GCEP Progress Report

Metal Oxide Nanotubes and Photo-Excitation Effects: New Approaches for Low-to-Intermediate Temperature Solid Oxide Fuel Cells to Enable Low GWG-Emission Transportation

Investigators

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Abstract

This collaborative project, involving Paul McIntyre's group at Stanford and Prof. Shriram Ramanathan's group at Harvard University, focuses on atomic layer deposition of ultrathin solid state electrolytes and electrodes for low-temperature SOFC operation, and incorporation of such materials in highly reticulated structures such as metal oxide nanotubes for high power density and clean energy conversion for transportation. The two groups are also studying the effects of nano-scale crystallite size in electrolytes on oxygen transport and of UV illumination on low-temperature electrochemical reaction kinetics at SOFC electrodes. The start date for the Stanford portion of the project was March 1, 2007. Work during the period from that date through early May of 2007 has concentrated on ALD precursor screening and thickness uniformity optimization, design of a simple new ALD chamber for rapid precursor screening studies, and selection of an impedance measurement system to be ordered and set up in McIntyre's laboratory. The Harvard subcontract for this project was not yet in effect, as of early May 2007; therefore, no results from Harvard are described in this report.

Introduction

The goal of this project is to enhance the power density and low-temperature efficiency of solid oxide fuel cells manufactured by atomic layer deposition. These enhancements will be achieved by engineering the morphology of the electrolyte at the nanoscale, and by photo-excitation of the membrane surface.

Background

The efficiency of a fuel cell is limited by the loss mechanisms inherent to its operation. The power density of a fuel cell is limited by the area of its electrolyte membrane. These two operational parameters are related by the fact that thinner electrolytes not only limit the resistive losses within the fuel cell, but they also allow the incorporation of more active area into a given stack volume.

Ultra-thin electrolyte membranes for solid oxide fuel cells (SOFCs) must meet at least two criteria: they must be free of pinholes through which gases could leak, and they must be of the correct chemical composition and crystalline structure. Atomic layer deposition (ALD) is capable of making a pinhole-free layer of material 2 to 3 orders of magnitude thinner than state-of-the-art electrolyte membranes. Furthermore, this layer is highly conformal to the substrate, even over rough or convolved surfaces. The chemical composition of the membrane is determined by the mix of precursors admitted to the deposition chamber, and it has been shown that the crystalline structure can be controlled through a sequence of deposition steps at different compositions and thicknesses, followed by annealing at a specified temperature.

Electrolyte thickness is not the only parameter that governs efficiency. The nature of the chemical reactions that take place at the surface of the membrane (the "triple phase boundary") is also responsible for lost work in a fuel cell. Exposure of the surface to photons in the ultraviolet range may reduce the activation energy for these reactions, thereby improving cell efficiency.

Results

As a newly-initiated project, activities to date have focused on optimization of ALD deposition parameters for growth of Y_2O_3-ZrO_2 nanolaminates, the initial step in forming ultra-thin yttria-stabilized zirconia (YSZ) alloy films for the electrolyte layer in SOFCs. Initial results on this methodology for YSZ alloy formation, obtained by the PIs prior to the start of the contract period, have recently been accepted for publication in Electrochemical and Solid State Letters.[1] In parallel, we have been investigating La, Sr, and Co metalorganic precursors for ALD of LSCO, a mixed ionic-electronic conductor that is a promising SOFC cathode material. Low volatility of Sr metalorganic precursors is particularly problematic, and we are investigating several different chemistries in an attempt to overcome this problem. In order to more efficiently survey different precursors and optimize deposition conditions, we have contracted with a machinist to fabricate a small, simpler ALD chamber which should be delivered during the upcoming summer quarter. We have also obtained quotes for an impedance system, required for electrochemical characterization of the ALD-grown SOFC materials, and will place an order for it soon.

Progress

Activities performed during the very brief period of the contract provide a foundation for more reproducible deposition of ultrathin, pin-hole free SOFC materials via atomic layer deposition. They are preparatory to the major tasks of the project which will depend in large part on the initiation of research at Harvard, once the subcontract there can be started.

Future Plans

During the coming year, we plan the following major activities –

1) Order and set up the impedance analysis system in McIntyre's laboratory. Fabricate a fixture for supporting micro-fabricated fuel cell arrays on Si wafers for impedance analysis with differing oxygen partial pressures on either side of the cell membrane.

2) Select precursors and investigate LSCO deposition process using new ALD "screening" chamber.

3) Investigate composition, grain size and thickness effects on the total conductivity and cubic phase stability of ultra-thin ALD-YSZ fuel cell membrane (w/ Harvard).

4) Study selective etching of Ge NWs coated with YSZ nanolaminates to produce YSZ nanotubes.

5) Begin Si microfabrication runs (patterning and selective etching) for fuel cell window fabrication.

Publications

No publications to report from research occurring so far during the contract period.

References

1. Ginestra, C., Sreenivasan, R., Karthikeyan, A., Ramanathan, S., & McIntyre, P.C., Atomic Layer Deposition of Y_2O_3/ZrO_2 Nanolaminates: A Route to Ultra-Thin Solid State Electrolyte Membranes. *Electrochem. Sol. Stat. Lett.*; in press.

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