Deposition of Ceramic Composites for Solid Oxide Fuel Cell Applications using Aerosol Jet Printing

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Outline

- **Fuel Cell – How it works and why we need**

- **Solid Oxide Fuel Cells (SOFCs)**
  - Material properties
  - Multi-layer configuration, electrochemistry
  - Conventional fabrication methods
  - Single cell fabrication and performance

- **Aerosol Jet Printing and Processing of SOFCs**
  - Electrochemical performance of cells & microstructure
    - *Single component- Electrolyte, YSZ*
    - *Composite Cathode layers- LSM and YSZ*
    - *Scanning Electron Microscopy(SEM)*
  - Anode Interlayer/Functional Gradation

- **Summary, Challenges and Future Work**
Hydrogen Fuel Cell

\[ \text{H}_2 + \frac{1}{2} \text{O}_2 = \text{H}_2\text{O} \]

\[ \Delta G^\circ = -nFE^\circ \]

\[ E^\circ = 1.23 \text{ V} \]
### Diverse Energy Sources/Fuels and Applications

#### Conventional Fuels
- Natural Gas
- Propane
- Diesel
- Other hydrocarbons

#### Biomass
- Methane
- Methanol

#### Renewable sources (wind, solar, biomass)
- Hydrogen

#### Nuclear
- Natural Gas
- Coal (with carbon sequestration)

#### Fuel Cells
- Alkaline
- Direct methanol
- Molten carbonate
- Polymer electrolyte membrane
- Phosphoric acid
- Solid Oxide

#### Clean and efficient Energy conversion

#### Stationary
- Primary Power and CHP (residential, commercial and industrial)
- Backup power

#### Transportation
- Auxiliary Power
  - Trucks
  - Trains
  - Aircraft
  - Ships
  - Specialty vehicles (e.g.- fork lift)
  - Buses
  - Automobiles

#### Portable Power
- Consumer Electronics
- Battery chargers
- Soldier power

Source: US DOE 2010
The Promise of Renewable Hydrogen from Wind and Solar Energy

- Hydrogen from renewable carbon free sources
- Needs advanced photoelectrolysis and photobiological technologies

## SOFC: Material Properties

<table>
<thead>
<tr>
<th>Materials</th>
<th>Electrical properties</th>
<th>Thermomechanical properties</th>
</tr>
</thead>
</table>
| Nickel-cermet (Ni-Yttria stabilized zirconia) | • el. Conductivity \( (\sigma_{el} + \sigma_{ion}) \)  
• Catalytic activity | • Porosity  
• Thermal expansion coefficient  
• Adhesion |
| Yttria doped Zirconia (YSZ) | • Ionic conductivity \( (\sigma_{ionic} \gg \sigma_{el}) \) | • Gas-tightness  
• Mechanical stability |
| Strontium doped lanthanum-manganate (La,Sr)MnO3 (LSM) | • el. Conductivity \( (\sigma_{el} + \sigma_{ion}) \)  
• Catalytic activity | • Adhesion  
• Thermal expansion coefficient  
• Porosity |

Color scheme in center: Courtesy - Robert Kee, Colorado School of Mines
Microstructure - “Triple Phase Boundary”

Ni-YSZ Anode

reaction at gas/electrode/electrolyte interface, a three phase boundary (TPB)

Adsorption, surface reaction and charge transfer

- dissociative adsorption of H\(_2\) (on Ni?)
- surface diffusion of H or (H+)
- ionization of surface H to Ni
- charge transfer reactions of H\(^+\) and O\(^2-\) and OH\(^-\) around the TPB
- desorption of H\(_2\)O

• Microstructure

  - particle size, Ni content, Ni dispersion in the cermet
  - preheating and heating temperatures
  - sintering temperature
Multi-layered SOFC Configuration

Electrode functional layers, electrolytes and barrier layers

- Extension of “Triple phase boundary” into bulk of the electrode
- Barrier layers to avoid deleterious reactions between components
- Match the thermal co-efficient of expansion between components
- Thinner electrolytes to compensate for ohmic loss at intermediate temperature operation
Fabrication Methods for SOFC Components

• Chemical methods
  - Chemical vapor deposition (1-10 µm/h)
  - Electrochemical vapor deposition (3-50 µm/h)
  - Sol-Gel (0.5 µm-1 µm for each coating)
  - Spray pyrolysis (5 -60µm /h)

• Physical Methods
  - Physical vapor
    - pulse laser (PLD)
    - sputtering (0.25-2.5 µm/h)
  - Laser Ablation
  - Molecular beam epitaxy
  - Atmospheric and vapor plasma spraying (100-500 µm/h)

• Ceramic Powder/Wet
  - Screen printing (10-100 µm)
  - Tape casting (25-200 µm)
  - Slip casting
  - Filter pressing
  - Slurry, spray, dip coating
  - Tape calendering
  - Transfer printing
  - Electrophoretic deposition
Characteristics of Different Methods

- **Chemical methods**
  - dense films
  - high reaction temperatures
  - limited range of compositions

- **Physical Methods**
  - reproducible, patterning with lithography/masks,
  - too expensive for scale-up

- **Ceramic Powder/Wet**
  - inexpensive, scale-up possible, prone to crack formation, inhomogenous thickness
Cell Fabrication: Electrolyte and Cathode Layers on Anode Support

Anode support Ni-YSZ

Paste or print LSM
Paste or print LSM/YSZ
Paste or print electrolyte, YSZ
Anode interlayer 50/50 wt% NiO/YSZ
Anode substrate- Ni-YSZ

Sinter- 1200 °C
Sinter- 1400 °C
Bisque- 950 °C
Comparison of Cell with Ink-jet Printed and Pasted Cathode

SEI - cell with printed cathode

SEI - cell with pasted cathode

Cell impedance

Cell impedance

Comparison of Performance of Cells with Ink-jet Printed and Pasted Cathode (Fuel-H₂; Oxidant- Air)

- comparable performance for both types
- reproducible performance

Aerosol Jet Printing: Electrolyte, YSZ

VM Tools™ Software

- patterns for material deposition designed using AutoCAD®.
- drawing files are converted into tool paths using VMTools™ (VMT)
- files generated by VMT integrate stage motion with deposition
Optimizing Nozzle-Substrate Distance

Optical Images of printed electrolyte surface

- A gap of up to 8mm between the nozzle and substrate gave homogenous deposits with no particulates
- longer transit distances lead to coalescence of smaller droplets

SEM: Surface of Printed Electrolytes

- printed (and sintered) electrolytes were dense
- grain size- 2- 5 µm

SEM: Cross-sectional View of Electrolytes

Electrolytes with different thicknesses printed by altering:

- deposition time
- speed
- line spacing
Mass calibration curves to determine the required gas flow conditions to establish desired compositions

- use single atomizer and determine individual deposition rates for a range of gas flow conditions

- plot calibration curves for the two individual materials

- select gas flow conditions corresponding to desired compositions

- use dual atomizers simultaneously to print the composites
Material Mixing: Composite Cathode

- individual components directly mixed on the fly offers potential for functional gradation

Calibration of Deposition Rate for Selection of Composition

- deposition rate of YSZ > LSM
- deposition rate likely depends on initial particle size distribution and aerosolized droplet distribution

sheath gas - 3000 sccm
SEM (Back scattered): Microstructure of Composite LSM/YSZ and LSM Layers

- cathode interlayer, LSM/YSZ about 12 µm thick and porous
- LSM layer about 3 µm thick and more dense than desired
- highly reproducible
The cells have open circuit voltages (OCV) ranging from 1.16-1.20V, depending on the temperature. The maximum power density at 850 °C for both cells is 250 mW/cm².
Cathode Optimization

Identically printed and processed YSZ, LSM/YSZ but different LSM printing/processing

<table>
<thead>
<tr>
<th>Ink composition</th>
<th>Thickness</th>
<th>Sintering Temperature</th>
</tr>
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<tbody>
<tr>
<td>(a) LSM Ink- 34 wt %, 40 passes,</td>
<td>-</td>
<td>1200 °C</td>
</tr>
<tr>
<td>(b) LSM Ink- 34 wt %, 60 passes,</td>
<td>-</td>
<td>1200 °C</td>
</tr>
<tr>
<td>(c) LSM Ink- 17 wt %, 40 passes,</td>
<td>-</td>
<td>1200 °C</td>
</tr>
<tr>
<td>(d) LSM Ink- 34 wt %, 40 passes,</td>
<td>-</td>
<td>1150 °C</td>
</tr>
</tbody>
</table>

Identical for all four cells
VI Curves of Different Printed Cells

- Panel a: 40 passes, sintering temp. 1300°C, solids wt% 34
- Panel b: 60 passes, sintering temp. 1200°C, solids wt% 34
- Panel c: 40 passes, sintering temp. 1200°C, solids wt% 17
- Panel d: 40 passes, sintering temp. 1150°C, solids wt% 34
Anode Interlayer: Functional Gradation Scheme

- **Non graded**
  - Electrolyte, YSZ
  - Anode support

- **Compositionally graded interlayer with NiO/YSZ**
  - Electrolyte, YSZ
  - NiO/YSZ
  - Anode support

The diagram illustrates the functional gradation scheme for the anode interlayer, showing a transition from non-graded to compositionally graded interlayer with NiO/YSZ.
VI Curves for Cells with Graded and Non-graded anode Functional Layer

Two identical sets

- reproducible performance
- graded cells show better performance compared to non-graded cells
Summary, Challenges and Conclusion

- SOFC anode, cathode, and electrolyte components were deposited using aerosol jet printing.
- Layer thickness and microstructure and hence electrochemical performance of cells incorporating printed components was reproducible.
- Functionally graded composite anode and composite cathode layers were printed and incorporated in button cells.
- Cells with functionally graded anode interlayers performed better than cells with non-graded anode interlayer.
- Low voltage scanning electron microscopy was used as a diagnostic tool for evaluating material mixing and elucidation of phases.
- Material mixing on anode side requires further optimization—modify inks, improve processing? Current overall cell performance is not satisfactory—requires further printing/processing optimization.

Additive deposition manufacturing methods enable printing of dense and porous SOFC Layers. The potential for electrode patterning, reproducibility of microstructures, and ease of mass manufacture make these deposition methods very advantageous compared to traditional methods of screen printing and spraying.
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