HIGH TEMPERATURE PROTONIC CONDUCTORS

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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 enhance 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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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

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

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

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

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

$\text{ABO}_3$ – $\text{Pm} \tilde{3} \text{m}$

Proton Insertion

Oxygen vacancies ($\text{V}_{\text{O}}^{**}$) needed for $\text{H}^+$ transport:
- B site doping: $2\text{B}_\text{B}^++\text{O}_\text{O}^++\text{M}_2\text{O}_3 \rightarrow 2\text{M}_{\text{Ce}}^++\text{V}_{\text{O}}^{**} + 2\text{BO}_2$
- Humid environment: $\text{H}_2\text{O}_{(g)} + \text{V}_{\text{O}}^{**} + \text{O}_\text{O} \rightarrow 2\text{OH}_\text{O}^•$
- $\text{H}_2$ environment: $\text{V}_{\text{O}}^{**} + \frac{1}{2}\text{O}_2 \rightarrow \text{O}_\text{O} + 2\text{h}^•$
  \[ \text{H}_2_{(g)} + 2\text{O}_\text{O} + 2\text{h}^• \rightarrow 2\text{OH}_\text{O}^• \]

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
• BO\(_6\) octahedra tilt to reduce A site volume
• SrCeO\(_3\) 11° & 12.5°
• BaCeO\(_3\) 6° & 8.8°

Cubic → Non-Cubic

Predominant proton transfer path

In-phase Antiphase

Independent Oxygen sites
Protonic Ceramic Development

Optimization of Composition

\[(A_xA_{1-x})(B_yB_{1-y})O_{3-\delta}\]

Maximize Proton Uptake

Solid State Sintering

Cermets

Argonne National Laboratory

Multiphase Materials

Maximize Ionic/Electronic Conductivity

Thin Film Structures

Maximize Permeation Rate

 Opportunities

A-Site Doping

• Proton Uptake
• Chemical Stability
• Mechanical Stability

B-Site Doping

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

Basic Science

• Crystal Structure
• Thermodynamics

Grain Boundary

• Detrimental to H⁺ transport

Environmental

• Reactive CO₂
• Reactive H₂O

Protonic Conduction

48 – 100 KJ/mol

σT (S/cm)

1000/RT

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

Nonporous Inorganic Membranes
Impedance Spectroscopy

**Experimental Set-Up**

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

**Conduction:** grain ≠ grain boundary

- \(\omega_0\) grain boundary \(<<\) \(\omega_0\) grain-Low T
- \(\omega_0\) grain boundary \(\sim\) \(\omega_0\) grain-High T
## Sintering Protonic Ceramics

![Co-precipitation](image1.png) ![Solid State](image2.png)

### High Sintering Temp.

<table>
<thead>
<tr>
<th>Composition</th>
<th>$T$ °C</th>
<th>$% \rho$</th>
<th>Composition</th>
<th>$T$ °C</th>
<th>$% \rho$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{BaZr}_{1-x}\text{Y}<em>x\text{O}</em>{3.5}$ (x=0.02-0.25)</td>
<td>1700</td>
<td>87</td>
<td>$\text{SrTi}_{1-x}\text{Sc}<em>x\text{O}</em>{3.5}$ (x=0.02-0.05)</td>
<td>1590</td>
<td>80</td>
</tr>
<tr>
<td>$\text{BaZr}<em>{0.9}\text{Sc}</em>{0.1}\text{O}_{3.5}$</td>
<td>1700</td>
<td>91</td>
<td>$\text{Sr}<em>{0.66}\text{Ba}</em>{0.33}\text{Ti}<em>{0.95}\text{Sc}</em>{0.05}\text{O}_{3.5}$</td>
<td>1560</td>
<td>90</td>
</tr>
<tr>
<td>$\text{BaZr}<em>{0.9}\text{In}</em>{0.1}\text{O}_{3.5}$</td>
<td>1700</td>
<td>93</td>
<td>$\text{Sr}<em>{0.33}\text{Ba}</em>{0.66}\text{Zr}<em>{0.56}\text{Y}</em>{0.1}\text{Ti}<em>{0.33}\text{O}</em>{3.5}$</td>
<td>1600</td>
<td>93</td>
</tr>
<tr>
<td>$\text{BaZr}<em>{0.9}\text{Gd}</em>{0.1}\text{O}_{3.5}$</td>
<td>1650</td>
<td>88</td>
<td>$\text{Sr}<em>{0.66}\text{Ba}</em>{0.33}\text{Zr}<em>{0.33}\text{Sc}</em>{0.05}\text{Ti}<em>{0.61}\text{O}</em>{3.5}$</td>
<td>1650</td>
<td>88</td>
</tr>
<tr>
<td>$\text{Ba}<em>{0.66}\text{Sr}</em>{0.33}\text{Zr}<em>{0.9}\text{Y}</em>{0.1}\text{O}_{3.5}$</td>
<td>1630</td>
<td>88</td>
<td>$\text{SrZr}<em>{0.33}\text{Sc}</em>{0.05}\text{Ti}<em>{0.61}\text{O}</em>{3.5}$</td>
<td>1590</td>
<td>94</td>
</tr>
<tr>
<td>$\text{SrZr}<em>{0.9}\text{Y}</em>{0.1}\text{O}_{3.5}$</td>
<td>1675</td>
<td>94</td>
<td>$\text{BaZr}<em>{0.45}\text{Y}</em>{0.1}\text{Ti}<em>{0.45}\text{O}</em>{3.5}$</td>
<td>1600</td>
<td>87</td>
</tr>
<tr>
<td>$\text{SrHf}<em>{0.9}\text{Y}</em>{0.1}\text{O}_{3.5}$</td>
<td>1600</td>
<td>82</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


![Counts](image3.png)

![Sintered Sample](image4.png)

![Powder](image5.png)
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
- \( \text{Sr}_3\text{Nb}_{1.82}\text{Ca}_{1.18}\text{O}_{9-\delta} \)

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

**Temp. gradient (+)**
- **Core**:
  - Higher \( [\text{V}^{\bullet\bullet}] \)
- **Shell**:
  - Lower \( [\text{V}^{\bullet\bullet}] \)
  - \( \text{Nb}^{5+}, \text{O}^{2-} \) rich shell
  - \( \text{Sr}^{2+}, \text{O}^{2-} \) rich core

**Liquid**

**Chemistry**

**Temp. gradient (+)**

**Seed**
- 100 wpp
- 5 mm
- Pull direction (15 mm/min)
\[ \sigma \cdot T = A \cdot \exp\left(-\frac{Q}{RT}\right) \]

**Activation Energy**

<table>
<thead>
<tr>
<th></th>
<th>( Q ) (KJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total ( \sigma )</td>
<td></td>
</tr>
<tr>
<td>( \text{SrCe}<em>{0.9} \text{Y}</em>{0.1} \text{O}_{3-\delta} ) Air</td>
<td>83.2</td>
</tr>
<tr>
<td>( \text{SrCe}<em>{0.9} \text{Y}</em>{0.1} \text{O}_{3-\delta} ) ( \text{H}_2 )</td>
<td>98.1</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></th>
<th>( Q ) (KJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total ( \sigma )</td>
<td></td>
</tr>
<tr>
<td>( \text{SrCe}<em>{0.9} \text{Y}</em>{0.1} \text{O}_{3-\delta} ) Air</td>
<td>84.6</td>
</tr>
<tr>
<td>( \text{SrCe}<em>{0.9} \text{Y}</em>{0.1} \text{O}_{3-\delta} ) ( \text{H}_2 )</td>
<td>98.1</td>
</tr>
<tr>
<td>Nowick ( \text{SrCe}<em>{1.06} \text{Nb}</em>{1.94} \text{O}_{9-\delta} )</td>
<td>66.5</td>
</tr>
<tr>
<td>Nowick ( \text{SrCe}<em>{1.18} \text{Nb}</em>{1.82} \text{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**

- SrC$_{0.95}$Yb$_{0.05}$O$_3$-$\delta$
- Hamakawa et al., SSI 48, 71, 2002

**GS Dependence**

- 3Y-ZrO$_2$, 550 °C
- Guo, Acta Mat. 51, 2539, 2003

**Porous Support**

Supported electrolyte fabrication difficult with high sintering temp.

**PVD Microstructure**

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

**Approach**

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

Deposition Chamber – \( P_{O_2} \) 30 mTorr

Target Rotator

Target

Plume
1-100 ev

Substrate

Substrate Heater
RT – 1000 °C

SiO\(_2\) Focusing Lens

SiO\(_2\) Window

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

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

$\text{BaCe}_{0.85}\text{Y}_{0.15}\text{O}_3-\delta$

700 °C

Thin Film Deposition - Silicon - 700 °C

Equivalent Circuit

Silicon

Solartron 1260/1287          0.1 – 1MHz          100 °C – 500 °C

Moist Argon – 25 °C Zplot/Zview Software
Total Conductivity
Silicon Substrates

\[ \sigma \cdot T = A \cdot \exp\left(-\frac{Q}{RT}\right) \]

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></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<sub>2</sub>O<sub>3</sub> Substrates

EIS

Ag Electrode

BCY

Porous Al<sub>2</sub>O<sub>3</sub>

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

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

Activation Energy

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Q (KJ/mol)</th>
<th>Film Thickness (μm)</th>
</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>
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<tr>
<td>900 °C/20 mT</td>
<td>75.4</td>
<td>3.2</td>
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<tr>
<td>900 °C/100 mT</td>
<td>54.1</td>
<td>4.8</td>
</tr>
<tr>
<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>

Conduction exhibits large dependence on process conditions.

Protonic Conduction – 48 – 100 KJ/mol
Porous BaZrO₃ Substrates

Solartron 1260/1296  0.1 – 1MHz  100 ºC – 950 ºC  
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

\[ \sigma \cdot T = A \cdot \exp\left(-\frac{Q}{RT}\right) \]

- Activation Energy
- \( \sigma \) less dependent upon process conditions
- Conduction change at \( T > 550 \, ^\circ C \)

<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></td>
<td></td>
</tr>
<tr>
<td>600 - 850</td>
<td>38.6</td>
<td>100.3</td>
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<tr>
<td>400 - 550</td>
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<td>850 °C/20 mT</td>
<td>550 – 900</td>
<td>89.7</td>
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<td></td>
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<td>600 °C/30 mT</td>
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<td>400 °C/20 mT</td>
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<td></td>
<td>100 – 550</td>
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<tr>
<td>600 °C/20 mT</td>
<td>550 – 900</td>
<td>102.9</td>
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<tr>
<td></td>
<td>100 – 550</td>
<td>45.7</td>
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<tr>
<td>900 °C/20 mT</td>
<td>550 – 900</td>
<td>112.2</td>
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<tr>
<td></td>
<td>100 – 550</td>
<td>62.5</td>
</tr>
</tbody>
</table>
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 protionic 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 protionic conduction.