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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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

\[
\begin{align*}
2H^+ + 2e^- & \rightarrow H_2 \\
ABO_3 & \\
H^+ & + e^- & \rightarrow H_2 \text{ gases}
\end{align*}
\]
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 – $\text{A}_2\text{B}_2\text{O}_7$

ABO$_3$ – Pm$\overline{3}$m

Proton Insertion

Oxygen vacancies ($V_0^{**}$) needed for $\text{H}^+$ transport:
- B site doping: $2\text{B}_{\text{B}^+} + \text{O}_0 + \text{M}_2\text{O}_3 \rightarrow 2\text{M}_{\text{Ce}^+} + V_0^{**} + 2\text{BO}_2$
- Humid environment: $\text{H}_2\text{O}_\text{(g)} + V_0^{**} + \text{O}_0 \rightarrow 2\text{OH}_0^*$
- $\text{H}_2$ environment: $V_0^{**} + \frac{1}{2}\text{O}_2 \rightarrow \text{O}_0 + 2h^*$
- $\text{H}_2\text{(g)} + 2\text{O}_0 + 2h^* \rightarrow 2\text{OH}_0^*$

Proton strongly associates with a neighbouring oxygen ion-represented as $\text{OH}$
Distorted Perovskite Structure

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

t < 0.96 tetragonal/orthorhombic

Octahedra Tilting

- \( \text{BO}_6 \) 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  |  Antiphase

\( \text{O}_1 \)  \( \text{O}_2 \)
Protonic Ceramic Development

Ceramic

Optimization of Composition

(A_xA_{1-x})(B_yB_{1-y})O_{3-δ}

Multiphase Materials

Maximize $\sigma$

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

B-Site Doping

• $O_2$ Vacancies
• Proton mobility
• Electron $\sigma$
• Proton Uptake
• Chemical Stability
• Mechanical Stability

Basic Science

• Crystal Structure
• Thermodynamics

Grain Boundary

• Detrimental to $H^+$ transport

Environmental

• Reactive $CO_2$
• Reactive $H_2O$

Protonic Conduction

48 – 100 KJ/mol

V.K. Gupt & J.Y.S. Lin

Nonporous Inorganic Membranes

σT (S/cm)

1000/RT

Environmental

• Reactive $CO_2$
• Reactive $H_2O$

Grain Boundary

• Detrimental to $H^+$ transport

Basic Science

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A-Site Doping

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• Proton mobility
• Electron $\sigma$
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Solid State Sintering

Cermets

Argonne National Laboratory

Opportunities

A-Site Doping

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• Chemical Stability
• Mechanical Stability

B-Site Doping

• $O_2$ Vacancies
• Proton mobility
• Electron $\sigma$
• Proton Uptake
• Chemical Stability
• Mechanical Stability

Basic Science

• Crystal Structure
• Thermodynamics

Grain Boundary

• Detrimental to $H^+$ transport

Environmental

• Reactive $CO_2$
• Reactive $H_2O$
Impedance Spectroscopy

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

- **Real Impedance (Ω)**
  - **Grain Interior**
  - **Grain Boundary**
  - **Electrodes**

- **Imaginary Impedance (Ω)**

- **Experimental Set-Up**

**Conduction:** grain ≠ grain boundary

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

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>91</td>
<td>SrTi_{1-x}Sc_{x}O_{3-δ}  x=0.02-0.05</td>
<td>1560</td>
<td>90</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_{0.66}Ba_{0.33}Zr_{0.56}Y_{0.1}Ti_{0.33}O_{3-δ}</td>
<td>1600</td>
<td>93</td>
</tr>
<tr>
<td>BaZr_{0.9}Gd_{0.1}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>1590</td>
<td>90</td>
</tr>
<tr>
<td>Ba_{0.66}Sr_{0.33}Zr_{0.9}Y_{0.1}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_{0.5}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

- Pull Outs

- Al 2nd phase contaminant – conc. between grains

Pre-fabrication contamination
Dense - Cellular growth

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

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

Liquid

Core: higher [V$^{••}$]
Shell: Lower [V$^{••}$]
Ca$^{2+}$, Sr$^{2+}$ rich core
Nb$^{5+}$, O$^{2-}$ rich shell

WDX maps

Microstructure - Sr$_3$(Ca$_{1+x}$Nb$_{2-x}$)O$_{9-\delta}$ - Chemistry
\[ \sigma \cdot T = A \cdot \exp(-Q/RT) \]

**Activation Energy**

<table>
<thead>
<tr>
<th>Total $\sigma$</th>
<th>$Q$ (KJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Sr}<em>{3}\text{Ca}</em>{1.06}\text{Nb}<em>{1.94}\text{O}</em>{9-\delta}$</td>
<td>84.6 98.1</td>
</tr>
<tr>
<td>$\text{Sr}<em>{3}\text{Ca}</em>{1.18}\text{Nb}<em>{1.82}\text{O}</em>{9-\delta}$</td>
<td>66.5</td>
</tr>
<tr>
<td>$\text{Sr}<em>{3}\text{Ca}</em>{1.18}\text{Nb}<em>{1.82}\text{O}</em>{9-\delta}$</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**

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

![Graph showing thickness dependence with various thicknesses and partial pressure of H$_2$ in the upstream, kPa](image)

**GS Dependence**

- $\log$(Conductivity / $\Omega \cdot cm^{-1}$) vs. Average Grain Size / nm
- $3\delta$-ZrO$_2$, 550 °C
- Guo, Acta Mat. 51, 2539, 2003

![Graph showing grain size dependence](image)

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

Targets
- Solid state synthesize powder
- Sintering – 1650 °C 10 hrs. air

Substrates
- Porous Al\(_2\)O\(_3\)
- Porous BaZrO\(_3\)
- Silicon

Deosition Chamber – \( \text{P}_{\text{O}_2} \) 30 mTorr

Target Rotator
Target
Plume 1-100 ev
SiO\(_2\) Focusing Lens
SiO\(_2\) Window
Substrate
Substrate Heater RT – 1000 °C

Solid state synthesize powder
Sintering – 1650 °C 10 hrs. air
Silicon Substrates

BaCe_{0.85}Y_{0.15}O_{3-δ}

700 °C

Thin Film Deposition - Silicon - 700 °C

Z' (ohms)

Z (ohms)

Thin Film Deposition - Silicon - 700 °C

EIS

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>Temperature</th>
<th>Q (KJ/mol)</th>
<th>Film Thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>600 °C/850</td>
<td>38.6</td>
<td></td>
</tr>
<tr>
<td>400 – 550</td>
<td>100.3</td>
<td></td>
</tr>
<tr>
<td>BaCe$<em>{0.85}$Y$</em>{0.15}$O$_3$ Sintered</td>
<td></td>
<td></td>
</tr>
<tr>
<td>800 °C/30 mT</td>
<td>33.4</td>
<td>6</td>
</tr>
<tr>
<td>700 °C/30 mT</td>
<td>38.2</td>
<td>6</td>
</tr>
<tr>
<td>600 °C/30 mT</td>
<td>29.9</td>
<td>2.4</td>
</tr>
</tbody>
</table>

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

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 °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>Sintered</td>
<td>600 - 850</td>
<td>38.6 100.3</td>
</tr>
<tr>
<td>950 °C/30 mT</td>
<td>200 - 900</td>
<td>74.8 3.6</td>
</tr>
<tr>
<td>950 °C/30 mT</td>
<td>200 - 900</td>
<td>75.4 3.2</td>
</tr>
<tr>
<td>900 °C/30 mT</td>
<td>200 - 600</td>
<td>54.1 4.8</td>
</tr>
<tr>
<td>800 °C/30 mT</td>
<td>200 - 600</td>
<td>98.1 3.6</td>
</tr>
<tr>
<td>700 °C/100 mT</td>
<td>350 - 900</td>
<td>115.6 1.7</td>
</tr>
<tr>
<td>700 °C/200 mT</td>
<td>350 - 700</td>
<td>108.2 4.1</td>
</tr>
</tbody>
</table>

Protonic Conduction – 48 – 100 KJ/mol

Conduction exhibits large dependence on process conditions.
Porous BaZrO₃ Substrates

EIS

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 BaZrO$_3$ Substrates

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

Activation Energy

<table>
<thead>
<tr>
<th>Process Conditions</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>56.8</td>
<td>9.4</td>
</tr>
<tr>
<td>850 °C/20 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></td>
</tr>
<tr>
<td>600 °C/30 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></td>
</tr>
<tr>
<td>400 °C/20 mT</td>
<td>550 – 900</td>
<td>102.9</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>100 - 550</td>
<td>45.7</td>
<td></td>
</tr>
<tr>
<td>600 °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></td>
</tr>
</tbody>
</table>

- \( \sigma \) 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.