Understanding electro-catalysis to design perovskite based electrodes for Solid Oxide Cells

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High Temperature Solid Oxide Cells

- Conversion at high efficiency
- Power Generation (> 60 % net)
- Possibility to co-electrolyse H₂O / CO₂ into syngas
- SOC are reversible

Same materials/catalysts for SOFC & SOE operation

Do SOFC perform well in Electrolysis? Specific degradation mechanisms? May optimized SOFC be further optimized for SOE operation?
Motivation – *Power generation*

- Ni based cermet SoA electrocatalysts
- Ni surface poisoned with $\text{H}_2\text{S}$

- Upstream desulfurizing unit
- Failure of desulfurizing unit?

Natural Gas → Sulfur compounds → Diesel
Motivation – *Power-to-X?*

High penetration of renewables induces mismatch between electricity generation and electricity consumption.

*Electricity price on the DE-AT market on 1st of May 2018* (Source EPEX)

Negative price

The energy transition requires large energy storage capacities

ca. 849 GWh at – 5€/MWh
Power-to-X – What is beyond the X?

- Store the surplus of energy in alternative vectors (*hydrogen, fuels, heat...*)

- Delocalize in the space and in the time the release of the energy surplus (*other infrastructures*)

- Place the kWh of stored energy on other markets with higher potential of gains
Do SOFC perform well in Electrolysis? Specific degradation mechanisms? May optimized SOFC be further optimized for SOE operation?
Air Electrode:
Lanthanum Strontium Cobalt Iron perovskite
mixed ionic and electronic conductor

1/2 O₂ + 2e⁻ → O²⁻

σ_{CGO} (e⁻) ≈ σ_{CGO} (O²⁻)
σ_{LSCF} (e⁻) ≥ σ_{LSCF} (O²⁻)

Porous Composite Gadolinia Doped Ceria – Lanthanum Strontium Cobalt Iron Oxide
Air Electrode: LSCF-CGO based materials

Reaction mechanism

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>$k^0$ (or $s_i^0$)</th>
<th>$E_{act}$ (kJ·mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>$O_2 + \square_{LSCF} \rightleftharpoons O_2,LSCF$</td>
<td>$s_i^0 = 5.0 \cdot 10^{-1}$</td>
<td>0</td>
</tr>
<tr>
<td>R2</td>
<td>$O_2,LSCF + \square_{LSCF} \rightleftharpoons 2 \cdot O_{LSCF}$</td>
<td>$1.0 \cdot 10^{22}$ cm$^2$·mol$^{-1}$·s$^{-1}$</td>
<td>20</td>
</tr>
<tr>
<td>R3</td>
<td>$O_{CGO}^- + V_{CGO}^- \rightleftharpoons O_{O,CGO}^+ + \square_{CGO}$</td>
<td>$1.6 \cdot 10^{22}$ cm$^2$·mol$^{-1}$·s$^{-1}$</td>
<td>90.9</td>
</tr>
</tbody>
</table>

Charge-transfer reactions

| C1  | $O_{LSCF} + e^- \rightleftharpoons O_{LSCF}^-$                         | $1.4 \cdot 10^{16}$ cm$^2$·mol$^{-1}$·s$^{-1}$ | 181.4                    |
| C2  | $O_{LSCF}^- + V_{CGO}^- + e^- \rightleftharpoons O_{O,CGO}^+$           | $8.9 \cdot 10^{15}$ cm$^2$·mol$^{-1}$·s$^{-1}$ | 99.7                     |

Reaction kinetics and thermodynamics derived

Experimental data recorded on **symmetrical button cell (CGO electrolyte)** with **LSCF & LSCF I CGO composite cathodes**

V. Yurkiv et al, JES, 161(4), F480 (2014)
Air Electrode: LSCF-CGO based materials

\[ O_{\text{LSCF}} + e^- \rightleftharpoons O_{\text{LSCF}}^1 \]

Charge Transfer 1

\[ O_{\text{LSCF}}^1 + V_{\text{CGO}}^- + e^- \rightleftharpoons O_{\text{CGO}}^x + \square_{\text{LSCF}} \]

Charge Transfer 2

Gas Conversion

V. Yurkiv, et al., JES, 161(4), F480 (2014)
Air Electrode: LSCF-CGO based materials

Performance governed by the surface of exchange between:

(1) between the LSCF and gas phase: Increase Specific Surface Area of LSCF
(2) between LSCF and CGO: Composite electrode LSCF-CGO

- 1 order of magnitude by increasing SSA by 3

Composite LSCF-CGO with surface modification
CGO content to be adapted as a function of op. T
Air Electrode: LSCF - CGO based materials

**LSM - YSZ**

\[ \sigma_{YSZ} (O^{2-}) \gg \sigma_{YSZ} (e^-) \]

\[ \sigma_{LSM} (e^-) \gg \sigma_{LSM} (O^{2-}) \]

**LSCF - CGO**

\[ \sigma_{CGO} (e^-) \approx \sigma_{CGO} (O^{2-}) \]

\[ \sigma_{LSCF} (e^-) \geq \sigma_{LSCF} (O^{2-}) \]
Fuel electrode:
Lanthanum doped Strontium Titanate (LST)
"mixed" ionic and electronic conductor

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

\[
\sigma_{\text{GDC}} (\text{O}^{2-}) \approx \sigma_{\text{GDC}} (\text{e}^{-})
\]
\[
\sigma_{\text{LST}} (\text{e}^{-}) \geq \sigma_{\text{LST}} (\text{O}^{2-})
\]

Porous Composite Gadolinia Doped Ceria – Lanthanum doped Strontium Titanate

sulfur tolerance
redox stable (dimensionally)
Lanthanum doped Strontium Titanate (LST) Fuel Electrode

- Perovskite structure with cubic unit cell
- 5 atoms at surface – only one oxygen
- $6.7 \cdot 10^{18}$ sites·m$^{-2}$ which lead to total surface site density of $1.0 \cdot 10^{-5}$ mol·m$^{-2}$
- Types of species:
  - Two types of surface sites $O_{\text{LST}}$
  - Two hydroxyl groups: $O\text{H}_{\text{LST}}$, $O\text{H}_{\text{Sr}}$
  - Theoretically $OH$ group can exist at La surface site
  - Hydrogen adsorbed on Sr site, $H_{\text{Sr}}$ (hydride)

$H_2 + 2 O_{\text{LST}} \rightleftharpoons OH_{\text{LST}} + OH_{\text{LST}}$

$H_2O + O_{\text{LST}} + \square_{\text{LST}} \rightleftharpoons 2 OH_{\text{LST}}$

$O_{\text{LST}} + O_{\text{LST}} \rightleftharpoons O_2 + \square_{\text{LST}}$

V. Yurkiv, G. Constantin, A. Hornes, A. Gondolini, E. Mercadelli, A. Sanson, L. dessemond, R. Costa, J. Power Sources (2015), 287, 58
Lanthanum doped Strontium Titanate (LST) Fuel Electrode

Charge Transfer 1

Charge Transfer 2

Water dissociation

97 % H₂, 3 % H₂O, OCV

V. Yurkiv, G. Constantin, A. Hornes, A. Gondolini, E. Mercadelli, A. Sanson, L. Dessemond, R. Costa, J. Power Sources (2015), 287, 58
Ni-YSZ vs LST-CGO anode / CGO not MIEC

Ni-YSZ
• Hydrogen Charge Transfer is the rate limiting step
• Performance is governed by the length of triple phase boundaries

LST-CGO
• Oxygen Charge Transfer is rate limiting
• Performance is governed by surfaces of exchange (LST I CGO & LST I Gas)

Surface to be increased
Thickness to be decreased

TPB length to be increased
Case Study - Sulfur Poisoning
**Ni-YSZ**
\[
\sigma_{\text{YSZ}}(O^2-) \gg \sigma_{\text{YSZ}}(e^-) \\
\sigma_{\text{LSM}}(e^-) \gg \sigma_{\text{LSM}}(O^2-) 
\]

**Ni-CGO**
\[
\sigma_{\text{CGO}}(O^2-) \approx \sigma_{\text{CGO}}(e^-) \\
\sigma_{\text{Ni}}(e^-) \gg \sigma_{\text{Ni}}(O^2-) 
\]

**LST-CGO**
\[
\sigma_{\text{CGO}}(O^2-) \approx \sigma_{\text{CGO}}(e^-) \\
\sigma_{\text{LST}}(e^-) \geq \sigma_{\text{LST}}(O^2-) 
\]

(tpb) length

\[
T < 600^\circ \text{C (?)} \\
\text{TPB} \\
T > 600^\circ \text{C (?)} \\
\text{TPB + CGO surface} 
\]
Sulfur poisoning in H₂/H₂O fuels: Ni/CGO vs. Ni/YSZ

850 °C, 0.5 A cm⁻², 97% H₂, 3% H₂O + 1, 2, 5, 10, 20 ppm H₂S

Different mechanisms
CGO as electro-active catalyst

Investigation of sulfur poisoning during reformate operation (CO/CO₂, CO/CO₂/H₂/H₂O, CH₄/H₂O)

Reversible short exposure poisoning

Methane steam reforming is inhibited under S-poisoning

CO Oxidation on Ni/CGO still possible even with 20 ppm H₂S (Not on Ni/YSZ) → higher sulfur tolerance

Eletrochemical conversion of CO on CGO surface

Sulfur Poisoning of Electrochemical Reformate Conversion on Nickel/Gadolinium-Doped Ceria Electrodes

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Fuel oxidation mechanism on Ni/CGO

CO oxidation on CGO surface possible
CO oxidation at TPB dominates, as CO strongly adsorbs on Ni
Fuel oxidation mechanism on Ni/CGO under Sulfur poisoning

CO oxidation

H₂ oxidation

WGS

Ni surface is blocked → CO oxidation at TPB deactivated
Surface process on CGO is still active

H₂ oxidation at TPB may still be active (smaller atom diameter)
Fuel oxidation mechanism on Ni/LST/CGO: Sulfur poisoning

Metal Supported Cell

LST – CGO seems to react faster to poisoning, higher degradation rate

LST – CGO – Ni seems more stable under poisoning conditions
Expected tolerance to Sulfur Poisoning

**Ni-YSZ**
\[
\sigma_{YSZ} (O^{2-}) \gg \sigma_{YSZ} (e^-)
\]
\[
\sigma_{LSM} (e^-) \gg \sigma_{LSM} (O^{2-})
\]
TPB length

**Ni-CGO**
\[
\sigma_{CGO} (O^{2-}) \approx \sigma_{CGO} (e^-)
\]
\[
\sigma_{Ni} (e^-) \gg \sigma_{Ni} (O^{2-})
\]
TPB length \( S_{CGO}=f(T) \)

**LST-CGO-Ni**
\[
\sigma_{CGO} (O^{2-}) \approx \sigma_{CGO} (e^-)
\]
\[
\sigma_{LST} (e^-) \geq \sigma_{LST} (O^{2-})
\]
TPB length
\[
S_{LST} \quad S_{CGO}=f(T)
\]

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(+++) \( tbc \)
Summary and conclusions

• **MIEC** materials offer increased electrochemically surfaces
• **TPB length** is not „always“ the critical parameter to control
• Optimal microstructure may differ depending on operating temperature

• *Multiplying reactive surfaces and the nature of those surfaces (metal, oxide) is a key to enhance tolerance of electrodes towards poisons*
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Thanks for your attention!