Reversible Solid Oxide Cells: Limitations and Possibilities

Mogensen, Mogens Bjerg; Ebbesen, Sune Dalgaard; Graves, Christopher R.; Sun, Xiufu; Tao, Youkun; Chen, Ming; Jacobsen, Torben

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REVERSIBLE SOLID OXIDE CELLS:
LIMITATIONS AND POSSIBILITIES

Mogens B. Mogensen, Sune D. Ebbesen,
Christopher R. Graves, Xiufu Sun, Youkun Tao, Ming Chen, Torben Jacobsen
Department of Energy Conversion and Storage

Invited presentation

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Outline

1. Introduction
2. SOC type and performance
3. Thermodynamic stability of materials and gases
4. Temperature gradients and mechanical stability
5. Possibilities - what to do?
6. Conclusions
Introduction

• We need conversion and storage devices to promote renewable energy from intermittent sources such as wind and solar

• Solid oxide cell (SOC) may be used as solid oxide electrolysis cell (SOEC) as well as solid oxide fuel cell (SOFC); it is fully reversible for \( \text{H}_2\text{O}/\text{H}_2 \) and \( \text{CO}_2/\text{CO} \) and mixtures of them

• SOC has a considerable potential in this context, but is not the market yet in spite of several decades of intense R&D

• What are the limitations?

• Are there possibilities to push the limitations?
SOC type

**Ni-YSZ supported**

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**Ni/YSZ support**

**Ni/YSZ electrode**

**YSZ electrolyte**

**LSM-YSZ electrode**

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10 μm      Acc. voltage: 12 kV      SE image

WD = 13 mm      Photo No. = 2165      Time: 14:58:29

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DTU Energy Conversion, Technical University of Denmark
SOEC Cell performance

World record?

\[ i - V \] curves for a Ni-YSZ-supported Ni/YSZ/LSM SOC: electrolyzer (negative current density) and fuel cell (positive current density) at different temperatures and steam or CO\(_2\) partial pressures - balance is H\(_2\) or CO. S.H. Jensen et al., International Journal of Hydrogen Energy, 32 (2007) 3253

DTU Energy Conversion, Technical University of Denmark
Thermodynamics of H$_2$O Electrolysis

H$_2$O → H$_2$ + $\frac{1}{2}$O$_2$

Energy demand (kJ/mol)

Temperature (°C)

Energy ("volt") = Energy (kJ/mol)/2F

E$_{tn}$ = $\Delta$H/2F

$\Delta$H/$\Delta$G > 1 , $\varepsilon$ = 100 % at E = E$_{tn}$ (if no heat loss)

Price $\propto$ 1/i [A/cm$^2$],

i $\propto$ E$_{cell}$ - $\Delta$G/2F
Thermodynamic stability of materials and gases

• Often degradation rates are reported as a function of current density even though it most often would be more appropriate to report as a function of electrode potentials and overpotentials.

• Naturally, the overvoltage and current density are directly related for a given cell, but

• Thermodynamic stability is directly related to electrode potential (vs. a reference, e.g. 1 atm. O₂ at given temperature) for given cell materials irrespective structural details such as particle size in composite electrodes.
Thermodynamic and mechanical stability of YSZ, Ni-YSZ, LSM-YSZ, CO etc.

- $\Delta G_f \approx -975 \text{ kJ/mol ZrO}_2$ at 800 °C - a voltage stability range of ca. 2.5 V - the very maximum, but realities are worse

- SOFC mode:
  - reactions between La,Sr based perovskite oxygen electrodes and YSZ
  - Re-oxidation of Ni in Ni-YSZ – the redox problem

- SOEC mode:
  - 1 ppm Zr into Ni at ca. -1.5 V, 850 °C - impurities make worse
  - carbon fiber formation in $\text{CO}_2-\text{H}_2\text{O}$ co-electrolysis if high diffusion limitation, Y. Tao et al., submitted to ECST
  - $\text{O}_2$ bubble formation with weakening of YSZ near LSM at high oxygen electrode overpotential ($\sim 60 \text{ mV at } 850 \degree \text{C}$), R. Knibbe et al., J. Electrochem. Soc., 157 (2010) B1209

- Mechanical strength: limitation for ceramic supported cells!
SOC degradation – in a bad case

850 °C, 10 % H₂ + 45 % H₂O + 45 % CO₂ to Ni/YSZ electrode and O₂ at LSM/YSZ electrode. Current density -1 A/cm², conversion degree 62 %.
Ni-YSZ cermet after test in previous graph

Detrimental nano-particle formation on Ni-particle surfaces breaking good contact to YSZ
Fast degradation > ca. 1 A cm\(^{-2}\)

- 850 °C, single cell, steam, -2 A cm\(^{-2}\) for 188 h
- Electrolyte conductivity degradation - near oxygen electrode
- TEM reveals that it is due to O\(_2\) bubble precipitation inside the electrolyte near the O\(_2\) LSM/YSZ-electrode destroying \(\sigma_{O_2^-}\)

This is to an extent a mechanical problem – O\(_2\) bubble formation is limited by YSZ creep only

Temperature measured outside cell - on O₂-electrode side
S. Ebbesen et al. Submitted to ECST
In-plane cracks in the YSZ near LSM electrode is often observed after test at high current density $> 1 \text{ A cm}^{-2}$

Could this be due to thermal gradients?
Heat sources

Diffusion

$i^2R_{p,Ni} - T\Delta S_{H2/H2O/O2-}$

$i^2R_s$

$i^2R_{p,O2} - T\Delta S_{O2-/O2}$

n-p recomb.

Support

Ni - YSZ

YSZ

LSM - YSZ
Heat sources

- \( i^2R \) is always positive heat irrespective of SOFC or SOEC
- Diffusion is always positive heat

- Reversible Peltier entropies of the single electrode reactions have a different nature:
  - Oxygen electrode, SOFC cathode: \( \Delta S_c = 46.9 \text{ J K}^{-1} (\text{mol e}^-)^{-1} \)
  - Hydrogen electrode, SOFC anode: \( \Delta S_a = -31.8 \text{ J K}^{-1} (\text{mol e}^-)^{-1} \)
  - \(-T\Delta S_c\) is positive heat in SOFC mode and negative heat (i.e. cooling) in SOEC mode

\[
2 \text{O}^{2-} \rightarrow \text{O}_2 + 4 \text{e}^- \quad 850 \, ^\circ \text{C}: \quad T\Delta S_c = +50.3 \text{ kJ (mol e}^-)^{-1} \\
2 \text{H}_2\text{O} + 4 \text{e}^- \rightarrow 2 \text{H}_2 + 2 \text{O}^{2-} \quad 850 \, ^\circ \text{C}: \quad T\Delta S_a = -34.1 \text{ kJ (mol e}^-)^{-1} \\
\]

\( \Delta S \) values from: Ahlgren and Poulsцен: SSI 70/71 (1994) 528

\[ n-p \text{ is again a different matter only important for EC mode } \]
## Data for calculations of electron conduction through the YSZ and p-n recombination heat

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrolyte thickness/µm</td>
<td>10</td>
</tr>
<tr>
<td>T/K</td>
<td>1123.15 = 850 °C</td>
</tr>
<tr>
<td>( pO_2 ) (left electrode)/bar</td>
<td>5.11E-18</td>
</tr>
<tr>
<td>( pO_2 ) (right electrode)/bar</td>
<td>1</td>
</tr>
<tr>
<td>Electrode resistance at left electrode/ohm cm²</td>
<td>0.4</td>
</tr>
<tr>
<td>Electrode resistance at right electrode/ohm cm²</td>
<td>0.05</td>
</tr>
<tr>
<td>Electronic charge transfer resistance (both electrodes)/ohm cm²</td>
<td>0.01</td>
</tr>
<tr>
<td>( \sigma_{YSZ} )/ S cm⁻¹</td>
<td>0.046</td>
</tr>
<tr>
<td>( D_h )/ cm²s⁻¹</td>
<td>1.59E-06</td>
</tr>
<tr>
<td>( D_e )/ cm²s⁻¹</td>
<td>2.44E-07</td>
</tr>
<tr>
<td>Cell voltage/V</td>
<td>1.3</td>
</tr>
<tr>
<td>( \phi_{right} - \phi_{left} )/V</td>
<td>0.015</td>
</tr>
<tr>
<td>Leak current ( i_{pn} )/A cm⁻²</td>
<td>-0.003</td>
</tr>
<tr>
<td>Total current, ( i )/A cm⁻²</td>
<td>-0.71</td>
</tr>
</tbody>
</table>
Potentials, e & p concentrations, 1.3 V

T. Jacobsen et al., to be published

Procedure given in:
T. Jacobsen et al., ECS Transactions, 13, 259 (2008)
Heat evolution at p-n junction - 1.3 V

-0.71 A cm$^{-2}$, e- leak: -3 mA cm$^{-2}$  850 °C
Potential and e & p concentrations, 1.7 V
Heat evolution at p-n junction - 1.7 V

-1.57 A cm$^{-2}$, e- leak: -77 mA cm$^{-2}$  850 °C
Possibilities that we see

1. Our state-of-the-art cell can now run stable over 1000 h at 800 °C with 1 A cm\(^{-2}\)

2. We are in the process of improving the basis for safe operation though further detailed measurements and modeling

3. Our improved understanding makes it possible accelerate the R&D further

4. We will look into several aspects of mechanical properties and cell design

5. We anticipate significant improvements though further basic materials and electrochemical research
SOC stability during constant current electrolysis test compared to reversible cycling test of 1 h EC + 5 h FC. During open-circuit and FC mode, ~25 L/h of pH₂/pH₂O ≈ 50/50 and EC mode ~13 L/h of pH₂/pH₂O≈10/90 gas was supplied. Pure O₂ at the O₂-electrode.
Conclusion

In spite of all the limitation we still think:

1. The reversible SOC has the greatest potential as an energy converter for chemical storage of renewable energy

2. There are still many possibilities for further significant improvement of the SOC

3. We must put more emphasis on mechanical properties and materials compatibility

4. We have already started 😊
Acknowledgement

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• Danish Programme Committee for Nano Science and Technology, Biotechnology and IT
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Thank you for your attention!