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
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
- \( \text{H}_2 \) transport – selectivity >1000

Applications

- Sensors - CO, CO\(_2\), H\(_2\), NO\(_x\) detection
- Power - Solid oxide fuel cells
- Electrolyzers
- Membrane reactors – chemical processing

\[ \text{CH}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2 \]

Fuel Cell

\[ \text{H}_2 \rightarrow 2\text{H}^+ + 2e^- \]

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

\[ \text{ABO}_3 \]

Fuel

Air

\[ \text{H}^+ \rightarrow \text{H}_2 \]

\[ 2\text{H}^+ + 2e^- \rightarrow \text{H}_2 \]

Cathode

Electrolyzer

\[ \text{ZrO}_2 \]

\[ \text{O}^- + 2e^- \rightarrow \text{O}_2 \]

Anode

Cathode

Gas Separation

\[ \text{H}_2 \rightarrow 2\text{H}^++2e^- \]

\[ \text{CO}, \text{CO}_2 \]

\[ 2\text{H}^++2e^- \rightarrow \text{H}_2 \]

\[ \text{Refined H}_2 \]

\[ \text{Gas mixture} \]

\[ \text{H}_2 \rightarrow 2\text{H}^++2e^- \]

\[ \text{CO} + 2\text{H}_2 \]
High Temperature Protonic Ceramics

Crystal Structures:
- Perovskite - $ABO_3$, $A_2(B'B'')O_{6-\delta}$ & $A_3(B'B_2'')O_{9-\delta}$
- Fluorite – $M_2O_3$
- Pyrochlore – $A_2B_2O_7$

$ABO_3$ – Pm3m

Proton Insertion

Oxygen vacancies ($V_O^{••}$) needed for $H^+$ transport:
- B site doping: $2B_B^+ + O_0 + M_2O_3 \rightarrow 2M_{Ce}^+ + V_O^{••} + 2BO_2$
- Humid environment: $H_2O(g) + V_O^{••} + O_0 \rightarrow 2OH_O^•$
- H$_2$ environment: $V_O^{••} + 1/2O_2 \rightarrow O_O + 2h^•$
  - $H_2(g) + 2O_0 + 2h^• \rightarrow 2OH_O^•$

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
• BO_6 octahedra tilt to reduce A site volume
• SrCeO_3 11° & 12.5°
• BaCeO_3 6° & 8.8°

Predominant proton transfer path

Independent Oxygen sites

Cubic \rightarrow Non-Cubic
Protonic Ceramic Development

**Optimization of Composition**

(A_xA_{1-x})(B_yB_{1-y})O_3-

Solid State Sintering

**Multiphase Materials**

Maximize $\sigma$

Ionic/Electronic

Cermets

Argonne National Laboratory

**Thin Film Structures**

Maximize Permeation Rate

**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 $H_2O$

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

Protonic Conduction

48 – 100 KJ/mol
Impedance Spectroscopy

Experimental Set-Up

- Imaginary Impedance (Ω)
- Real Impedance (Ω)

Grain Interiors
Grain Boundaries
Electrodes

Series (⊥) grain boundaries
Parallel (∥) grain boundaries
Electrode

conduction: grain ≠ grain boundary

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

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>(\text{BaZr}<em>{1-x}\text{Y}</em>{x}\text{O}_{3-δ})</td>
<td>1700</td>
<td>87</td>
<td>(\text{SrTi}<em>{1-x}\text{Sc}</em>{x}\text{O}_{3-δ})</td>
<td>1590</td>
<td>80</td>
</tr>
<tr>
<td>(x=0.02-0.25)</td>
<td></td>
<td></td>
<td>(x=0.02-0.05)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{BaZr}<em>{0.9}\text{Sc}</em>{0.1}\text{O}_{3-δ})</td>
<td>1700</td>
<td>91</td>
<td>(\text{Sr}<em>{0.66}\text{Ba}</em>{0.33}\text{Ti}<em>{0.95}\text{Sc}</em>{0.05}\text{O}_{3-δ})</td>
<td>1560</td>
<td>90</td>
</tr>
<tr>
<td>(\text{BaZr}<em>{0.9}\text{In}</em>{0.1}\text{O}_{3-δ})</td>
<td>1700</td>
<td>93</td>
<td>(\text{Sr}<em>{0.33}\text{Ba}</em>{0.66}\text{Zr}<em>{0.56}\text{Y}</em>{0.1}\text{Ti}<em>{0.33}\text{O}</em>{3-δ})</td>
<td>1600</td>
<td>93</td>
</tr>
<tr>
<td>(\text{BaZr}<em>{0.9}\text{Gd}</em>{0.1}\text{O}_{3-δ})</td>
<td>1650</td>
<td>88</td>
<td>(\text{Sr}<em>{0.66}\text{Ba}</em>{0.33}\text{Zr}<em>{0.33}\text{Sc}</em>{0.05}\text{Ti}<em>{0.61}\text{O}</em>{3-δ})</td>
<td>1650</td>
<td>88</td>
</tr>
<tr>
<td>(\text{Ba}<em>{0.66}\text{Sr}</em>{0.33}\text{Zr}<em>{0.9}\text{Y}</em>{0.1}\text{O}_{3-δ})</td>
<td>1630</td>
<td>88</td>
<td>(\text{SrZr}<em>{0.33}\text{Sc}</em>{0.05}\text{Ti}<em>{0.61}\text{O}</em>{3-δ})</td>
<td>1590</td>
<td>94</td>
</tr>
<tr>
<td>(\text{SrZr}<em>{0.9}\text{Y}</em>{0.1}\text{O}_{3-δ})</td>
<td>1675</td>
<td>94</td>
<td>(\text{BaZr}<em>{0.45}\text{Y}</em>{0.1}\text{Ti}<em>{0.45}\text{O}</em>{3-δ})</td>
<td>1600</td>
<td>87</td>
</tr>
<tr>
<td>(\text{SrHf}<em>{0.9}\text{Y}</em>{0.1}\text{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$^{\text{nd}}$ 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**

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

**WDX maps:**
- **Ca**
- **Sr**
- **Nb**

**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

**Microstructure**

- **Temp. gradient (+)**
  - Core: higher \( V \)
  - Shell: lower \( V \)

**Liquid**

- **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
**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>(\text{SrCe}<em>{0.9}Y</em>{0.1})O(_{3-\delta}) Air (\text{H}_2)</td>
<td>83.2</td>
</tr>
<tr>
<td>De Vries (\text{H}_2)</td>
<td>53.6</td>
</tr>
<tr>
<td>Nowick (\text{H}_2)</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>(\text{Sr}<em>3\text{Ca}</em>{1.18}\text{Nb}_{1.82}\text{O}_9) Air (\text{H}_2)</td>
<td>84.6</td>
</tr>
<tr>
<td>Nowick (\text{Sr}<em>3\text{Ca}</em>{1.06}\text{Nb}_{1.94}\text{O}_9) (\text{H}_2)</td>
<td>66.5</td>
</tr>
<tr>
<td>Nowick (\text{Sr}<em>3\text{Ca}</em>{1.18}\text{Nb}_{1.82}\text{O}_9) (\text{H}_2)</td>
<td>63.6</td>
</tr>
</tbody>
</table>

Protonic Conduction

48 – 100 KJ/mol
Nano-Structure Domains

Nanostructures → Protonic transport ?

SR$_3$(Ca$_{1+x}$Nb$_{2-x}$)O$_{9-\delta}$

SrCe$_{0.9}$Y$_{0.1}$O$_{3-\delta}$

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

Disordered Domains
Ordered Domains
Antiphase Boundaries
Vacancy loops

1650 °C 10 Hrs.
**Thin Film Electrolytes**

**Thickness Dependence**

- $\text{SrCe}_{0.95} \text{Yb}_{0.05} \text{O}_3 - \delta$

**GS Dependence**

- $3\text{Y-ZrO}_2$, 550 °C

**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
- Recrystallized grain structure
- Porous structure consisting of tapered crystallites separated by voids
**Pulsed Laser Deposition**

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

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

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

**Deposition Chamber – P\(_0\)\(_2\) 30 mTorr**

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

![Image of deposition process](image_url)
Silicon Substrates

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

700 °C

High (400) orientation

Thin Film Deposition - Silicon - 700 °C

Equivalent Circuit

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_{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></td>
<td></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 Al$_2$O$_3$ Substrates

![X-ray diffraction pattern of (002) and (400) peaks of Al$_2$O$_3$/BCY at different temperatures: 950°C, 900°C, 700°C, and 800°C.](image)

![Equivalent circuit diagram with labeled components: R1, CPE1, R2, CPE2, R3, and BCY layer.](image)

![Graph showing Z' and Z(10^6 ohms) at various temperatures: 568°C, 525°C, 495°C, 461°C, and 430°C.](image)

**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 ºC Deposition Temperature

Dense films fabricated at 600-950 ºC
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**

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

**Activation Energy**

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Q (KJ/mol)</th>
<th>Film Thickness (μm)</th>
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<tbody>
<tr>
<td>Sintered</td>
<td></td>
<td></td>
</tr>
<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>950 900 mT</td>
<td>74.8</td>
<td>3.6</td>
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<tr>
<td>950 900 mT</td>
<td>75.4</td>
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<td>900 900 mT</td>
<td>54.1</td>
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<td>800 900 mT</td>
<td>98.1</td>
<td>3.6</td>
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<tr>
<td>700 900 mT</td>
<td>115.6</td>
<td>1.7</td>
</tr>
<tr>
<td>700 900 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 BaZrO$_3$ Substrates

Solartron 1260/1296 0.1 – 1MHz 100 °C – 950 °C
Air, 5%H$_2$/N$_2$ Zplot/Zview Software
Microstructure Characterization

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

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

$\text{BaZrO}_3$
Growth Segregation

amorphous nano-grains

amorphous

BaZrO$_3$

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

~20 nm grains

EDX Ba Deficient

EDX Ce Deficient
Total Conductivity
Porous BaZrO$_3$ Substrates

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

Activation Energy

<table>
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<th>Temp. (°C)</th>
<th>Q (KJ/mol)</th>
<th>Film Thickness (μm)</th>
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<td>Sintered</td>
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<td></td>
</tr>
<tr>
<td>600 - 850</td>
<td>38.6</td>
<td>100.3</td>
</tr>
<tr>
<td>400 - 550</td>
<td>89.7</td>
<td>9.4</td>
</tr>
<tr>
<td>550 - 900</td>
<td>106.7</td>
<td>5.9</td>
</tr>
<tr>
<td>100 - 550</td>
<td>111.5</td>
<td>3.8</td>
</tr>
<tr>
<td>600 - 600</td>
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<td>1.0</td>
</tr>
<tr>
<td>750 - 800</td>
<td>112.2</td>
<td>3.1</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 produced unique microstructures that can not 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.