High Temperature Protonic Conductors (HTPC) with the perovskite structure are envisioned for electrochemical membrane applications such as H$_2$ separation, H$_2$ sensors and fuel cells. Successive membrane commercialization is dependent upon addressing issues with H$_2$ permeation rate and environmental stability with CO$_2$ and H$_2$O. HTPC membranes are conventionally fabricated by solid-state sintering. Grain boundaries and the presence of intergranular second phases reduce the proton mobility by orders of magnitude than the bulk crystalline grain. To enhanced protonic mobility, alternative processing routes were evaluated. A laser melt modulation (LMM) process was utilized to fabricate bulk samples, while pulsed laser deposition (PLD) was utilized to fabricate thin film membranes.

Sr$_3$Ca$_{1+x}$Nb$_{2-x}$O$_9$ and SrCe$_{1-x}$Y$_x$O$_3$ bulk samples were fabricated by LMM. Thin film BaCe$_{0.85}$Y$_{0.15}$O$_3$ membranes were fabricated by PLD on porous substrates. Electron microscopy with chemical mapping was done to characterize the resultant microstructures. High temperature protonic conduction was measured by impedance spectroscopy in wet air or H$_2$ environments. The results demonstrate the advantage of thin film membranes to thick membranes but also reveal the negative impact of defects or nanoscale domains on protonic conductivity.
High Temperature Protonic Conductors
F.W. Dynys
NASA-Glenn Research Center

M. H. Berger
Ecole des Mines de Paris

A. Sayir
CWRU/NASA-Glenn Research Center

Sponsors: NASA Glenn Research Center Internal Research and Development Program.

European Office of Aerospace Research & Development by AFOSR under Grant # FA8655-03-1-3040.
Outline

A. Introduction

B. Sintering
  ● $\text{BaCe}_{0.85}\text{Y}_{0.15}\text{O}_{3-\delta}$

C. Directional Solidification
  ● $\text{SrCe}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$
  ● $\text{Sr}_3\text{Ca}_{1.18}\text{Nb}_{1.82}\text{O}_{9-\delta}$

C. Thin Film Deposition
  ● $\text{BaCe}_{0.85}\text{Y}_{0.15}\text{O}_{3-\delta}$

D. Summary
World Energy Demand Growing Dramatically

- Finite fossil fuel supply ≠ demand
- Energy poverty - Competition for limited energy resources.
- Rising CO₂ emissions
- Cost

Challenges
- Renewable energy supply will be essential: Wind, Solar, Bio-fuels Geothermal & Solar thermal
- New forms of energy are vital: H₂
- New sources: Methane hydrates
- Improve efficiency: Extend finite resources
- Technology: Drive energy cost reduction
Functional Oxide Materials for Energy Applications

Oxide ceramics – Electrochemical properties

- Oxygen transport – selectivity >1000
- H₂ transport – selectivity >1000

Applications

- Sensors - CO, CO₂, H₂, NOₓ detection
- Power - Solid oxide fuel cells
- Electrolyzers
- Membrane reactors – chemical processing
High Temperature Protonic Ceramics

Crystal Structures: Perovskite - $\text{ABO}_3$, $\text{A}_2(\text{B'} \text{B''})\text{O}_{6-\delta}$ & $\text{A}_3(\text{B'} \text{B''})\text{O}_{9-\delta}$
Fluorite – $\text{M}_2\text{O}_3$
Pyrochlore – $\text{A}_2\text{B}_2\text{O}_7$

$\text{ABO}_3$ – Pm\,3\,m

Proton Insertion

Oxygen vacancies ($V_0^{\bullet\bullet}$) needed for $\text{H}^+$ transport:
B site doping: $2\text{B}_B^+ + \text{O}_0 + \text{M}_2\text{O}_3 \rightarrow 2\text{M}_{\text{Ce}}^+ + V_0^{\bullet\bullet} + 2\text{BO}_2$
Humid environment: $\text{H}_2\text{O}_\text{(g)} + V_0^{\bullet\bullet} + \text{O}_0 \rightarrow 2\text{OH}_\text{O}^*$
H$_2$ environment: $V_0^{\bullet\bullet} + \frac{1}{2}\text{O}_2 \rightarrow \text{O}_0 + 2\text{h}^*$
H$_2(\text{g}) + 2\text{O}_0 + 2\text{h}^* \rightarrow 2\text{OH}_\text{O}^*$
Proton strongly associates with a neighbouring oxygen ion-represented as OH
Distorted Perovskite Structure

tolerance factor = \( \frac{R_A + R_O}{\sqrt{2 \cdot (R_B + R_O)}} \)

t<0.96 tetragonal/orthorhombic

Octahedra Tilting

- BO₆ octahedra tilt to reduce A site volume
- SrCeO₃ 11° & 12.5°
- BaCeO₃ 6° & 8.8°

Predominant proton transfer path

Independent Oxygen sites
Protonic Ceramic Development

Optimization of Composition

\[(A_{x}A_{1-x})(B_{y}B_{1-y})O_{3-\delta}\]

Solid State Sintering

Multiphase Materials

Maximize \(\sigma\) Ionic/Electronic

Cermets

Argonne National Laboratory

Thin Film Structures

Maximize Permeation Rate

Opportunities

Protonic Conduction

48 – 100 KJ/mol

A-Site Doping

- Proton Uptake
- Chemical Stability
- Mechanical Stability

Basic Science

- Crystal Structure
- Thermodynamics

Grain Boundary

- Detrimental to H\(^+\) transport

Environmental

- Reactive CO\(_2\)
- Reactive H\(_2\)O
Impedance Spectroscopy

Experimental Set-Up

- Series (⊥) grain boundaries
- Parallel (∥) grain boundaries
- Grain interiors
- Electrode

conduction: grain ≠ grain boundary

ω₀ grain boundary << ω₀ grain-Low T
ω₀ grain boundary ~ ω₀ grain-High T
Sintering Protonic Ceramics

![Chemical Structures and Data](image)

**High Sintering Temp.**

<table>
<thead>
<tr>
<th>Composition</th>
<th>T °C</th>
<th>% ρ</th>
<th>Composition</th>
<th>T °C</th>
<th>% ρ</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaZr$<em>{0.9}$Sc$</em>{0.1}$O$_{3-δ}$</td>
<td>1700</td>
<td>91</td>
<td>Sr$<em>{0.66}$Ba$</em>{0.33}$Ti$<em>{0.95}$Sc$</em>{0.05}$O$_{3-δ}$</td>
<td>1560</td>
<td>90</td>
</tr>
<tr>
<td>BaZr$<em>{0.9}$In$</em>{0.1}$O$_{3-δ}$</td>
<td>1700</td>
<td>93</td>
<td>Sr$<em>{0.33}$Ba$</em>{0.66}$Zr$<em>{0.56}$Y$</em>{0.1}$Ti$<em>{0.33}$O$</em>{3-δ}$</td>
<td>1600</td>
<td>93</td>
</tr>
<tr>
<td>BaZr$<em>{0.9}$Gd$</em>{0.1}$O$_{3-δ}$</td>
<td>1650</td>
<td>88</td>
<td>Sr$<em>{0.66}$Ba$</em>{0.33}$Zr$<em>{0.33}$Sc$</em>{0.05}$Ti$<em>{0.61}$O$</em>{3-δ}$</td>
<td>1650</td>
<td>88</td>
</tr>
<tr>
<td>Ba$<em>{0.66}$Sr$</em>{0.33}$Zr$<em>{0.9}$Y$</em>{0.1}$O$_{3-δ}$</td>
<td>1630</td>
<td>88</td>
<td>SrZr$<em>{0.33}$Sc$</em>{0.05}$Ti$<em>{0.61}$O$</em>{3-δ}$</td>
<td>1590</td>
<td>94</td>
</tr>
<tr>
<td>SrZr$<em>{0.9}$Y$</em>{0.1}$O$_{3-δ}$</td>
<td>1675</td>
<td>94</td>
<td>BaZr$<em>{0.45}$Y$</em>{0.1}$Ti$<em>{0.45}$O$</em>{3-δ}$</td>
<td>1600</td>
<td>87</td>
</tr>
<tr>
<td>SrHf$<em>{0.9}$Y$</em>{0.1}$O$_{3-δ}$</td>
<td>1600</td>
<td>82</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Directional Solidification

Sintered rod

Laser heating

Melt

Seed

Low energy/coherent interfaces
High Density
Microstructure-SrCe\textsubscript{0.9}Y\textsubscript{0.1}O\textsubscript{3-δ} - Chemistry

Textured Microstructure

- Al 2\textsuperscript{nd} phase contaminant – conc. between grains
  Pre-fabrication contamination
Microstructure - $\text{Sr}_3(Ca_{1+x} Nb_{2-x})O_{9-\delta}$ - Chemistry

Dense - Cellular growth

Core: $\text{Ca}^{2+}$, $\text{Sr}^{2+}$ rich
Shell: $\text{Nb}^{5+}$, $\text{O}^2-$ rich
$2^{nd}$ phases: $\text{Sr}^{2+}$, $\text{O}^2-$ rich

Source rod:
Polycrystalline
$\text{Sr}_3\text{Nb}_{1.82}\text{Ca}_{1.18}\text{O}_{9-\delta}$

Liquid

Core: higher $\{V\}$
Shell: lower $\{V\}$

Temp. gradient (+)

WDX maps

Ca
Sr
Nb

Seed

5 mm pull direction (15 mm/min)
**SrCe$_{0.9}$Y$_{0.1}$O$_{3-\delta}$**

\[ \sigma \cdot T = A \cdot \exp(-Q/RT) \]

**Activation Energy**

<table>
<thead>
<tr>
<th>Total $\sigma$</th>
<th>Q (KJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrCa$<em>{0.9}$Y$</em>{0.1}$O$_{3-\delta}$ Air</td>
<td>83.2</td>
</tr>
<tr>
<td>De Vries</td>
<td>53.6</td>
</tr>
<tr>
<td>Nowick</td>
<td>60.8</td>
</tr>
</tbody>
</table>

**Sr$_3$(Ca$_{1+x}$Nb$_{2-x}$)O$_9$-\(\delta\)**

**Activation Energy**

<table>
<thead>
<tr>
<th>Total $\sigma$</th>
<th>Q (KJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr$<em>3$Ca$</em>{1.18}$Nb$_{1.82}$O$_9$-(\delta) Air</td>
<td>84.6</td>
</tr>
<tr>
<td>Nowick Sr$<em>3$Ca$</em>{1.06}$Nb$_{1.94}$O$_9$-(\delta)</td>
<td>66.5</td>
</tr>
<tr>
<td>Nowick Sr$<em>3$Ca$</em>{1.18}$Nb$_{1.82}$O$_9$-(\delta)</td>
<td>63.6</td>
</tr>
</tbody>
</table>

Protonic Conduction

48 – 100 KJ/mol
Nano-Structure Domains

Nanostructures ➔ Protonic transport ?
**Thin Film Electrolytes**

### Thickness Dependence

- Sr$_{0.95}$Yb$_{0.05}$O$_{3-\delta}$
- Hamakawa1 et al., SSI 48, 71, 2002

### GS Dependence

- Guo, Acta Mat. 51, 2539, 2003

Porous Support

Supported electrolyte fabrication difficult with high sintering temp.

### Approach

**Pulsed Laser Deposition**
- Stoichiometry
- Simple
- High Energy
- High Deposition Rate

**PVD Microstructure**

- Transition structure consisting of densely packed fibrous grains
- Columnar grains
- Porous structure consisting of tapered crystallites separated by voids
- Recrystallized grain structure
**Pulsed Laser Deposition**

Excimer Laser
- $\lambda = 248 \text{ nm} - \text{KrF}$
- Energy: $1 - 3 \text{ J/cm}^2$
- Frequency: $<10 \text{ Hz}$
- Pulse: $25 \text{ ns}$

**Targets**
- Solid state synthesize powder
- Sintering – $1650 \text{ oC} 10 \text{ hrs. air}$

**Substrates**
- Porous $\text{Al}_2\text{O}_3$
- Porous $\text{BaZrO}_3$
- Silicon

**Deposition Chamber – $P_{O_2} 30 \text{ mTorr}$**

- Target Rotator
- Target
- Plume 1-100 ev
- SiO$_2$ Focusing Lens
- SiO$_2$ Window
- Substrate
- Substrate Heater RT – 1000 °C
- Targets

SiO$_2$ Window

Substrates

Porous $\text{Al}_2\text{O}_3$

Porous $\text{BaZrO}_3$

Silicon
Silicon Substrates

BaCe$_{0.85}$Y$_{0.15}$O$_{3-\delta}$

700 °C

High (400) orientation

Thin Film Deposition - Silicon - 700 °C

Z($) (ohms)

Z (ohms)

Solartron 1260/1287

0.1 – 1MHz

Moist Argon – 25 °C

Zplot/Zview Software
Total Conductivity
Silicon Substrates

\[ \sigma \cdot T = A \cdot \exp(-Q/RT) \]

Activation Energy

<table>
<thead>
<tr>
<th>Material</th>
<th>Temp. (°C)</th>
<th>Q (KJ/mol)</th>
<th>Film Thickness (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaCe_{0.85}Y_{0.15}O_{3}</td>
<td>600 - 850</td>
<td>38.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>400 - 550</td>
<td>100.3</td>
<td></td>
</tr>
<tr>
<td>Sintered</td>
<td>800 °C/30 mT</td>
<td>100 - 500</td>
<td>33.4 6</td>
</tr>
<tr>
<td></td>
<td>700 °C/30 mT</td>
<td>200 – 500</td>
<td>38.2 6</td>
</tr>
<tr>
<td></td>
<td>600 °C/30 mT</td>
<td>100 – 500</td>
<td>29.9 2.4</td>
</tr>
</tbody>
</table>

Protonic Conduction – 48 – 100 KJ/mol
Porous Al$_2$O$_3$ Substrates

![Graph showing EIS data and equivalent circuit](image)

- **Counts**
  - 20° to 70° (002) and (400)
  - 800°C

- **Equivalent Circuit**
  - Grain
  - Grain Boundary
  - Electrode
  - R1, CPE1, R2, CPE2, R3

- **EIS**
  - Ag Electrode
  - BCY
  - Porous Al$_2$O$_3$

- **Solartron 1260/1296**
  - 0.1 – 1 MHz
  - 100°C – 950°C

- **Air**
  - 25°C

- **Zplot/Zview Software**

- **Graphs**
  - Z’ (10^6 ohms)
  - Z (10^6 ohms)

- **Temperatures**
  - 568°C
  - 525°C
  - 495°C
  - 461°C
  - 430°C

---

**950°C  900°C  700°C**

**Counts**

**EIS**

**Ag Electrode**

**BCY**

**Porous Al$_2$O$_3$**

**Solartron 1260/1296**

**Air – 25°C**

**Zplot/Zview Software**
Microstructure Characterization

BaCe$_{0.85}$Y$_{0.15}$O$_3$-δ Film
800 °C Deposition Temperature

Dense films fabricated at 600-950 °C
No inclusions from PLD

Al$_2$O$_3$ particles determine column width.
Dense films form by impinging column growth.
No long range defects

Numerous BCY nano-crystals nucleate at the Al$_2$O$_3$ particle surface.
Thin amorphous layer
Interface Characterization

BaCe$_{0.85}$Y$_{0.15}$O$_{3-\delta}$ Film

950 °C Deposition Temperature

BCY Film

Al$_2$O$_3$

Sharp Interface
Total Conductivity
Porous Al₂O₃ Substrates

σ·T = A·exp(-Q/RT)

Activation Energy

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Q (KJ/mol)</th>
<th>Film Thickness (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>600 - 850</td>
<td>38.6</td>
<td>100.3</td>
</tr>
<tr>
<td>400 - 550</td>
<td></td>
<td></td>
</tr>
<tr>
<td>950°C/30 mT</td>
<td>74.8</td>
<td>3.6</td>
</tr>
<tr>
<td>950°C/30 mT</td>
<td>75.4</td>
<td>3.2</td>
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<tr>
<td>900°C/30 mT</td>
<td>54.1</td>
<td>4.8</td>
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<tr>
<td>950°C/20 mT</td>
<td></td>
<td></td>
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<td>800°C/30 mT</td>
<td>98.1</td>
<td>3.6</td>
</tr>
<tr>
<td>700°C/100 mT</td>
<td>115.6</td>
<td>1.7</td>
</tr>
<tr>
<td>700°C/200 mT</td>
<td>108.2</td>
<td>4.1</td>
</tr>
</tbody>
</table>

Protonic Conduction – 48 – 100 KJ/mol

Conduction exhibits large dependence on process conditions.
Porous BaZrO₃ Substrates

Solartron 1260/1296  0.1 – 1MHz  100 °C – 950 °C  
Air, 5%H₂/N₂  Zplot/Zview Software
Microstructure Characterization
BaCe$_{0.85}$Y$_{0.15}$O$_{3-\delta}$ Film

- Columnar grains
- No particle inclusions from PLD
- Low defects
- No long range ordering
Growth Segregation

Small domains 2 nm visible
3.1 Ang … make the continuous circle

~20 nm grains
Total Conductivity
Porous BaZrO₃ Substrates

σ·T = A·exp(-Q/RT)

Activation Energy

<table>
<thead>
<tr>
<th></th>
<th>Temp. (°C)</th>
<th>Q (KJ/mol)</th>
<th>Film Thickness (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sinter</td>
<td>600 - 850</td>
<td>38.6</td>
<td>100.3</td>
</tr>
<tr>
<td></td>
<td>400 - 550</td>
<td>89.7</td>
<td>9.4</td>
</tr>
<tr>
<td>850 °C/20 mT</td>
<td>550 – 900</td>
<td>56.8</td>
<td>5.9</td>
</tr>
<tr>
<td></td>
<td>100 - 550</td>
<td>106.7</td>
<td>5.9</td>
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<tr>
<td>600 °C/30 mT</td>
<td>550 – 900</td>
<td>106.7</td>
<td>5.9</td>
</tr>
<tr>
<td></td>
<td>100 - 550</td>
<td>55.2</td>
<td>5.9</td>
</tr>
<tr>
<td>400 °C/20 mT</td>
<td>550 – 900</td>
<td>111.5</td>
<td>3.8</td>
</tr>
<tr>
<td></td>
<td>100 - 550</td>
<td>48.1</td>
<td>3.8</td>
</tr>
<tr>
<td>600 °C/20 mT</td>
<td>550 – 900</td>
<td>102.9</td>
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<td>100 - 550</td>
<td>45.7</td>
<td>1.0</td>
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<td>900 °C/20 mT</td>
<td>550 – 900</td>
<td>112.2</td>
<td>3.1</td>
</tr>
<tr>
<td></td>
<td>100 - 550</td>
<td>62.5</td>
<td>3.1</td>
</tr>
</tbody>
</table>

- σ less dependent upon process conditions
- Conduction change at T >550 °C
Summary

- Directionally solidified samples exhibit similar ionic conduction to reported data for sintered samples.
- Directional solidification produces nano-sized structural defects. Influence of defects on proton mobility remains unknown.
- Directional solidification can produce unique microstructures that cannot be achieved by solid state sintering.
- Dense protonic films can be fabricated on porous substrates by PLD in the temperature range of 600-950 °C.
- Columnar growth morphologies are observed at temperature <950 °C. Process dependent oriented crystal growth occurs among the [100] and [001] directions.
- Matching crystal symmetry between substrate & film is essential to maximize protonic conduction.