Metal Oxide Nanotubes and Photo-Excitation Effects: New Approaches for Low Temperature Solid Oxide Fuel Cells

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Trends in Personal Mobility

- Transportation accounts for ~ 24% of GWG emissions currently
- Increasing relative impact in future due to growing adoption of automotive transportation world-wide (e.g. personal automobile ownership increasing ~ 20% per annum in China)
- Great interest in **greener engine technologies** and **low-GWG fuels**

Source: GCEP Advanced Transportation Assessment, Spring 06
Reduced-GWG Automobile Propulsion Technologies

- Improved internal combustion engines (evolutionary)
  - hybrids
  - flexible-fuel IC engines burning hydrogen-rich hydrocarbons

- All electric vehicles

*Low temperature fuel cells*

Major potential impact, but breakthroughs needed → esp. in materials & catalysts
Fuel Cell Basics

Example: PEM fuel cell

Hydrogen is typical fuel for PEM cells, but this is not necessarily the case for other fuel cell types.

Key idea: Electrochemical reduction and oxidation reactions on either side of an ion-conducting membrane set up a steady-state voltage difference across the cell - voltage difference (EMF) can do work (e.g. move a vehicle)

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Solid oxide fuel cells

Operating Principle

YSZ is a crystalline alloy of ZrO₂ and Y₂O₃
- Oxygen fast ion conductor
- Electronic insulator

Siemens-Westinghouse Tubular SOFC
- High operating temperatures
- Target fixed power generation


SOFC's – high efficiency, flex fuel, simple operation, but high temperature
Fuel cell power output

The open circuit voltage is given by the Nernst equation:

\[ E^o = \frac{RT}{4F} \ln \frac{P_{O_2(c)}}{P_{O_2(a)}} \]

at 1000°C:

\[ \frac{RT}{4F} \ln \frac{0.2}{10^{-18}} = 1.1 \text{ V} \]

- OCV is theoretical maximum EMF available to drive electron current from anode to cathode (through interconnect) and do work.

- Actual EMF is less than OCV at a given current density
- Portion of OCV is consumed in resistance loss across YSZ membrane and charge transfer losses at electrodes
- \textbf{Reducing these losses is critical to lowering SOFC operating temperature}
Our approach

Reduce SOFC operating temperature while maintaining high efficiency, power density, and fuel flexibility

Methods under investigation

- Lower Ohmic resistance loss across YSZ membrane by depositing ultrathin YSZ films via *atomic layer deposition* (ALD) - decrease membrane thickness from 10’s of mm to 10’s of nm.
- Increase power density by exploring high-aspect ratio membranes, including YSZ nanotubes
- *UV-modification* of nano-scale electrode structures and properties
Outline

• Introduction

• \textit{ALD of nanocrystalline YSZ electrolytes}

• UV illumination effects on SOFC electrolytes and electrodes

• Microfabricated membranes and oxide nanotubes

• Summary
ALD: Ultrathin, conformal metal oxide film deposition

- ALD: cyclic surface-saturating chemical reactions separated by inert gas purges
- Capable of producing fully conformal ultrathin films over convolved substrate surfaces

**ALD Nanolaminate Approach:**

Use ALD to deposit ZrO$_2$ and Y$_2$O$_3$ films with desired thickness

Deposit nanolaminate

Anneal nanolaminate to form YSZ

YSZ

HfO$_2$
Long-period YSZ nanolaminates

As-grown

- 20 nm total thickness
- Tetragonal ZrO$_2$
- Amorphous Y$_2$O$_3$

Annealed

- Appreciable, yet incomplete interdiffusion
- Interfacial SiO$_2$ growth
  - 1 nm $\longrightarrow$ 15 nm

Raw Zr and Y counts calibrated using standard 8% YSZ
Y:Zr content ratio plotted vs sample depth
Further evidence of layer interdiffusion

Crystal phase evolution for varying $Y_2O_3$ content of ALD-YSZ

- Selected area electron diffraction indicates formation of the cubic, fast ion conducting, YSZ phase for 10 mol% $Y_2O_3$ dopant, similar to bulk YSZ.
Effect of substrate on in-plane YSZ electrical conductivity

- Unexpected decrease in electrical conductivity for 6 mol% Y$_2$O$_3$ sample on MgO (100) single crystal compared to 2 mol% and 3 mol% Y$_2$O$_3$ YSZ films on SiO$_2$/Si (100).
- Apparent activation energy for conductivity does not change.
- Suggests the removal of a shunt current component through the Si substrate for these in-plane conductivity measurements.

Need through thickness measurement of electrical conductivity (fuel cell tests)
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Photo-excitation effects example: Room temperature oxidation of Zr

- The rate of oxidation of metals and self-limiting thickness can be influenced by photons even at room temperature
- Surface oxygen incorporation rate increased

Film grain size control under illumination: YSZ ultra-thin electrolyte membrane

- In addition to the rate of oxidation, the evolution of oxide film grain size during Y-Zr alloy oxidation can be greatly altered by UV illumination.

- Mechanism requires further investigation; may involve modification of point defect concentrations and charge states to decrease drag force on grain boundaries.

Electrical conductivity of Y$_2$O$_3$-doped ZrO$_2$ thin films grown by alloy oxidation under UV

- Reduction in ionic conductivity compared to thermally oxidized films
- Grain size effect?
- Not advantageous for SOFC electrolyte (want large $\sigma_{\text{ion}}$)
Structural evolution of SOFC electrodes under UV illumination

Under review, 2009

LSCF mixed electronic/ionic conducting oxides

• promising cathode materials for SOFC’s

• we have demonstrated that UV exposure during crystallization leads to a reproducible enhancement in conductivity (electronic) and crystallization kinetics

• structural and compositional tuning with UV excitation is a promising approach to designing oxide materials for energy applications
Structural evolution of SOFC electrodes under UV illumination

Growth of thin $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-d}$ films by rf-sputtering, annealed at 450°C with and without UV exposure

Slight shift in x-ray diffraction peak (+ 0.1 deg) in films exposed to UV consistent with oxygen enrichment

Surface morphology is similar in both cases
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Free Standing SOFC Membrane Microfabrication

Use ALD-HfO₂ membranes to develop methodology – chemically similar to YSZ but easier to deposit

Best result: 27 nm-thick HfO₂ free-standing membranes with 125x125 µm² area were fabricated with yield of 100% (complete absence of broken/cracked windows)
Electrode Microfabrication

Porous Pt Deposition Optimization

Pressure: 75 mTorr  Ar flow rate: 75 sccm

Pressure: 95 mTorr  Ar flow rate: 100 sccm

4.8 % pore area

8.7 % pore area

Preparation: DC magnetron sputtering (power: 100 Watt, film thickness: 50nm)
HfO₂ SOFC Membrane Characterization

Sample photograph

Measurement station

25 mm

Cathode probe

Sealed chamber

AC Impedance Properties of HfO₂ Membranes

68 nm HfO₂, 500°C

Z' (Ohm·cm²)

Z'' (Ohm·cm²)
YSZ nanotube synthesis & properties

Top left: vertical Ge nanowire array (40 nm diameter)

Bottom left: conformal ALD-HfO₂ coating on Ge nanowire (40 nm diameter)

Top right: Schematic of high aspect-ratio YSZ membrane composed of metal oxide nanotubes
- note: Ge etches readily in dilute H₂O₂/H₂O solution
- YSZ functions as an etch stop
Thin-wall oxide nanotube experiments

Initially, 1.5mm-long Ge vertical nanowires were used as template for growth of HfO$_2$ nanotubes.

Chemical mechanical polishing (CMP) to expose HfO$_2$ nanotubes.

Processing conditions for ALD of HfO$_2$ ultra-thin layers:

- **Precursor (Temp.):** Hf[N-(CH$_3$)$_2$]$_4$ (90°C)
- **Oxidant (Temp.):** H$_2$O (25°C)
- **Growth per cycle:** 0.85Å
- **Film roughness:** 2Å
- **Substrate temp.:** 300°C

Deposition of 2-8nm-thick HfO$_2$ layer using ALD followed by anneal at 800°C for 3hrs in Ar.

Ge selective wet etch out of HfO$_2$ nanotubes.

Deposition of 1.5mm-thick SiO$_2$ encapsulation layer using plasma enhanced chemical vapor deposition (PECVD).

Buffered oxide etch (BOE) of SiO$_2$ encapsulation layer.
Vertical, having ultra-thin walls, crystalline (except 2nm-thick sample) HfO$_2$ nanotubes were observed. Additionally, HfO$_2$ nanocrystalline films on Si(111)surface were characterized.
Nanotubes after selective Ge core etching

SEM images of hollow vertical HfO₂ nanotubes: plan view

- Ge is easily etched in oxidative aqueous solutions (solubility of GeO₂).
- Ge nanowire cores were dissolved after few minutes in 30% H₂O₂ aqueous solution at 40°C in ultrasonic bath, without etching of HfO₂ nanotubes.
- SEM of the etched samples showed hollow broken HfO₂ nanotubes. Unbroken HfO₂ nanotubes were not etched.
Metal oxide nanotubes – cross-section images

(a) TEM image of hollow HfO$_2$ nanotubes synthesized by ALD of HfO$_2$ on Ge NWs of 20nm diameter, and selective wet etching of the Ge in dilute H$_2$O$_2$

(b) cross-section view of a HfO$_2$ nanotube.
Selective etching of Ge NW template

Energy dispersive spectroscopy (EDS) analysis shows absence of residual Ge inside HfO₂ nanotubes after selective wet etching. Note that Cu contamination is from TEM grid after ion milling of the sample.
Summary

• Atomic layer deposition of nanoscale metal oxides provides new opportunities for energy-focused materials research.

• Ultra-thin solid state electrolyte membranes can reduce the Ohmic barrier to oxygen ion current transport in SOFC’s.
  - ALD nanolaminates to tune composition and the crystal structure of YSZ electrolytes
  - Innovative approaches to reducing activation losses at the air/cathode interface are still required.

• UV illumination during annealing of LSCO electrodes produces a large enhancement in electrical conductivity.
  - Need to test effects on SOFC performance

• Microfabricated oxide windows with membrane thickness < 30 nm fabricated successfully by ALD and MEMS etching methods.

• Metal oxide nanotubes grown on vertical Ge NW templates
  - Selective removal of Ge successful
  - Future work: combine ALD SOFC membranes and NT fabrication