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

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

Gas Separation
- CH₄ + 1/2O₂ → CO + 2H₂

Electrolyzer
- H₂ → 2H⁺ + 2e⁻
- H₂O → 2H⁺ + O²⁻ + 2e⁻
- ZrO₂

Fuel Cell
- H₂ → 2H⁺ + 2e⁻
- 2H⁺ + 1/2O₂ → H₂O
- ABO₃

Cathode
- e⁻

Anode
- H⁺

Electrolyzer
- Refined H₂
- 2H⁺ + 2e⁻ → H₂
- ABO₃

Cathode
- CO, CO₂

Gas Mixture
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 (V$_{O^{••}}$) needed for H$^+$ transport:
  - B site doping: $2\text{BB}^+ + \text{O}_0^+ + \text{M}_2\text{O}_3 \rightarrow 2\text{M}_{\text{Ce}}^+ + \text{V}_O^{••} + 2\text{BO}_2$
  - Humid environment: $\text{H}_2\text{O}_{(g)} + \text{V}_O^{••} + \text{O}_0 \rightarrow 2\text{OH}_0^•$
  - H$_2$ environment: $\text{V}_O^{••} + \frac{1}{2}\text{O}_2 \rightarrow \text{O}_0 + 2\text{h}^•$
  - $\text{H}_2_{(g)} + 2\text{O}_0 + 2\text{h}^• \rightarrow 2\text{OH}_0^•$

- Proton strongly associates with a neighbouring oxygen ion-represented as 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
• \( \text{SrCeO}_3 11^\circ & 12.5^\circ \)
• \( \text{BaCeO}_3 6^\circ & 8.8^\circ \)

Cubic \( \rightarrow \) 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-δ}

Multiphase Materials

Maximize σ
Ionic/Electronic

Thin Film Structures

Maximize Permeation Rate

Solid State Sintering

Cermets

Argonne National Laboratory

Opportunities

Protonic Conduction

48 – 100 KJ/mol

Basic Science

• Crystal Structure
• Thermodynamics

Environmental

• Reactive CO₂
• Reactive H₂O

Grain Boundary

• Detrimental to H⁺ transport

A-Site Doping

• Proton Uptake
• Chemical Stability
• Mechanical Stability

B-Site Doping

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

Solid State Sintering

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

σT (S/cm)

1000/RT

0.01 0.1 1 10 100

Protonic Conduction

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

100 10 1

1000 °C

Grain Boundary

• Detrimental to H⁺ transport

Environmental

• Reactive CO₂
• Reactive H₂O

Basic Science

• Crystal Structure
• Thermodynamics

A-Site Doping

• Proton Uptake
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• Mechanical Stability

B-Site Doping

• O₂ Vacancies
• Proton mobility
• Electron σ
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Solid State Sintering

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

σT (S/cm)

1000/RT

0.01 0.1 1 10 100

Protonic Conduction

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

100 10 1

1000 °C
Impedance Spectroscopy

Experimental Set-Up

- Series (⊥) grain boundaries
- Parallel (∥) grain boundaries
- Grain interiors
- Electrodes

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_{0.9}O_{3-δ} x=0.02-0.25</td>
<td>1700</td>
<td>87</td>
<td>SrTi_{1-x}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_{0.6}In_{0.1}O_{3-δ}</td>
<td>1700</td>
<td>93</td>
<td>Sr_{0.33}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>1650</td>
<td>88</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_{0.9}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 2nd phase contaminant – conc. between grains
- Pre-fabrication contamination
**Microstructure - $\text{Sr}_3(\text{Ca}_{1+x}\text{Nb}_{2-x})\text{O}_{9-δ}$ - Chemistry**

Dense - Cellular growth

- **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
- $\text{Sr}_3\text{Nb}_{1.82}\text{Ca}_{1.18}\text{O}_{9-δ}$

**Chemistry**
- Core: higher $[\text{V}^{-}]$
- Shell: Lower $[\text{V}^{-}]$

**WDX maps**
- $\text{Ca}$
- $\text{Sr}$
- $\text{Nb}$

**Temp. gradient (+)**
- Core: higher $[\text{V}^{-}]$
- Shell: Lower $[\text{V}^{-}]$
- $\text{Ca}^{2+}$, $\text{Sr}^{2+}$ rich core
- $\text{Nb}^{5+}$, $\text{O}^{2-}$ rich shell
- Liquid
\[ \sigma \cdot T = A \cdot \exp(-\frac{Q}{RT}) \]

**Activation Energy**

<table>
<thead>
<tr>
<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}) Air</td>
<td>184.6</td>
</tr>
<tr>
<td>De Vries ( \frac{1}{2})</td>
<td>53.6</td>
</tr>
<tr>
<td>Nowick ( \frac{1}{2})</td>
<td>60.8</td>
</tr>
</tbody>
</table>

Protonic Conduction

48 – 100 KJ/mol
Nano-Structure Domains

Nanostructures → Protonic transport ?
Thin Film Electrolytes

**Thicknness Dependence**

\[
\text{Thickness} \quad \begin{array}{c}
\text{2 \, \mu m} \\
80 \, \mu m \\
140 \, \mu m \\
1 \, \text{mm}
\end{array}
\]

\[\text{log} (\text{Conductivity}, \ \Omega \cdot \text{cm}^{-1})\]

- **SrC_{0.95}Yb_{0.05}O_{3-\delta}**
- Hamakawa1 et al., SSI 48, 71 2002

**GS Dependence**

\[3\text{Y-ZrO}_2, \ 550 \, ^\circ\text{C}\]

- Bulk, Hahn et al.
- Grain Boundary, Hahn et al.

Guo, Acta Mat. 51, 2539, 2003

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

Targets
- Solid state synthesize powder
- Sintering – 1650 $^\circ$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

Solartron 1260/1287

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>Sample</th>
<th>Temp. (°C)</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>
<td>100.3</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

EIS
Ag Electrode
BCY
Porous Al$_2$O$_3$

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

950°C
900°C
700°C

Counts

2θ

(002) (400)

Al$_2$O$_3$/BCY
Al$_2$O$_3$

800°C

5 µm

Grain R1
Grain Boundary R2
Electrode R3

CPE1
CPE2

Equivalent Circuit

Z'(10^6 ohms)

Z(10^6 ohms)

Solartron 568 °C
Solartron 525 °C
Solartron 495 °C
Solartron 461 °C
Solartron 430 °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

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

$950 \, ^\circ\text{C}$ Deposition Temperature

BCY Film

$\text{Al}_2\text{O}_3$

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>
</tr>
<tr>
<td>900 °C/30 mT</td>
<td>75.4</td>
<td>3.2</td>
</tr>
<tr>
<td>700 °C/100 mT</td>
<td>54.1</td>
<td>4.8</td>
</tr>
<tr>
<td>950 °C/20 mT</td>
<td>98.1</td>
<td>3.6</td>
</tr>
<tr>
<td>600 - 900</td>
<td>115.6</td>
<td>1.7</td>
</tr>
<tr>
<td>350 - 700</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

Equivalent Circuit

2nd Arc
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
Growth Segregation

amorphous nano-grains

amorphous

BaZrO$_3$ 100 nm

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

EDX Ba Deficient

EDX Ce Deficient

~20 nm grains
Total Conductivity
Porous BaZrO₃ Substrates

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

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>Sintered BaCe₀.₈₅Y₀.₁₅O₃₋δ</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 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.