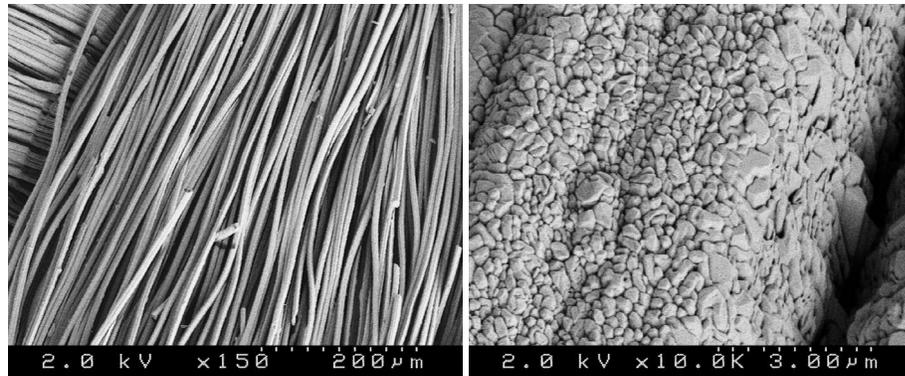


Fig. 3. Scanning electron microscope images of Ni-coated zirconia fibers at low magnification (left) reveal the porous structure to the composite membrane and at high magnification (right) reveal the *nano* structure of the Ni coating.

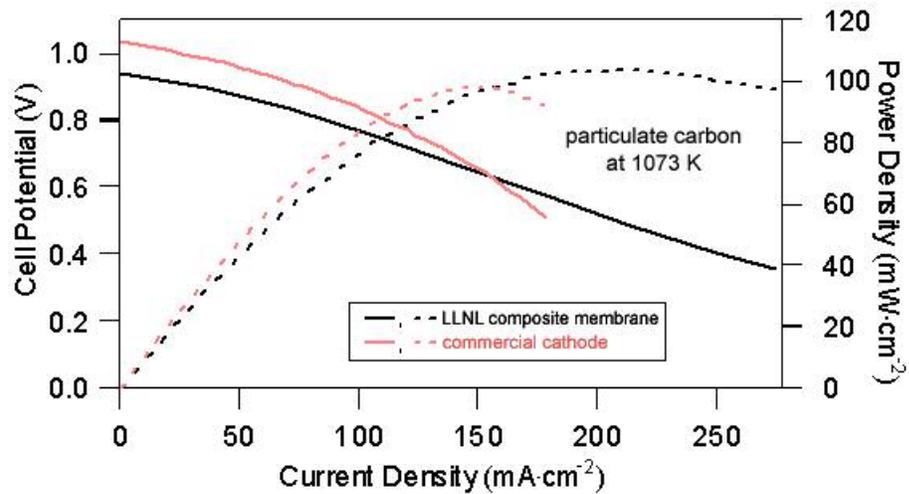


Fig. 4. The output of a carbon fuel cell operated at 1073 K using particulate carbon as the fuel and the Ni-coated zirconia cloth as the electrodes out performs cells constructed with commercial cathodes.

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