Requirements, selection and electrochemical studies of new cathode materials for proton ceramic fuel cells

F. Mauvy\textsuperscript{(a)}, A. Grimaud\textsuperscript{(a)}, J. M. Bassat\textsuperscript{(a)}, J. C. Grenier\textsuperscript{(a)}, J. Dailly\textsuperscript{(b)} and M. Marrony\textsuperscript{(b)}

\textsuperscript{(a)}ICMCB-CNRS, 87. Av. du Dr Schweitzer, F-33608 Pessac cedex, France
\textsuperscript{(b)}EDF- ElfER Emmy-Noether-Strasse 11, 76131 Karlsruhe- Germany
Introduction Protonic Conducting Solid Oxide Fuel Cell H⁺-SOFC

Electrochemical system:

H₂ + ½ O₂ → H₂O  ∆rG° < 0

Chemical energy (H₂) ➔ Electrical energy and heat

Increase the temperature

Decrease the temperature

2H₂O ➔ 2H₂ + O₂

Hydrogen oxidation

H₂ → 2H⁺ + 2e⁻

Oxygen reduction

½ O₂ + 2H⁺ + 2e⁻ → H₂O

Water formation at the cathode = main issue
Introduction Protonic Conducting Solid Oxide Fuel Cell H⁺-SOFC

1) Oxygen reduction on electrode surface

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

2) \text{O}^{2-} \text{ diffusion and water creation at electrode / electrolyte interface}

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

Mechanism we are looking for

1) \text{H}^+ \text{ transfer and diffusion}
2) Water formation at the air / electrode interface

\[
\frac{1}{2} \text{O}_2 + 2 \text{e}^- + 2 \text{H}^+ \rightarrow \text{H}_2\text{O}
\]
Requirements for H⁺-SOFC cathode:

- Electronic conductivity > 100 S.cm⁻¹
  Four probes measurement

- Ionic conductivity
  \[ H^+ \sim 10^{-2} - 10^{-3} \text{ S.cm}^{-1} (\sigma_{\text{electrolyte}}) \]
  No methods to measure

- Good electrocatalytic properties towards oxygen reduction
  Impedance Spectroscopy measurements

- Stability under wet air
1) Selection of Mixed Ionic Electronic Conducting oxides MIEC and study of their conductivities

2) Hydration studies and Electrochemical measurements

3) Study of the influence of the physical properties (oxygen non-stoichiometry, electronic conductivity)

4) Conclusion
1. Selection of electrode materials

Mixed Protonic Electronic Conducting oxides

Non stoichiometric oxides

Transition metal

Oxygen non-stoichiometry

Hydration

Perovskites

AMO$_{3-\delta}$

Ln$_2$MO$_4+\delta$

Double perovskites

LnBaM$_2$O$_{5+\delta}$

(Ln,Ba)MO$_3-\delta$

Ruddlesden-Popper phases

Ln$_2$MO$_{4+\delta}$

La$_{0.6}$Sr$_{0.4}$Fe$_{0.8}$Co$_{0.2}$O$_3-\delta$

Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_3-\delta$

PrBaCo$_2$O$_{5+\delta}$

Pr$_2$NiO$_{4+\delta}$

Mixed Protonic Electronic Conducting oxides

O$_{2(g)}$

H$_2$O$_{(g)}$

e$^-$

H$^+$

Transition metal

σ$_e$

σ$_{O_2^-}$

Hydration

σ$_{H^+}$

Mixed Protonic Electronic Conducting oxides

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Mixed Protonic Electronic Conducting oxides

O$_{2(g)}$

H$_2$O$_{(g)}$

e$^-$

H$^+$

Transition metal

σ$_e$

σ$_{O_2^-}$

Hydration

σ$_{H^+}$
1. Characterization of electrode materials

- Physical characterizations

**Oxygen content (dry air)**

![Graph of oxygen content vs. temperature for various materials](image1.png)

- Large oxygen non-stoichiometry for $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$, $\text{PrBaCo}_2\text{O}_{5+\delta}$ and $\text{Pr}_2\text{NiO}_4+\delta$

- Low oxygen non-stoichiometry for $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_{3-\delta}$

**Electrical conductivity (dry air)**

![Graph of electrical conductivity vs. temperature for various materials](image2.png)

- $\sigma_e >$ several dozens of $\text{S.cm}^{-1}$ at 600°C
- Large enough for cathode application

⇒ What about the hydration in these MIEC oxides?
2) Hydration properties and Electrochemical measurements

- are electrode materials hydrated or not ?

- Determination of the RDS of the electrode reaction
2.1. Hydration properties of electrode materials

Measure hydration in oxides is technically complicated

**Hydration step**
500°C / 12h under air / 0.10 bar H₂O

**Dehydration step**
TGA (1°C/min) under dry air up to 1000°C
2.1. Hydration properties of electrode materials

Measure hydration in oxides is technically complicated

**Hydration step**
- 500°C / 12h under air / 0.10 bar H₂O

**Dehydration step**
- TGA (1°C/min) under dry air up to 1000°C

**Barium containing oxides** = large hydration but low stability (BaCO₃ formation)

⇒ Basic properties of barium
2.2. Electrochemical performances of electrode materials

1) Preparation of symmetrical half-cell

2) Electrochemical Impedance Spectroscopy (EIS) measurements

**Polarization resistances Rp (I_{dc}=0)**

- Air / 0.03 bar H₂O
  - La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-δ}
  - Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ}
  - Pr_{2}NiO_{4+δ}

**Tafel Plots (I_{dc} ≠ 0)**

- Air / 0.03 bar H₂O
  - La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-δ}
  - Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ}
  - Pr_{2}NiO_{4+δ}

- Pr_{2}NiO_{4+δ} and PrBaCo_{2}O_{5+δ} give the best performances (lowest Rp and overpotentials)
2.3. Electrochemical behaviors vs p(H₂O)

- Determination of rate determining steps: measurements vs. pH₂O

![Graph showing electrochemical behaviors vs pH₂O for different materials.](image)

- Rp increases vs. pH₂O for La₀.₆Sr₀.₄Fe₀.₈Co₀.₂O₃₋δ
- Rp decreases vs. pH₂O for Ba₀.₅Sr₀.₅Co₀.₈Fe₀.₂O₃₋δ
2.3. Study of rate determining steps

- Determination of rate determining steps: measurements vs. pH$_2$O

```
<table>
<thead>
<tr>
<th>pH$_2$O values</th>
<th>0.03 bar</th>
<th>0.06 bar</th>
<th>0.10 bar</th>
<th>0.15 bar</th>
<th>0.20 bar</th>
<th>0.30 bar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr$<em>2$NiO$</em>{4+δ}$</td>
<td>□</td>
<td>■</td>
<td>▲</td>
<td>▼</td>
<td>□</td>
<td>□</td>
</tr>
<tr>
<td>La$<em>{0.6}$Sr$</em>{0.4}$Fe$<em>{0.8}$Co$</em>{0.2}$O$_3$-δ</td>
<td>□</td>
<td>■</td>
<td>▲</td>
<td>▼</td>
<td>□</td>
<td>□</td>
</tr>
</tbody>
</table>
```

pH$_2$O increases

2.4. Study of rate determining steps / Conclusion

**MIEC (O²⁻ / e⁻) oxides**

La₀.₆Sr₀.₄Fe₀.₈Co₀.₂O₃₋δ

- Low δ₀ and no hydration
- Water formation at the electrolyte / electrode interface
- ➔ Blocking effect and low electrochemical performances

**MIEC (O²⁻ / H⁺ / e⁻) oxides**

Ba₀.₅Sr₀.₅Co₀.₈Fe₀.₂O₃₋δ, PrBaCo₂O₅₊δ and Pr₂NiO₄₊δ

- Large δ₀ and hydration (even low)
- Proton transfer and OHΟ⁻ formation under high pH₂O
- ➔ Good electrochemical performances
3) Study of the influence of the physical properties (oxygen non-stoichiometry, electronic conductivity, etc …)

exemple of the oxygen over-stoichiometric $\text{Pr}_{2-\delta}\text{Sr}_x\text{NiO}_{4+\delta}$
3.1. Influence of physical properties / Pr$_{2-x}$Sr$_x$NiO$_{4+\delta}$

Modification of oxygen over-stoichiometric phase: Pr$_{2-x}$Sr$_x$NiO$_{4+\delta}$ ($x = 0, 0.1, 0.2$ and $0.5$)

**Stoichiometric Pr$_2$NiO$_4$**

- Orthorhombic (Bmab)

**Pr$_{2-x}$Sr$_x$NiO$_{4+\delta}$**

- Orthorhombic (Bmab or Fmmm)

**Stabilization process**

**Oxygen over-stoichiometry decreases**

**Structural stresses in stoichiometric compound:**
- Pr$^{3+}$ small cation $\rightarrow$ Pr$_2$O$_2$ in extension
- Ni$^{2+}$ large cation $\rightarrow$ NiO$_2$ in compression

**Pr$^{3+}$ substitution by Sr$^{2+}$:**
- Sr$^{2+}$ larger than Pr$^{3+}$ (1.31 $\rightarrow$ 1.179 Å)
- Ni$^{2+}$ oxidation into Ni$^{3+}$ (0.69 $\rightarrow$ 0.60 Å)
3.1. Influence of physical properties / Pr$_{2-x}$Sr$_x$NiO$_{4+δ}$

Modification of oxygen over-stoichiometric phase: Pr$_{2-x}$Sr$_x$NiO$_{4+δ}$ ($x = 0, 0.1, 0.2$ and $0.5$)

$$H_2O + O^{x}_O \rightarrow OH^\cdot_0 + OH^\cdot_i$$

Slight increase of $\sigma_\varepsilon$ vs. [Sr$^{2+}$]

$\Rightarrow$ Ni$^{2+}$ oxidation into Ni$^{3+}$

by charge compensation

3.1. Influence of physical properties / Pr$_{2-x}$Sr$_x$NiO$_{4+\delta}$

Modification of oxygen over-stoichiometric phase: Pr$_{2-x}$Sr$_x$NiO$_{4+\delta}$ ($x = 0, 0.1, 0.2$ and $0.5$)

\[ H_2O + O^x_O \rightarrow OH^+_O + OH^-_i \]

- Oxygen content decreases
- Water insertion sites increases
- Use of cation Sr$^{2+}$ with basic properties

3.2. Electrochemical measurements / Pr\(_{2-x}\)Sr\(_x\)NiO\(_{4+\delta}\)

Modification of oxygen over-stoichiometric phase: Pr\(_{2-x}\)Sr\(_x\)NiO\(_{4+\delta}\) (x = 0, 0.1, 0.2 and 0.5)

\[ H_2O + O_\text{O}^x \rightarrow OH_\text{O}^- + OH_i^- \]

- Rp increases vs. [Sr\(^{2+}\)]

**Graph:**

- Plot of \(R_p\) vs. \(1000/T\) for different compositions.

- Air / 0.03 bar H\(_2\)O

- \(R_p\) values for different compositions:
  - Pr\(_2\)NiO\(_{4+\delta}\)
  - Pr\(_{1.5}\)Sr\(_{0.5}\)NiO\(_{4+\delta}\)
  - Pr\(_{1.8}\)Sr\(_{0.2}\)NiO\(_{4+\delta}\)
  - Pr\(_{1.9}\)Sr\(_{0.1}\)NiO\(_{4+\delta}\)

3.2. Electrochemical measurements / Pr$_{2-x}$Sr$_x$NiO$_{4+\delta}$

Modification of oxygen over-stoichiometric phase: Pr$_{2-x}$Sr$_x$NiO$_{4+\delta}$ ($x = 0$, 0.1, 0.2 and 0.5)

- R$_{LF}$ increases vs. [Sr$^{2+}$]
- No more effect of pH$_2$O on LF resistances
  ➞ No hydration?

- Strong increase of R$_{MF}$ vs. [Sr$^{2+}$]
- R$_{MF}$ increases vs. pH$_2$O for Pr$_{1.5}$Sr$_{0.5}$NiO$_{4+\delta}$
  ➞ No more proton transfer

➢ To stabilize the structure decreases the hydration

Improvement of the electrochemical performances with ionic and protonic conduction

4. Characterization of electrode materials / Conclusion

Improvement of the electrochemical performances with ionic and protonic conduction

Rp (Ω·cm²) 600°C

10⁴

10²

10⁰

e⁻ Conduction

O²⁻ / e⁻ Conduction

H⁺ / O²⁻ / e⁻ Conduction

La₀.₆Sr₀.₄Fe₀.₈Co₀.₂O₃₋δ

Ba₀.₅Sr₀.₅Co₀.₈Fe₀.₂O₃₋δ

PrBaCo₂O₅₋δ

Pr₂NiO₄₊δ

Pt
4. Conclusion / Prospects

- Selection of Mixed Ionic Electronic Conducting oxides
  - Characterization of their conductivity (O^{2-} and e^-)
  - Study of their hydration properties
  - Characterization of their electrochemical behavior
    - Evidence of the role of proton on the oxygen reduction reaction

- Understanding of the influence of oxygen non-stoichiometry on electrochemical behavior

- Development of H^+-SOFC single cell with optimized materials

~ 180 mW.cm\(^{-2}\) at 0.6 V and 600°C
Thank you very much for your attention
2.3. Definition of the elementary steps of the oxygen reduction

Definition of steps involved in the oxygen reduction and water formation at the H⁺-SOFC cathode.

**Triple conducting O²⁻ / H⁺ / e⁻ perovskite**

1. $\text{O}_2(\text{g}) \rightarrow \text{O}_2(\text{ads})$

2. $\text{O}_2(\text{ads}) \rightarrow 2\text{O}(\text{ads})$

3. $\text{O}(\text{ads}) + 2\text{e}^- + \text{V}_0 \rightarrow \text{O}_0^x$

4. $\text{OH}_0^{-} (\text{BCY10}) + \text{O}_0^x(\text{cath}) \rightarrow \text{O}_0^x(\text{BCY10}) + \text{OH}^{-}(\text{cath})$

5. $2\text{OH}^- \rightarrow \text{H}_2\text{O}(\text{ads}) + \text{O}_0^x + \text{V}_0$

6. $\text{H}_2\text{O}(\text{ads}) \rightarrow \text{H}_2\text{O}(\text{g})$

2.3. Definition of the elementary steps of the oxygen reduction

Definition of steps involved in the oxygen reduction and water formation at the H⁺-SOFC cathode

Triple conducting O²⁻ / H⁺ / e⁻ perovskite

\[ Rp \propto pO_2^{-n} \times pH_2O^{-m} \]

<table>
<thead>
<tr>
<th>Steps</th>
<th>( pO_2^{-n} )</th>
<th>( pH_2O^{-m} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>1/2</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>1/4</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>1/2</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>6</td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>

2.3. Study of rate determining steps

- Middle and low frequencies resistances dependence vs. pH\(_2\)O

**Middle frequency**

- Middle frequency Low frequency

  - \(R_{\text{MF}}\) increases for \(\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_{3-\delta}\) vs. pH\(_2\)O
  - Does not correspond to any elementary step
  - pH\(_2\)O\(^{-1/2}\) dependence for \(R_{\text{MF}}\text{ Pr}_2\text{NiO}_{4+\delta}\)
  - Proton transfer as rate determining step

**Low frequency**

- ~ pH\(_2\)O\(^{-1}\) dependence for \(R_{\text{LF}}\) \(\text{Pr}_2\text{NiO}_{4+\delta}\), \(\text{PrBaCo}_2\text{O}_{5+\delta}\) and \(\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}\)
  - Water formation and/or exhaust on the surface of the electrode as rate determining step