

Design and Synthesis of Oriented Guest-Host Nanostructures For Enhanced Membrane Performances

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Abstract

This project has demonstrated a novel nanomaterial design concept and a synthesis method for “guest-host” type superionic-conducting nanocomposite membranes. This concept consists of nanophases of oxide electrolyte nanograins (*guest*) encapsulated inside the nanopore channels of an oxide layer matrix (*host*), with channels oriented perpendicular to the layer surface. Using ionic conducting YSZ (yttrium stabilized zirconia) as a special case, we have shown that the host-guest design allows orientation of a large number channels, allowing a high density of of nanograin boundaries/interfaces to be built into the film to enhance cross-membrane conductivity. This structure allowed conductivity measurements with impedance spectroscopy to be performed for the first time at room temperature. Cross-membrane conductivity values at low temperature ranges of interest are the higher than any reported values. The conductivity-enhancing mechanisms could be attributed to (1) controlled orientation and increased number density of YSZ nanograin-host interfaces and (2) creation and stabilization of YSZ nanocrystalline phases inside nanopore channels (<10 nm dia.). This successful initial demonstration of host-guest nanostructures is expected to have direct impact on fuel cell technologies, and may also have beneficial use in a broad range of applications such as in solar cells, sensors, chemical/gas separations, catalysis, and magnetic memory devices. This work may also lead to a new way to develop membrane technologies that offer orders-of-magnitude higher permeability and selectivity, as well as improved thermal stability of the desirable nanocrystalline phases.

Introduction

Oxide ionic conductors, such as oxygen- or proton-conducting ceramic membranes, are very important materials for a wide range of applications, such as in fuel cells, microbatteries, and other solid-state ionics-based devices. Solid oxide fuel cells (SOFCs) present an efficient and ecologically acceptable way to simultaneously generate heat/electricity with theoretical efficiency as high as 70%. One future development goal is to introduce intermediate-temperature solid oxide fuel cells (IT-SOFCs) by considering alternative materials (such as electrolyte and electrode) that would enable lowering the operating temperature from 1000°C to below 800°C without loss of performance. Lower-temperature operation will reduce the system materials requirement and cost, and also avoid many undesirable interfacial reactions between electrode and electrolyte materials. At low operating temperatures, superior ionic conductivity of the oxide electrolyte layer ($> 10^{-2}$ S/cm) is required for success in fuel cell applications. A technical challenge lies in the creation of a stable membrane nanostructure that offers cross-membrane conductivity far above what is available today.

Nanomaterials have been considered promising in improving materials performance for solid-state ionics and SOFCs. The objectives of this project are to:

1. Demonstrate that novel host-guest nanocomposite membrane can be synthesized,
2. Prove that the designed nanostructure (i.e., large number density of oriented guest-host interfaces and nanocrystalline grain boundaries) can enhance cross-membrane ionic conductivity, and
3. Demonstrate improved thermal stability of nanocrystalline phases due to host nanopore confinement.

Technical Approach

Our nanocomposite membrane design, conceptually illustrated in Fig. 1a, consists of nanocrystalline phases of oxide electrolyte (*guest*, i.e., YSZ nanosized grains) encapsulated inside a *host*, which is a rigid solid (Al_2O_3 or SiO_2) matrix layer containing high-density arrays of oriented, uniform, nanopore cylinder channels (ideally <10 nm in diameter). This novel membrane approach integrates three potential conductivity-enhancement mechanisms:

- (1) Oriented guest-host interfaces, aligned parallel to the current flow direction (i.e., across the membrane layer),
- (2) Large number density of nanograin boundaries and nanograin-host interfaces via creation of nanocrystalline phases inside a host nanopore channels, and
- (3) Enhanced thermal stability of nanocrystalline phases due to confinement of grain growth inside nanopore channels.

This approach creatively allows the utilization of a large number of oriented guest-host interfaces as well as nanophase grain boundaries by stabilizing nanograins within designed nanopore channels.

Validation of conductivity enhancement through orientated crystal-substrate interfaces. This interface-orientation mechanism can be supported by the current understanding of the advantageous effect of crystal-substrate interface orientation on conductivity:

- Using a single-crystal YSZ film on MgO substrate, previous studies at ORNL have shown enhancement of ionic conductivity (measured with current flow parallel to the crystal-substrate interface) when film thickness decreased below 60 nm [Kosacki et al., 2004]. A 15-nm thick film exhibited the highest ionic conductivity ever reported, approximately 200-fold greater than that of conventional coarse-grained zirconia electrolyte at 400°C .
- Similar interface-orientation effect has been also reported for $\text{BaF}_2/\text{CaF}_2$ multilayers of epitaxial films where an increase of ionic conductivity (parallel to the layered interfaces) of over three orders of magnitude was observed relative to the bulk materials [Sata et al., 2000].
- A study in a large bulk single crystal YSZ clearly demonstrated the oriented interfacial effect on ionic conductivity enhancement due to dislocations (i.e., oriented interfaces of micro-cracks inside one piece of single crystal, parallel to the current flow direction) generated by plastic deformation [Otsuka, et al. 2003]. The conductivity increased with the increase of number density of microcracks in the crystal.

Justification of conductivity enhancement through nanocrystalline phases. For nanocrystalline ceramic electrolytes, the following have been established [Kharton and Marques, 2002]:

- large number and volume of grain boundaries ($\sim 10^{19} \text{ cm}^{-3}$), resulting in a large ratio of atoms in grain boundaries to grain volume (ca. 30-60%);
- grain boundary impurity segregation, and thus considerably lower concentration of impurity phases, which blocks ionic conduction per unit of grain boundary area;
- increased contribution of space-charge effects;
- grain-size-dependent defect thermodynamics (i.e., increased vacancy concentration in the grain-boundary area; $D_{\text{GB}} \gg D_{\text{B}}$). Ionic mobility due to a higher number density of nanograin boundaries and higher interfacial concentration of defects (oxygen vacancies) is superior to the ionic diffusion through the bulk grains.

Results from supported nanocrystalline ScSZ thin films have shown that the enhanced electrical conductivity was due to the changes of ion mobility, which occurs in grain-boundary interfaces oriented parallel to the current flow [Kosacki et al., 2001]. Such an idea of interface orientation effect has been also reported for nanocrystalline CaF_2 [Puin et al., 2000]. In addition, grain-substrate interfacial contributions are enhanced in a substrate-supported nanocrystalline film [Suzuki et al., 2002]. These factors have been shown to contribute enhanced conductivity in the direction parallel to a film-substrate

interface. We have aimed at a proving the concept of a nanostructured material designed to maximize the grain boundary and grain-substrate interfacial effects.

Results and Discussion

Proof-of-principle studies have focused on development of membrane synthesis by infiltrating and growing YSZ (typically $\text{ZrO}_2:16\% \text{Y}$) nanophases inside oriented nanoporous host layers of anodized alumina discs, with pore-channel diameters in the range of 10-100nm.

Synthesis of host-guest nanocomposite membranes. Initial effort to prepare ordered nanopore host materials was by an “engineered molecular assembly templated synthesis” (EMATS) [Hu et al., 2003], which allows the formation of large-area domains of hexagonally ordered cylinder channels (<10 nm), perpendicular to the layer surface. However, at this stage, oriented mesoporous silica in the form of membrane discs is difficult to make. Alternatively, we have been cooperating with Synkera Technologies and have successfully obtained anodized aluminum oxide (AAO) discs of various desirable pore channel diameters (13 ± 2 , 18 ± 3 , 35 ± 3 , 55 ± 6 , and 73 ± 7 nm). Various methods have been attempted to infiltrate guest YSZ nanophases into host matrix. A vacuum-assisted polymer or nanoparticle precursor infiltration method has been developed to infiltrate or impregnate YSZ precursor into the host nanopore channels, followed by thermally induced crystallization and grain growth. The nanostructures of the resulting composite materials (e.g., pore channels and confined nanograins) were examined by scanning transmission electron microscope (STEM) and X-ray diffraction (XRD), showing ~ 5nm nanocrystalline grains present at typical 600°C, 4h calcination. Back-scatter SEM images have shown long YSZ nanowires across the channels, in some cases segmented wires.

Conductivity enhancement in oriented guest-host nanocomposite membranes. The conductivity of the nanostructured samples were measured by impedance spectroscopy (IS), which allows the separation of resistances related to grains, grain boundaries, and electrode effects. The diffusivity of ions in nanocrystalline materials corresponds to the results of conductivity measurement by impedance spectroscopy. The cross-membrane conductivity at room temperature of the materials synthesized in this study was the highest ever reported for YSZ materials; in fact, this is the first time values have been obtainable at room temperature. As shown in Figure 1b, the oriented host-guest interfaces further enhance the conductivity beyond what grain boundaries in nanocrystalline phase can provide. It is noted that conductivity of the materials from this study is lower than other nanocrystalline YSZ at high temperatures; low guest density and nanowire discontinuity and interface segmentation at high temperatures might have contributed to this reduced performance at high temperature.

Stability and maintenance of high-conductivity nanostructures. Thermal stability of nanocrystalline phases, which is related to grain growth phenomena under relatively high temperature processing or operation conditions, is known to be a technology bottleneck for maintaining nanophase-enhanced conductivity in conventionally supported nanocrystalline films [Dong and Hu et al., 2002]. Our STEM examinations have visually proven the nanopore-confinement effect that has restricted the growth of grain size within the dimension of nanopore channels of the AAO host. In an extreme case, a single crystal nanowire may form, but still provide the desirable nanograin dimension and the oriented guest-host interfaces. Therefore, this guest-host design resolves the thermal stability problem by surviving the desirable nanograin size in the nanocomposite membrane.

Future work. The demonstration of the enhanced conductivity and improved thermal stability for our nanocomposite membrane samples is expected to attract follow-on funding for further development of the membrane fabrication method for fuel cells and other applications. Future development needs to address various issues, including systematic studies of nanostructure and composition; improvement of YSZ nanophase density, homogeneity, and the contact interface between electrode and the membrane; the effect of channel diameter, aspect ratio, channel length, and host and guest composition effect. The size of

the membrane area needs to be scaled up for future practical technology development. Mechanical properties of the membrane under various temperatures need to be also evaluated.

Benefits

The novel concept demonstrated here is not limited to ionic oxide material. Beyond fuel-cell applications, the host layer materials (if functionalized with appropriate ligands) could potentially serve as membranes for waste water clean-up, biomolecule separation, synthesis of uniform macromolecules (dendrimers), and mining applications. Furthermore, many different kinds of nanocrystalline oxides or non-oxides (metals/alloys, nitrides) can be developed in the nanopore channels of our unique host matrix layer to take advantage of the nanocrystal confinement and oriented interfacial effects. For example, proton-conducting oxides or polymers can be prepared as guest phases confined in nanopore channels for proton membranes. Such nanocomposite membranes could also lead to a new generation of electrochemical sensor materials for H_2 , NO_x , etc. The designed nanocomposite membranes could be used for solar cells, membrane catalytic reactors (desulfurization by hosted Mo_2N nanophase), hard-disk memory (magnetic recording with high signal-to-noise ratio), or for electronic/optical devices (when guests are semiconductors such as CdS). In summary, the R&D and application opportunities for our novel nanostructured membranes are very broad.

References

- Dong, J.; Hu, Michael Z.; Payzant, E. A.; Armstrong, T. R.; and Becher, P. F. 2002. "Grain growth in nanocrystalline yttrium-stabilized zirconia thin films synthesized by spin coating of polymeric precursors," *J. Nanosci. Nanotechnol.*, 2, 161.
- Hu, Michael Z.; de Almeida, V.; Blom, D. A.; Allard, L.; Dai, S.; Tsouris, C.; and Zhang Z. 2003. "Pore Channel Orientation In Self-assembled Inorganic Mesostructures," a poster presented at the Microscopy and Microanalysis 2003 Meeting, San Antonio, Texas, 3-7 August 2003.
- Kharton, V. V. and Marques, F. M. B. 2002. "Mixed ionic-electronic conductors: effects of ceramic microstructure on transport properties," *Current Opinion in Solid State and Materials Science*, 6, 261.
- Kosacki, I.; Becher, P. F.; Rouleau, C. M.; Lowndes, D. H.; and Bentley, J. 2004. "Observation of superionic conductivity in highly oriented nanometer scale ZrO_2 -10 mol % Y_2O_3 (10YSZ) film," unpublished results.
- Kosacki, I.; Suzuki, T.; and Anderson, H. U. 2001. Proc. 7th Intern. Sym. In Solid Oxide Fuel Cells, Tsukuba, *The Electrochem. Soc. Proc.*, vol. 2001-2016, pp. 284-292.
- Otsuka, K.; Kuwabara, A.; Nakamura, A.; Yamamoto, T.; Matsunaga, K.; and Ikuhara, Y. 2003. "Dislocation-enhanced ionic conductivity of yttria-stabilized zirconia," *Appl. Phys. Lett.*, 82, 877.
- Puin, W.; Rodewald, S.; Ramlau, R.; Heitjans, P.; Maimer, J. 2000. "Local and overall ionic conductivity in nanocrystalline CaF_2 ," *Solid State Ionics*, 131, 159.
- Sata, N.; Eberman, K.; Eberl, K.; and Mailer, J. 2000. "Mesoscopic fast ion conduction in nanometer-scale planar heterostructures," *Nature*, 408, 946.
- Suzuki, T.; Kosacki, I.; and Anderson, H. U. 2002. "Microstructure-electrical conductivity relationships in nanocrystalline ceria thin films," *Solid State Ionics*, 151, 111.

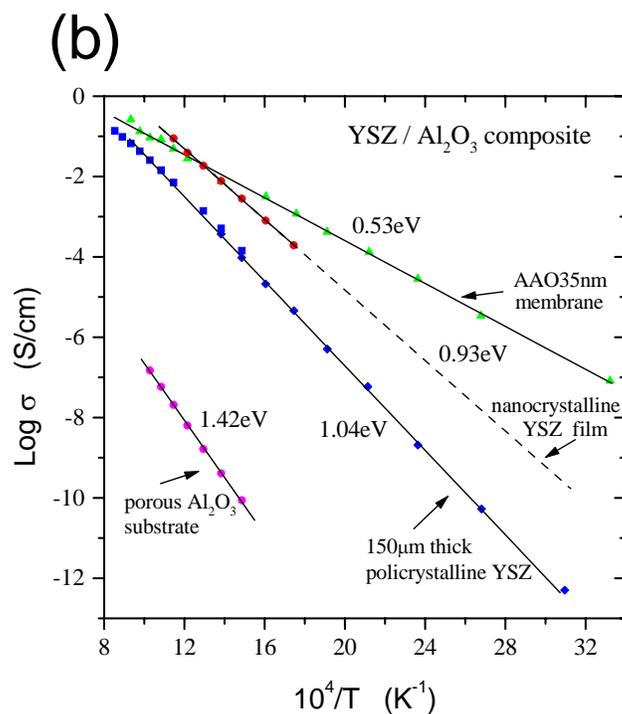
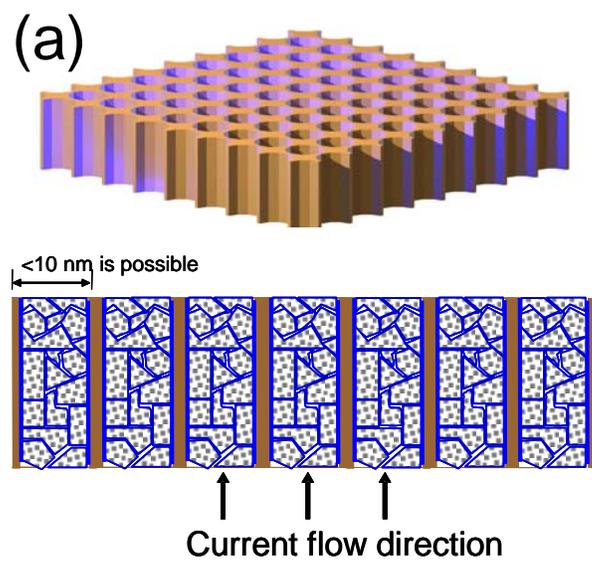


Fig. 1. (a) Schematic illustration of the nanostructure design of oriented guest-host nanocomposite membranes. (b) The measurable room temperature ($1/T = 33 \times 10^{-4} \text{ K}^{-1}$) and low-temperature conductivity data provide proof-of-principle demonstration of the effects of nanostructure and orientation on the enhancement of conductivity in nanocomposite membranes.