High Temperature Protonic Conductors (HTPC) with the perovskite structure are envisioned for electrochemical membrane applications such as H₂ separation, H₂ sensors and fuel cells. Successive membrane commercialization is dependent upon addressing issues with H₂ permeation rate and environmental stability with CO₂ and H₂O. 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.

Sr₃Ca₁₊ₓNb₂₋ₓO₉ and SrCe₁₋ₓYₓO₃ bulk samples were fabricated by LMM. Thin film BaCe₀.₈₅Y₀.₁₅O₃ 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 H₂ 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
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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
- $\text{H}_2$ transport – selectivity >1000

Applications

- Sensors - CO, CO$_2$, H$_2$, NO$_x$ detection
- Power - Solid oxide fuel cells
- Electrolyzers
- Membrane reactors – chemical processing
High Temperature Protonic Ceramics

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

$\text{ABO}_3$ – $\text{Pm}3\text{m}$

Proton Insertion

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

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

\[ t < 0.96 \text{ tetragonal/orthorhombic} \]

Octahedra Tilting
- \( \text{BO}_6 \) octahedra tilt to reduce A site volume
- \( \text{SrCeO}_3 \) 11° & 12.5°
- \( \text{BaCeO}_3 \) 6° & 8.8°

Cubic  \[ \rightarrow \]  Non-Cubic

Predominant proton transfer path

Independent Oxygen sites

In-phase  \[ \rightarrow \]  Antiphase
Protonic Ceramic Development

Ceramic

Optimization of Composition

(A_xA_{1-x})(B_yB_{1-y})O_{3-δ}

Multiphase Materials

Maximize σ
Ionic/Electronic

Thin Film Structures

Maximize Permeation Rate

Solid State Sintering

Cermets

Argonne National Laboratory

Opportunities

A-Site Doping

• Proton Uptake
• Chemical Stability
• Mechanical Stability

Basic Science

• Crystal Structure
• Thermodynamics

Grain Boundary

• Detrimental to H⁺ transport

Environmental

• Reactive CO₂
• Reactive H₂O

B-Site Doping

• O₂ Vacancies
• Proton mobility
• Electron σ
• Proton Uptake
• Chemical Stability
• Mechanical Stability

Protonic Conduction
48 – 100 KJ/mol

σT (S/cm)

0.09 0.10 0.11 0.12 0.13 0.14 0.15 0.16

1000 °C 900 °C 800 °C 700 °C 600 °C 500 °C

V.K. Gupta & J.Y.S. Lin
Nonporous Inorganic Membranes

V.K. Gupta & J.Y.S. Lin
Nonporous Inorganic Membranes
Impedance Spectroscopy

-\[ V(\omega) \]

- Series (\( \perp \)) grain boundaries
- Parallel (\( \parallel \)) grain boundaries
- Grain interiors
- Electrode

-\[ R \] Grain Boundary
-\[ R \] Grain
-\[ C \] Grain Interior

- Imaginary Impedance (\( \Omega \))
- Real Impedance (\( \Omega \))

Conduction: grain \( \neq \) grain boundary

\( \omega_0 \) grain boundary \( \ll \) \( \omega_0 \) grain-Low T

\( \omega_0 \) grain boundary \( \sim \) \( \omega_0 \) grain-High T

Experimental Set-Up
**Sintering Protonic Ceramics**

Co-precipitation  Solid State

### 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_{1-x}Y_{0.15}O_{3-δ} x=0.02-0.25</td>
<td>1700</td>
<td>87</td>
<td>SrTi_{1-δ}Sc_{x}O_{3-δ} x=0.02-0.05</td>
<td>1590</td>
<td>80</td>
</tr>
<tr>
<td>BaZr_{0.9}Sc_{0.1}O_{3-δ}</td>
<td>1700</td>
<td>91</td>
<td>Sr_{0.66}Ba_{0.33}Ti_{0.95}Sc_{0.05}O_{3-δ}</td>
<td>1560</td>
<td>90</td>
</tr>
<tr>
<td>BaZr_{0.85}In_{0.1}O_{3-δ}</td>
<td>1700</td>
<td>93</td>
<td>Sr_{0.33}Ba_{0.66}Zr_{0.56}Y_{0.1}Ti_{0.33}O_{3-δ}</td>
<td>1600</td>
<td>93</td>
</tr>
<tr>
<td>BaZr_{0.8}Gd_{0.2}O_{3-δ}</td>
<td>1650</td>
<td>88</td>
<td>Sr_{0.66}Ba_{0.33}Zr_{0.33}Sc_{0.05}Ti_{0.61}O_{3-δ}</td>
<td>1650</td>
<td>88</td>
</tr>
<tr>
<td>Ba_{0.66}Sr_{0.33}Zr_{0.9}O_{1.1}O_{3-δ}</td>
<td>1630</td>
<td>88</td>
<td>SrZr_{0.33}Sc_{0.05}Ti_{0.61}O_{3-δ}</td>
<td>1590</td>
<td>94</td>
</tr>
<tr>
<td>SrZr_{0.9}Y_{0.1}O_{3-δ}</td>
<td>1675</td>
<td>94</td>
<td>BaZr_{0.45}Y_{0.1}Ti_{0.45}O_{3-δ}</td>
<td>1600</td>
<td>87</td>
</tr>
<tr>
<td>SrHf_{0.9}Y_{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$_{0.9}$Y$_{0.1}$O$_{3-\delta}$ - Chemistry

Textured Microstructure

- Al 2$^{nd}$ phase contaminant – conc. between grains
- Pre-fabrication contamination
**Microstructure - \( \text{Sr}_3(\text{Ca}_{1+x}\text{Nb}_{2-x})\text{O}_{9-\delta} \) - Chemistry**

**Dense - Cellular growth**

- **BSE - SEM**

Core: \( \text{Ca}^{2+}, \text{Sr}^{2+} \) rich

Shell: \( \text{Nb}^{5+}, \text{O}^{2-} \) rich

2nd 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 \([V\text{••}]\)

Shell: lower \([V\text{••}]\)

2nd phases: \( \text{Sr}^{2+}, \text{O}^{2-} \) rich

**WDX maps**

- **Ca**
- **Sr**
- **Nb**

**Temp. gradient (+)**

**Seed**

- 100 µm
- 5 mm
- Pull direction (15 mm/min)
**σ·T = A·exp(-Q/RT)**

### Activation Energy

<table>
<thead>
<tr>
<th></th>
<th>Total σ</th>
<th>Q (KJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>SrCe_{0.9}Y_{0.1}O_{3-δ}</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>De Vries</td>
<td>H₂</td>
<td>83.2</td>
</tr>
<tr>
<td>Nowick</td>
<td>H₂</td>
<td>98.1</td>
</tr>
<tr>
<td>Nowick</td>
<td></td>
<td>60.8</td>
</tr>
</tbody>
</table>

### Activation Energy

<table>
<thead>
<tr>
<th></th>
<th>Total σ</th>
<th>Q (KJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sr_{3}(Ca_{1+x}Nb_{2-x})O_{9-δ}</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nowick</td>
<td>Sr_{3}Ca_{1.18}Nb_{1.82}O_{9-δ}</td>
<td>66.5</td>
</tr>
<tr>
<td>Nowick</td>
<td>Sr_{3}Ca_{1.18}Nb_{1.82}O_{9-δ}</td>
<td>63.6</td>
</tr>
</tbody>
</table>

Protonic Conduction
48 – 100 KJ/mol
Nano-Structure Domains

Nanostructures [image]

Protonic transport? [image]
Thin Film Electrolytes

**Thickness Dependence**

- SrC_{0.95}Yb_{0.05}O_{3-δ}
- Hamakawa et al., SSI 48, 71, 2002

**GS Dependence**

- 3Y-ZrO_{2}, 550 °C
- Guo, Acta Mat. 51, 2539, 2003

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
- Recrystallized grain structure
- Porous structure consisting of tapered crystallites separated by voids

**Slurry Process**
Pulsed Laser Deposition

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

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

**Substrates**
- Porous Al$_2$O$_3$
- Porous BaZrO$_3$
- Silicon

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

- Targets
  - Solid state synthesize powder
  - Sintering – 1650 $^\circ\text{C}$ 10 hrs. air

- Substrates
  - Porous Al$_2$O$_3$
  - Porous BaZrO$_3$
  - Silicon

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

- SiO$_2$ Focusing Lens
- SiO$_2$ Window
- Target Rotator
- Target
- Plume 1-100 ev
- Substrate
- Substrate Heater
  - RT – 1000 $^\circ\text{C}$

- Targets
  - Solid state synthesize powder
  - Sintering – 1650 $^\circ\text{C}$ 10 hrs. air

- Substrates
  - Porous Al$_2$O$_3$
  - Porous BaZrO$_3$
  - Silicon
Silicon Substrates

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

700 °C

Solartron 1260/1287 0.1 – 1MHz 100 °C – 500 °C
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></th>
<th>Temp. (°C)</th>
<th>Q (KJ/mol)</th>
<th>Film Thickness (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaCe$<em>{0.85}$Y$</em>{0.15}$O$_3$ Sintered</td>
<td>600 - 850 400 - 550</td>
<td>38.6 100.3</td>
<td></td>
</tr>
<tr>
<td>800 °C/30 mT</td>
<td>100 - 500</td>
<td>33.4</td>
<td>6</td>
</tr>
<tr>
<td>700 °C/30 mT</td>
<td>200 – 500</td>
<td>38.2</td>
<td>6</td>
</tr>
<tr>
<td>600 °C/30 mT</td>
<td>100 – 500</td>
<td>29.9</td>
<td>2.4</td>
</tr>
</tbody>
</table>

Protonic Conduction – 48 – 100 KJ/mol
Porous Al₂O₃ Substrates

EIS

Ag Electrode

BCY

Porous Al₂O₃

Solartron 1260/1296 0.1 – 1MHz 100 °C – 950 °C
Air – 25 °C Zplot/Zview Software
Microstructure Characterization

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

800 ℃ Deposition Temperature

Dense films fabricated at 600-950 ℃

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 nanocrystals 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>Sintered</td>
<td>600 - 850</td>
<td>38.6</td>
</tr>
<tr>
<td></td>
<td>400 - 550</td>
<td>100.3</td>
</tr>
<tr>
<td>950 °C/30 mT</td>
<td>200 - 900</td>
<td>74.8</td>
</tr>
<tr>
<td>950 °C/30 mT</td>
<td>200 - 900</td>
<td>75.4</td>
</tr>
<tr>
<td>900 °C/30 mT</td>
<td>200 - 600</td>
<td>54.1</td>
</tr>
<tr>
<td>800 °C/30 mT</td>
<td>200 - 600</td>
<td>98.1</td>
</tr>
<tr>
<td>700 °C/100 mT</td>
<td>350 - 900</td>
<td>115.6</td>
</tr>
<tr>
<td>700 °C/200 mT</td>
<td>350 - 700</td>
<td>108.2</td>
</tr>
</tbody>
</table>

Conduction exhibits large dependence on process conditions.

Protonic Conduction – 48 – 100 KJ/mol
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

BaZrO$_3$
Growth Segregation

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

~20 nm grains
Total Conductivity
Porous \( \text{BaZrO}_3 \) Substrates

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

- \( \sigma \) 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.