Reversible Solid Oxide Cells: Limitations and Possibilities

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REVERSIBLE SOLID OXIDE CELLS: LIMITATIONS AND POSSIBILITIES

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Invited presentation

SSI-19 Kyoto, Japan, June 2 - 7, 2013
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

Ni/YSZ support

Ni/YSZ electrode

YSZ electrolyte

LSM-YSZ electrode

10 µm  Acc. voltage: 12 kV  SE image

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

$-V$ 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 H₂O Electrolysis**

\[ \text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2 \]

**Energy demand (kJ/mol)**

- **Liquid**
- **Gas**

**Total energy demand (\(\Delta H_f\))**

**Energy (“volt”)** = Energy (kJ/mol)/2F

\[ E_{\text{tn}} = \frac{\Delta H}{2F} \]

\[ E_{\text{cell}} = E_{\text{tn}} \]

\[ \frac{\Delta H}{\Delta G} > 1 \quad , \quad \varepsilon = 100 \% \quad \text{at} \ E = E_{\text{tn}} \quad \text{(if no heat loss)} \]

\[ i \propto E_{\text{cell}} - \frac{\Delta G}{2F} \]

\[ \text{Price} \propto \frac{1}{i} \quad [\text{A/cm}^2] \]

**Temperature (°C)**

- 0 100 200 300 400 500 600 700 800 900 1000
- 0 50 100 150 200 250 300

**Energy demand (Volt)**

- 0.00
- 0.26
- 0.52
- 0.78
- 1.04
- 1.30
- 1.55
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 of 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 CO$_2$-H$_2$O co-electrolysis if high diffusion limitation, Y. Tao et al., submitted to ECST
  - O$_2$ bubble formation with weakening of YSZ near LSM at high oxygen electrode overpotential (~ 60 mV at 850 °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 A cm$^{-2}$

Could this be due to thermal gradients?
Heat sources

Diffusion

$\frac{i^2 R_{p,Ni}}{-T \Delta S_{H_2/H_2O/O_2^-}}$

$\frac{i^2 R_s}{-T \Delta S_{O_2^-/O_2}}$

$n-p$ recomb.
Heat sources

- $i^2R_x$ 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: $\Delta S_c = 46.9 \text{ J K}^{-1} \text{ (mol e}^{-}\text{)}^{-1}$
  - Hydrogen electrode, SOFC anode: $\Delta S_a = -31.8 \text{ J K}^{-1} \text{ (mol e}^{-}\text{)}^{-1}$
- $-T\Delta S_c$ is positive heat in SOFC mode and negative heat (i.e. cooling) in SOEC mode

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

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

n-p 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>Parameter</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>$p_{O_2}$(left electrode)/bar</td>
<td>5.11E-18</td>
</tr>
<tr>
<td>$p_{O_2}$(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>$D_n$/ 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 1.5 1.7</td>
</tr>
<tr>
<td>$(\varphi_{right} - \varphi_{left})$/V</td>
<td>0.015 0.024 0.032</td>
</tr>
<tr>
<td>Leak current $i_{pn}$/A cm⁻²</td>
<td>-0.003 -0.014 -0.077</td>
</tr>
<tr>
<td>Total current, $i$/A cm⁻²</td>
<td>-0.71 -1.14 -1.57</td>
</tr>
</tbody>
</table>
Potentials, e & p concentrations, 1.3 V

π, φ, cₑ, cₜ

T. Jacobsen et al. to be published

Procedure given in:
T. Jacobsen et al., ECS Transactions, 13, 259 (2008)

6 January 2014
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.

C. Graves et al., submitted.
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
• The work of many colleagues over the years

Thank you for your attention!