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 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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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

\[ \text{Fuel Cell} \]
- H₂ \rightarrow 2\text{H}^+ + 2e^-\quad \text{Anode}
- \text{H}^+ + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}\quad \text{Cathode}

\[ \text{Electrolyzer} \]
- 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\quad \text{Anode}
- \text{O}^2- \rightarrow \text{O}_2\quad \text{Cathode}

\[ \text{Gas Separation} \]
- CH₄ + \frac{1}{2}\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2
- \text{H}_2 \rightarrow 2\text{H}^+ + 2e^-\quad \text{Anode}
- 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\quad \text{Cathode}

\[ \text{CH}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2 \]
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 – $\text{A}_2\text{B}_2\text{O}_7$

$\text{ABO}_3$ – $\text{Pm}3\text{m}$

Proton Insertion

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

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

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

t<0.96 tetragonal/orthorhombic

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

Cubic → Non-Cubic

Predominant proton transfer path

Independent Oxygen sites

In-phase

Antiphase
Protonic Ceramic Development

Ceramic

Optimization of Composition

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

Multiphase Materials

Maximize \(\sigma\) Ionic/Electronic

Thin Film Structures

Maximize Permeation Rate

Solid State Sintering

Cermets

Argonne National Laboratory

Opportunities

Protonic Conduction

48 – 100 KJ/mol

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 \(H_2\)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

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>BaZrₓ₀.₈₅ Yₓ₀.₁₅ O₃₋δ</td>
<td>1700</td>
<td>87</td>
<td>SrTi₁₋ₓ Scₓ O₃₋δ, x=0.02-0.05</td>
<td>1590</td>
<td>80</td>
</tr>
<tr>
<td>x=0.02-0.25</td>
<td>1700</td>
<td>91</td>
<td>Sr₀.₆₆ Ba₀.₃₃ Ti₀.₉₅ Sc₀.₀₅ O₃₋δ</td>
<td>1560</td>
<td>90</td>
</tr>
<tr>
<td>BaZrₓ₀.₉ Scₓ₀.₁ O₃₋δ</td>
<td>1700</td>
<td>93</td>
<td>Sr₀.₃₃ Ba₀.₆₆ Zr₀.₅₆ Y₀.₀₁ Ti₀.₃₃ O₃₋δ</td>
<td>1600</td>
<td>93</td>
</tr>
<tr>
<td>BaZrₓ₀.₉ Inₓ₀.₁ O₃₋δ</td>
<td>1650</td>
<td>88</td>
<td>Sr₀.₆₆ Ba₀.₃₃ Zr₀.₃₃ Sc₀.₀₅ Ti₀.₆₁ O₃₋δ</td>
<td>1650</td>
<td>88</td>
</tr>
<tr>
<td>Ba₀.₆₆ Sr₀.₃₃ Zrₓ₀.₉ Yₓ₀.₁ O₃₋δ</td>
<td>1630</td>
<td>88</td>
<td>SrZr₀.₃₃ Sc₀.₀₅ Ti₀.₆₁ O₃₋δ</td>
<td>1590</td>
<td>94</td>
</tr>
<tr>
<td>SrZrₓ₀.₉ Yₓ₀.₁ O₃₋δ</td>
<td>1675</td>
<td>94</td>
<td>BaZr₀.₄₅ Y₀.₀₁ Ti₀.₄₅ O₃₋δ</td>
<td>1600</td>
<td>87</td>
</tr>
<tr>
<td>SrHfₓ₀.₅ Yₓ₀.₁ O₃₋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
• Al 2\textsuperscript{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
  - 2\text{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••]
- Nb\text{O}^{2-} \text{rich shell}
- Ca\text{O}^{2-} \text{rich core}

**WDX maps**
- \( \text{Ca} \)
- \( \text{Sr} \)
- \( \text{Nb} \)

**Temp. gradient (+)**

**Seed**
- 100 mm
- 5 mm pull direction (15 mm/min)
\[ \sigma \cdot T = A \cdot \exp(-Q/RT) \]

**Activation Energy**

<table>
<thead>
<tr>
<th></th>
<th>Total $\sigma$</th>
<th>$Q$ (KJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr$<em>{3}$(Ca$</em>{1+x}$Nb$<em>{2-x}$)O$</em>{9-\delta}$</td>
<td>Sr$<em>{3}$Ca$</em>{1.06}$Nb$<em>{1.94}$O$</em>{9-\delta}$</td>
<td>84.6 98.1</td>
</tr>
<tr>
<td>Nowick Sr$<em>{3}$Ca$</em>{1.18}$Nb$<em>{1.82}$O$</em>{9-\delta}$</td>
<td>66.5 63.6</td>
<td></td>
</tr>
<tr>
<td>De Vries Sr$<em>{3}$Ca$</em>{1.18}$Nb$<em>{1.82}$O$</em>{9-\delta}$</td>
<td>53.6 60.8</td>
<td></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$_{3-\delta}$

1650 °C 10 Hrs.

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

**Thickness Dependence**

![Chart showing thickness dependence](chart.png)

**GS Dependence**

![Graph showing grain size dependence](graph.png)

**Porous Support**

Supported electrolyte fabrication difficult with high sintering temp.

**Approach**

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

Excimer Laser
- λ = 248 nm -KrF
- Energy: 1 – 3 J/cm²
- Frequency: <10 Hz
- Pulse: 25 ns

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

Substrates
- Porous Al₂O₃
- Porous BaZrO₃
- Silicon
Silicon Substrates

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

700 °C

High (400) orientation

Thin Film Deposition - Silicon - 700 °C

$Z'(\text{ohms})$

$Z(\text{ohms})$

EIS

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

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

σ·T = A·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} 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 Al$_2$O$_3$ Substrates

Counts

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

EIS

Ag Electrode

Porous Al$_2$O$_3$

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

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

<table>
<thead>
<tr>
<th>Temperature (℃)</th>
<th>Q (KJ/mol)</th>
<th>Film Thickness (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaCe₀.₈₅Y₀.₁₅O₃ Sintered</td>
<td>600 - 850</td>
<td>38.6</td>
</tr>
<tr>
<td>400 - 550</td>
<td>100.3</td>
<td></td>
</tr>
<tr>
<td>950 °C/30 mT</td>
<td>200 - 900</td>
<td>74.8</td>
</tr>
<tr>
<td>3.6</td>
<td></td>
<td></td>
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<tr>
<td>950 °C/30 mT</td>
<td>200 - 900</td>
<td>75.4</td>
</tr>
<tr>
<td>3.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>900 °C/30 mT</td>
<td>200 - 600</td>
<td>54.1</td>
</tr>
<tr>
<td>4.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>800 °C/30 mT</td>
<td>200 - 600</td>
<td>98.1</td>
</tr>
<tr>
<td>3.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>700 °C/100 mT</td>
<td>350 - 900</td>
<td>115.6</td>
</tr>
<tr>
<td>1.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>700 °C/200 mT</td>
<td>350 - 700</td>
<td>108.2</td>
</tr>
<tr>
<td>4.1</td>
<td></td>
<td></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
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

EDX
Ba Deficient

EDX
Ce Deficient
Total Conductivity
Porous BaZrO₃ Substrates

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

Activation Energy

<table>
<thead>
<tr>
<th>Process</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>850 °C/20 mT</td>
<td>550 – 900</td>
<td>89.7</td>
<td>9.4</td>
</tr>
<tr>
<td>600 °C/30 mT</td>
<td>550 – 900</td>
<td>106.7</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>600 °C/20 mT</td>
<td>550 – 900</td>
<td>102.9</td>
<td>1.0</td>
</tr>
<tr>
<td>900 °C/20 mT</td>
<td>550 – 900</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.