Proton Conducting ceramic Cells: Status and Prospects

M. Marrony
Project Manager in Fuel Cell
Outline

• Introduction

• Materials and processes

• Scale-up processes

• Performance and durability

• Conclusion and prospects
Outline

• Introduction
  – Research overview
  – Context & roadmap: case in fuel cell

• Materials and processes

• Scale-up processes

• Performance and reliability

• Conclusion and prospects
Introduction: PCC research in the literature...

- More and more interests...
  - Better understanding of proton diffusion phenomena through the material
  - Optimization of intrinsic properties of materials and cell manufacturing (mechanical strength, performances)
  - Diversity of applications
    - Fuel cell
    - Hydrogen pumping
    - Ammonia synthesis
    - Electrolysis

*source: science direct
Keyword: proton conducting ceramic fuel cell
Introduction: PCC research mapping*

- > 15 countries
- > 9 industrials
- >30 laboratories and Institutes

*List non exhaustive
Introduction: PCC in Fuel cell: Context & roadmap

- Assessment of PCFC technology as electrochemical devices vs. other FC technologies (SOFC, PEMFC)
  - Simplification of reforming step (vs. PEMFC)
  - (Potentially) use of common metallic materials (reduction of cost) (vs. SOFC)
  - (Potentially) better stability under dynamic/thermal cycles (vs. SOFC)
  - (Potentially) better energetic efficiency (no dilution of fuel @anode side) (vs. SOFC)
  - Better diffusion kinetics of H+ elements (vs. O2-)

- Opening market target: beginning 2020
  - Competition with LT SOFC technology
Outline

• Introduction

• Materials and processes
  – Criteria and status
  – Strategic approach
  – Nanopowder synthesis method

• Scaling-up

• Performance and reliability

• Conclusion and prospects
**Materials and processes: the ideal PCC…**

- Operating domain in PCFC research: 500 -700°C
  - >600°C: competition with IT-SOFC (2nd generation) and now LT-SOFC (3rd generation)
  - <600°C: non mature domain

<table>
<thead>
<tr>
<th>600°C</th>
<th>Anode</th>
<th>Electrolyte</th>
<th>Cathode</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H₂/ H₂O</td>
<td>Air / H₂ / H₂O</td>
<td>Air / H₂O</td>
</tr>
<tr>
<td></td>
<td>H₂/ H₂O</td>
<td>H₂/ H₂O</td>
<td>H₂/ H₂O</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chemical stability</th>
<th>H₂/ H₂O</th>
<th>Air / H₂ / H₂O</th>
<th>Air / H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂/CO tolerance</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>Ionic/protonic conductivity</td>
<td>&gt; 10⁻² S·cm⁻¹</td>
<td>&gt; 10⁻² S·cm⁻¹</td>
<td>&gt; 10⁻² S·cm⁻¹</td>
</tr>
<tr>
<td>Electronic conductivity</td>
<td>&gt;1000 S·cm⁻¹</td>
<td>~ 0 S·cm⁻¹</td>
<td>&gt;100 S·cm⁻¹</td>
</tr>
<tr>
<td>ASR</td>
<td>&lt; 0.15 Ω·cm²</td>
<td>&lt; 0.15 Ω·cm²</td>
<td>&lt; 0.15 Ω·cm²</td>
</tr>
<tr>
<td>Catalytic activity</td>
<td>yes</td>
<td>no</td>
<td>yes</td>
</tr>
<tr>
<td>Mechanical properties</td>
<td>Porous ~50% 300-800µm Thick</td>
<td>Dense &gt;95% 10-30µm Thick</td>
<td>Porous ~30% 20-40µm Thick</td>
</tr>
<tr>
<td>Industrial aspects</td>
<td>Easy and not costly synthesis &amp; manufacturing processes</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Electrolyte materials**
- Perovskite type AMₓX₁₋ₓO₃₋δ
  - (with A=Ba, Sr, M=Ce, Zr, Ta et X=Y, Yb, In)
    - 
    - 
  - Other perovskites:
    - Ba (Ce₀.6 Y₀.3 Nb₀.1)O₃₋δ (BCNY)
    - La₆₋ₓWO₁₂₋₅ (LWO)
    - …

**Anode materials**
- Corresponding cermet (NiO-EI)

**Cathode materials**
- Commonly SOFC materials
  - LSM, LSCF, BSCF, Ln₂NiO₄
  - others:
    - Cobalt-containing perovskite-type materials
      - Sm₀.₅Sr₀.₅CoO₃₋δ
      - Ce₀.₈Sm₀.₂O₂₋δ (SSC – SDC) (Sun et al. 2011)
    - …
Materials and processes: strategic approach

• Starting point: Perovskite BCY based materials as electrolyte
  – Need of thin and dense electrolyte with high mechanical strength and high performance stability
    ➢ Reduction of electrolyte resistance
    ➢ Use of nanopowder to enhance
      – Ionic grain boundary conductivity
      – The gastightness
    ➢ Insertion of new doping elements (Zr, Zn...) (better CO2 tolerance, lower sintering temperature...)

• Need of optimal microstructure and composition of the porous electrode for:
  – A good catalyst activity
  – To match TEC of materials
  – To improve adhesion between components
    ➢ Use of Nanostructured electrode to get
      – High electro catalytic activity
      – Large TPB

Advanced MIEC cathodes

Composite approach

Optimization of intrinsic properties of baseline materials

Advanced electrolyte materials

Porous cathode structure

Porous anode structure

Multi layer anode cermet
Materials and processes: nanopowder synthesis

- **Flash Combustion method**
  - Effective method used for the production of more than 1000 fine complex oxide powders
  - A self-sustained reaction of metal nitrates and different fuels

- **Advantages**
  - The liquid state allows mixing the reactants on the molecular level permitting uniform formulation
  - The high reaction temperature ensures high product purity and crystallinity
  - Short process duration promotes synthesis of nano-size powders with high specific surface area

\[
\text{Nitrates} + \text{H}_2\text{O} + \text{Glycine} \\
\text{Dehydration } @ 200^\circ \text{C} \\
\text{Ignition/Combustion} @ 600^\circ \text{C}
\]

Outline

• Introduction

• Materials and processes

• **Scaling-up**
  – Powder synthesis: the first level of maturity system
  – Cell manufacturing: the second level of maturity system…

• Performance and reliability

• Conclusion and prospects
Scaling-up step 1: powder synthesis

- Validation of the up-scaling step for lab powder synthesis process:
  - Combustion and solid state reaction
  - Good quality and reproducibility (>1 kg)

<table>
<thead>
<tr>
<th>1st generation</th>
<th>2nd generation</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaCe$<em>{0.9}$Y$</em>{0.1}$O$_{3-\delta}$ (BCY10)</td>
<td>Ba$<em>2$(In$</em>{0.8}$Ti$_{0.2}$)$<em>2$O$</em>{5.2-\delta}$ (BIT02)</td>
</tr>
<tr>
<td>NiO / BaCe$<em>{0.9}$Y$</em>{0.1}$O$_{3-\delta}$</td>
<td>NiO / Ba$<em>2$(In$</em>{0.8}$Ti$_{0.2}$)$<em>2$O$</em>{5.2-\delta}$</td>
</tr>
<tr>
<td>Pr$<em>2$NiO$</em>{4+\delta}$</td>
<td>Ba(Ce$<em>{0.6}$Zr$</em>{0.1}$Y$_{0.1}$)$<em>3$O$</em>{3-\delta}$ (BCZY)</td>
</tr>
<tr>
<td>NiO / Ba(Ce$<em>{0.6}$Zr$</em>{0.1}$Y$_{0.1}$)$<em>3$O$</em>{3-\delta}$</td>
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</tr>
</tbody>
</table>

Delivery of powders to the partners

Cell elaboration

Quality control OK
Scaling-up step 2: Anode Supported cell manufacturing (1)

- Target: elaboration of cells at industrial level (> φ 80 mm):
  - Easy and industrial methods
  - Low manufacturing cost
- Evaluation of co-pressing method for half-cells (commonly used in the literature)

- φ 25 mm 😊 → φ 40 mm 😊 → φ 80 mm 😞
  - Difficulty with feasibility & reproducibility for bigger cells
    - Co-pressing method can not be easily used for mass production
    - Introduction of wet chemical routes

Dailly J., Marrony M. et al, under manuscript
### Scaling-up step 2: Anode Supported Cell manufacturing (2)

<table>
<thead>
<tr>
<th>Anode</th>
<th>Electrolyte</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressing</td>
<td>Tape-casting, screen-printing, slip-casting</td>
</tr>
<tr>
<td>Tape-casting</td>
<td></td>
</tr>
</tbody>
</table>

#### Tape-casting

- NiO/BCY10

#### Screen-printing

- BCY10

#### Co-sintering

- 1400°C / 10h

#### Screen-printing (PrN, BSCF, $\text{Nd}_2\text{NiO}_{4+x}$)

- 1200°C / 1h

#### GENERATION 2: preliminary results

<table>
<thead>
<tr>
<th></th>
<th>Thickness</th>
<th>Porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode</td>
<td>430 µm</td>
<td>2% ( cellForRowAt)</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>25 µm</td>
<td>3% ( Crescent)</td>
</tr>
<tr>
<td>Cathode</td>
<td>17 µm</td>
<td>30% ( Smile)</td>
</tr>
</tbody>
</table>

**SEM observations**
- **Before reduction**:
  - Anode: 430 µm, 2% (EndElement)
  - Electrolyte: 25 µm, 3% (EndElement)
  - Cathode: 17 µm, 30% (EndElement)
Outline

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• Scale-up processes

• Performance and durability

• Conclusion and prospects
Performance and reliability: status (1)

- Actual average cell performance:
  - 100 - 250 mW/cm²@600°C
  - Cell diameter below 10 mm
  - BCZY and BCY based cells
  - Many cathode/electrolyte couples

- Targeted cell Performances:
  - >400 mW/cm², 600°C
    - …LT-SOFC > 500 mW/cm², 600°C
Performance and reliability: status (2)

- **Cell Reliability target**
  - Few thousand hours under static mode (@0.7-0.8V)
  - >100 dynamic cycles

- **Lifetime tests in PCFC:**
  - No real data in the literature:
    - Few tens hours... @700°C!!!
Performance and durability: BCY10/PrN based cell

Cell performance and reliability improved
- 180 mW/cm², 600°C
- >250h

SEM/EDX analysis
- Electrolyte layer:
  - Porosity and quality improved
  - Thickness to be reduced (< 20 μm)
- Anode layer
  - Better homogenity
- Cathode Layer:
  - High reactivity PrN / BCY
  - Delamination effect

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Performance and durability: advanced substituted perovskite based cell

$\text{Ba(Ce}_{0.9}\text{Y}_{0.1})\text{O}_{3-d} \rightarrow \text{BCY10}$
$\text{Ba(Ce}_{0.8}\text{Zr}_{0.1}\text{Y}_{0.1})\text{O}_{3-d} \rightarrow \text{BCZY}$
$\text{Ba(Ce}_{0.6}\text{Y}_{0.3}\text{Nb}_{0.1})\text{O}_{3-d} \rightarrow \text{BCYN30}$

Influence of material electrolyte (NiO-electrolyte / electrolyte/BSCF) on cell performance

- Electrolyte based PCFC cell:
  - $\text{BCY} > \text{BCYN} > \text{BCZY}$

- $\text{P} = 125 \text{ mW/cm}^2, 600^\circ\text{C}$ without composite,
- $\text{P} = 200 \text{ mW/cm}^2, 600^\circ\text{C}$ with composite
  - Case of BSCF
Performance and reliability: BCY stable?

- Performance to be optimized
  - 1000h @0.8V without degradation! 😊
  - $P_{\text{max}} = 60 \text{ mW/cm}^2$ 😊
  - …but OCV > 1 V 😊, even after 1000h!

- SEM/EDX observations
  - No diffusion of elements through layers 😊
  - Slight increase of porosity of electrolyte 😊
    - Because power density is nearly constant with time, the properties of BCY is not the parameter key of degradation…
      - Cathode interface layer to be optimized (protective coating interface?)

<table>
<thead>
<tr>
<th>Thickness (μm)</th>
<th>Porosity After test</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode</td>
<td>430  2% → 18%</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>25     3% → 10%</td>
</tr>
<tr>
<td>Cathode</td>
<td>17     30% → 25%</td>
</tr>
</tbody>
</table>

Dry H₂/air

$600^\circ\text{C}$

$1.2$  
$1.1$  
$1.0$  
$0.9$  
$0.8$  
$0.7$  
$0.6$  
$0.5$  
$0.4$  
$0.3$  
$0.2$  
$0.1$  
$0$  

$0$  
$100$  
$200$  
$300$  
$400$  
$500$  
$600$  
$700$  
$800$  
$900$  
$1000$

$E (\text{Volts})$  
$\text{Time (Hours)}$

$E (\text{Volts})$  
$i (\text{A/cm}^2)$

$0.00$  
$0.01$  
$0.02$  
$0.03$  
$0.04$  
$0.05$  
$0.06$  
$0.07$  
$0.08$  
$0.09$  
$0.10$

$0.00$  
$0.01$  
$0.02$  
$0.03$  
$0.04$  
$0.05$  
$0.06$  
$0.07$  
$0.08$  
$0.09$  
$0.10$

$\text{Power (W/cm}^2\text{)}$

$\text{IV curves of NiO-BCY/BCY/NdN cell vs. time (h)}$

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• Performance and durability

• Conclusion and prospects
Conclusions

- Promising technology in fuel cell but not enough mature materials and processes used
  - Research activity growing up for the 10 last years

- Materials & processes
  - Validation of the scale up of material synthesis
  - Cell manufacturing to be improved
    - Wet chemical routes

- Cell Performances
  - Actually: ~200 mW/cm², 600°C
    - BCY based cell
    - In the literature: 350 mW/cm², 600°C
  - To be reached:
    - >400-500 mW/cm², 600°C...
    - ...vs. LT-SOFC > 500 mW/cm², 600°C

- Cell reliability
  - >1000h with BCY based cell without any degradation
Propects (1)

• In order to reduce technological bottlenecks...
  – Towards « Nafton® » or YSZ references
    ➢ Understanding of proton diffusion mechanisms through materials
    ➢ Innovative materials
  – Towards the best couple electrolyte/cathode
    ➢ Better compatibility (TEC, chemical reactivity…)
      – Composite system?
  – Towards the best microstructure
    ➢ Composition gradient
    ➢ Innovative materials: MIEC (H+/e) for both cathode and anode layers
  – Towards the best operating conditions
    ➢ Standard criteria
    ➢ Vs. Application profile
Prospects (2)

Opening to electrolysis @ intermediate temperature (500-700°C): energy storage via H2

- ☹ PO2 ↑ @ H2 side by shifting SOFC/SOEC modes
- ☺ PO2 ↑ @ O2 side by shifting PCFC/PCEC modes
  - High produced H2 quality
  - Better stability of material properties (Ni elements especially)
  - Reversibility concept more acceptable

- … but poor state of the art
  - 2-3 recent scientist articles
Acknowledgments and informations…

CONDOR team…

Financial supports…

More information on PCFC results: www.pcfc-condor.org
www.metprocell.eu

EVENT in 2013 in Montpellier (France) → 1st announcement come soon…

PROSPECTS PCC 2013 (n°2)
Proton Ceramics cells in applied research:
* Fuel cell
* Electrolysis
* Ammonia synthesis
* H2 pumping

Thank you for your attention!
Materials and processes: electrolytes (1)

- **Substituted Perovskites and derivates**
  - **Generation 1:**
    - \( \text{BaCe}_{0.9} \text{Y}_{0.1} \text{O}_{3-d} \) (BCY10)
      - BCY10: \( s(\text{H}^+) = 1-10 \text{ mS/cm}, 400-600^\circ \text{C} \)
    - \( \text{BaZr}_{0.9} \text{Y}_{0.1} \text{O}_{3-d} \) (BZY10)
  - **Generation 2:**
    - \( \text{Ba(Ce}_{0.6} \text{Y}_{0.3} \text{Nb}_{0.1})\text{O}_{3-d} \) (BCYN)
    - \( \text{BaCe}_{0.8} \text{Zr}_{0.1} \text{Y}_{0.1} \text{O}_{3-d} \) (BCZY)
    - \( \text{Ba}_2\text{In}_{2-x}\text{Ti}_x \text{O}_{5+d} \) (avec \( x=0.2 \)) (BIT02)

- **Nanopowdered approach**
  - High sinterability
  - High apparent density
    - Ex: BZY10: sintering temperature 200°C lower than those described in the literature (ref: 1700°C)

---

**Conductivity measurements vs. \( T(\circ \text{C}) \) [Ar/H2, H2O 3%]**

**Sintering Temperature °C**

- \( \text{BCY} \)
- \( \text{BZY} \)
- \( \text{BCZY} \)
- \( \text{BCYN} \)

**Compacty %**

- \( \text{BIT02} \)

---


Materials and processes: electrolytes (2)

4% CO₂/He 700°C/10h

- Substituted Perovskites
  - Reactivity ranking
    - BCYN30 > BCZY >> BCY
      - Powder level
      - Dense material: reactivity less pronounced
        » Kinetics effect

Materials and processes: anode cermet (1)

- Characteristics of the support
  - Mechanical strength
  - Gas permeability (~ 40 % porosity)
  - Total conductivity higher than 100 mS/cm

- Structuration of Functional layer
  - Fine microstructure, large TPB

- Control of microstructure (porosity) vs. synthesis methods
  - Flash combustion
  - Infiltration
  - Physical mixture
  - Gelling starch as porogen

Materials and processes: anode cermet (2)

- Pure Ni-BCY cermet after reduction @ 700°C

- Metallic behavior, percolation of the Ni phase
- $\sigma > 1000$ S/cm, @ 600°C attributed to high homogeneity

- EIS on symmetrical cell (anode/electrolyte/anode)
  - Low polarisation ASR $\approx 0.1$ Ω cm² @ 600°C for any synthesis methods

Materials and processes: Cathode (1)

- Cathode materials
  - Water insertion abilities in oxides materials
  - 3 structural types

\[
A_xB_yO_2 + \frac{n}{2}H_2O \rightarrow A_xB_yO_{2-n\frac{1}{2}}(OH)_n
\]

Perovskites

\[A_{1-x}A'_xM_{1-x}M'_xO_3-\delta\]

- AO layer
- MO\(_2\) layer
- \(H_2O\) insertion
- Oxygen vacancies

- Ba\(_{0.5}\)Sr\(_{0.5}\)Co\(_{0.8}\)Fe\(_{0.2}\)O\(_{3-\delta}\)
- La\(_{0.6}\)Sr\(_{0.4}\)Fe\(_{0.8}\)Co\(_{0.2}\)O\(_{3-\delta}\)

Double Perovskites

- LnBaM\(_2\)O\(_{5+\delta}\)

- AO layer
- MO\(_2\) layer
- LnO\(_{0.5}\) layer
- \(H_2O\) insertion

- GdBaCo\(_2\)O\(_{5+\delta}\)
- NdBaCo\(_2\)O\(_{5+\delta}\)
- PrBaCo\(_2\)O\(_{5+\delta}\)

Ruddlesden-Popper

- Ln\(_2\)MO\(_{4+\delta}\)

- Oxygen vacant sites
- \(H_2O\) insertion
- Couche Ln\(_2O_2\)
- Couche MO\(_2\)

- La\(_2\)NiO\(_{4+\delta}\)
- Nd\(_2\)NiO\(_{4+\delta}\)
- Pr\(_2\)NiO\(_{4+\delta}\)

Materials and processes: Cathode (2)

- Electrochemical measurements
  - Symmetric electrode/electrolyte/electrode half cells
    - Preparation of dense BaCe$_{0.9}$Y$_{0.1}$O$_{3-d}$ electrolyte pellets
    - Electrode ink (particle size < 1 mm) screen printed
    - Electrode layer sintered between 1000 and 1200 °C
  - Electrode layers with controlled microstructure (thickness and porosity)

\[ \eta \text{ cath (V / Pt)} \]

\[ \log (I_{dc}) \]

\[ \text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_{3-d} \]

\[ \text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-d} \]

\[ \text{Pr}_2\text{NiO}_{4+\delta} \]

\[ \text{PrBaCo}_2\text{O}_{5+\delta} \]

- BSCF (ASR ≈ 1Ω cm$^2$ @ 600°C) appear as the most promising cathode materials for H$^+$-SOFC