Metal Oxide Nanotubes and Photo-Excitation Effects

New Approaches for Low-Temperature Solid Oxide Fuel Cells for Low GWG-Emission Transportation

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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)

Source: GCEP Advanced Transportation Assessment, Spring 06

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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)
# Fuel Cell Types

<table>
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<tr>
<th>Fuel Cell Type</th>
<th>Common Electrolyte</th>
<th>Operating Temperature</th>
<th>System Output</th>
<th>Efficiency</th>
<th>Applications</th>
<th>Advantages</th>
<th>Disadvantages</th>
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<tr>
<td>Polymer Electrolyte Membrane (PEM)*</td>
<td>Solid organic polymer poly-perfluorosulfonic acid</td>
<td>50 - 100°C 122 - 212°F</td>
<td>~1kW – 250kW</td>
<td>50-60% electric</td>
<td>Back-up power • Portable power • Small distributed generation • Transportation</td>
<td>Solid electrolyte reduces corrosion &amp; electrolyte management problems • Low temperature • Quick start-up</td>
<td>Requires expensive catalysts • High sensitivity to fuel impurities • Low temperature waste heat</td>
</tr>
<tr>
<td>Alkaline (AFC)</td>
<td>Aqueous solution of potassium hydroxide soaked in a matrix</td>
<td>90 - 100°C 194 - 212°F</td>
<td>10kW – 100kW</td>
<td>60-70% electric</td>
<td>Military • Space</td>
<td>Cathode reaction faster in alkaline electrolyte so high performance</td>
<td>Expensive removal of CO₂ from fuel and air streams required</td>
</tr>
<tr>
<td>Phosphoric Acid (PAFC)</td>
<td>Liquid phosphoric acid soaked in a matrix</td>
<td>150 - 200°C 302 - 392°F</td>
<td>50kW – 1MW (250kW module typical)</td>
<td>80 to 85% overall with combined heat and power (CHP 36-42% electric)</td>
<td>Distributed generation</td>
<td>High efficiency • Increased tolerance to impurities in hydrogen • Suitable for CHP</td>
<td>Requires platinum catalysts • Low current and power • Large size/weight</td>
</tr>
<tr>
<td>Molten Carbonate (MCFC)</td>
<td>Liquid solution of lithium, sodium, and/or potassium carbonates, soaked in a matrix</td>
<td>600 - 700°C 1112 - 1292°F</td>
<td>~1kW – 1MW (250kW module typical)</td>
<td>85% overall with CHP (60% electric)</td>
<td>Electric utility • Large distributed generation</td>
<td>High efficiency • Fuel flexibility • Can use a variety of catalysts • Suitable for CHP</td>
<td>High temperature speeds corrosion and breakdown of cell components • Complex electrolyte management • Slow start-up</td>
</tr>
<tr>
<td>Solid Oxide (SOFC)</td>
<td>Solid zirconium oxide to which a small amount of yttria is added</td>
<td>650 - 1000°C 1202 - 1832°F</td>
<td>9kW – 3MW</td>
<td>85% overall with CHP (60% electric)</td>
<td>Auxiliary power • Electric utility • Large distributed generation</td>
<td>High efficiency • Fuel flexibility • Can use a variety of catalysts • Solid electrolyte reduces electrolyte management problems • Suitable for CHP</td>
<td>High temperature enhances corrosion and breakdown of cell components • Slow start-up</td>
</tr>
</tbody>
</table>

SOFC's – high efficiency, flex fuel, simple operation, but high temperature


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Solid Oxide Fuel Cells

Operating Principle

YSZ is a crystalline alloy of $\text{ZrO}_2$ and $\text{Y}_2\text{O}_3$

- **Oxygen fast ion conductor**
- **Electronic insulator**


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Fuel Cell Power Output

The open circuit voltage is given by the Nernst equation:

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

at 1000°C:

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

- 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}

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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.

• Study the possibility of reducing Ohmic and activation losses by using current output to produce UV light, which may enhance bulk conductivity and the rate of interface oxygen exchange between electrode & electrolyte

• Increase power density by exploring high-aspect ratio membranes, including YSZ nanotubes
UV Illumination to Reduce Losses

- UV illumination may change the surface structure and improve the catalytic properties of the fuel cell electrodes
- Electrode/electrolyte exchange kinetics also can be affected
- May alter charge state of point defects in YSZ layer, changing its resistance

**Example:** UV-ozone oxidation of ultrathin metals forms high quality metal oxide layers at room temperature at oxidation rates many orders of magnitude greater than for thermal oxidation

\[
O_2 + h\nu' = 2O \\
O + O_2 = O_3 \\
O_3 + h\nu'' = O_2 + O
\]
YSZ Nanotube Synthesis & Properties

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

**Bottom left:** conformal ALD-HfO\textsubscript{2} 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 H\textsubscript{2}O\textsubscript{2}/H\textsubscript{2}O solution
- YSZ functions as an etch stop

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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 arbitrary 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

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Recent Results: Long-Period YSZ Nanolaminates

As-grown
- 20 nm total thickness
- Tetragonal ZrO₂
- Amorphous Y₂O₃

Annealed
- Appreciable, yet incomplete interdiffusion
- Interfacial SiO₂ growth
  - 1 nm → 15 nm

SIMS Chemical Depth Profile
(raw data by EAG Labs, Sunnyvale, CA)
- Raw Zr and Y counts calibrated using standard 8% YSZ
- Y:Zr content ratio plotted vs sample depth
- Further evidence of layer interdiffusion


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Recent Results: Short-Period YSZ Nanolaminates (3% Y₂O₃)

As-grown

- Amorphous structure
- 20-35 nm total thickness

Annealed

- YSZ containing 2-4 mol% Y₂O₃
- Polycrystalline tetragonal structure (same as bulk at this composition)
- Columnar grain structure that spans entire film thickness (5–25 nm grain diameter)
- Density increase from 5.8 to 6.1 g/cc

C. Ginestra et al.,

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Recent Results: Electrical Characterization of ALD-YSZ

Conductivity vs Frequency

- 30 nm thick sample
- Additional 6 hour anneal (900°C)
  - Point defect equilibration
  - SiO$_2$ interface layer thickens
- Voltage measurements (1Hz–300kHz)
- Total conductivity from complex impedance

Conductivity vs Temperature

- ~10x higher than bulk polycrystalline 3YSZ
- ~15x higher than polycrystalline 2YSZ
- Comparable to bulk cubic YSZ (8-10 mol% yttria)

Sample conductivity


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Recent Results: Thickness Effects on Structural Evolution in Evaporated YSZ Films

Change in crystalline structure on \textit{in-situ} heating from room temperature to 600°C.

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Phase Transformation Sequence: Size Dependence

Tsuchiya et al., Phil. Mag. (in press, 2007)

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Oxygen Ambient Effects in Post-Deposition Anneals

Oxygen annealing (“ex-situ” condition) leads to tetragonal phase formation in e-beam deposited YSZ films.

We will investigate similar processes in ALD-laminate derived YSZ thin films.

Tsuchiya et al., Phil. Mag. (in press, 2007)
Summary and Future Work

• Initial results on ALD-YSZ nanolaminates suggest this is a promising approach for making ultra-thin SOFC membranes

• Reason for enhanced total electrical conductivity of nanolaminate-derived samples and composition tuning of oxygen ion conductivity are now under investigation

• Perovskite SOFC electrode deposition studies by ALD are under way

• Next year's effort at Stanford will focus on electrode studies and development of microfabrication techniques to prepare thin film fuel cell arrays

• Postdoc arriving at Stanford Nov. 1 will lead fuel cell microfabrication work

• Ongoing work at Harvard emphasizes UV illumination studies on oxygen transport in YSZ and across YSZ/electrode interfaces