Physical Modeling of Solid Oxide Electrolysis Cells in CO-electrolysis mode

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Motivation

- Electricity from wind turbines and solar panels fluctuates.

- How can we store and use this surplus electricity?
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Power-to-Gas with SOECs in co-electrolysis operation:
- Simultaneous reduction of $\text{H}_2\text{O}$ and $\text{CO}_2$
- Production of syngas ($\text{H}_2 + \text{CO}$)

$\rightarrow$ Subsequent production of synthetic fuels, …

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Motivation

• Electricity from wind turbines and solar panels fluctuates.

Power-to-Gas with SOECs in co-electrolysis operation:
• Simultaneous reduction of H₂O and CO₂
• Production of syngas (H₂ + CO)

→ Subsequent production of synthetic fuels, …

• How can we store and use this surplus electricity?
• Control of the exhaust gas composition of SOECs
• Understanding of degradation phenomena
Numerical Framework NEOPARD-X\textsuperscript{[1,2]}

**Numerical Environment for the Optimization of Performance And Reduction of Degradation of $X$ (= energy conversion device)**

Developed at DLR since 2013 based on the open source software DuMu$^X$\textsuperscript{[3]} and DUNE \textsuperscript{[4]}

**NEOPARD-X\textsuperscript{[1,2]} features**
- 2D and 3D discretization of the cells
- Transport models for the cell layers
- Detailed electrochemical models
- Suitable for different technologies
- Transient simulations

**Fields of Application:**
- DMFC
- PEMFC
- SOEC
- ...

\textsuperscript{[1]}: Futter et al., JPS, 391(2018) 148.
\textsuperscript{[2]}: Futter et al., JPS, 410-411 (2019) 78-90.
\textsuperscript{[3]}: Flemisch et al., 2011, Adv. Water Resour., 34(9).
\textsuperscript{[4]}: https://dune-project.org/
SOEC Model

- Modeling domain & features

- Elementary kinetic modeling of co-electrolysis and RWGS

- Model validation under various operating conditions

- Impedance analysis & predictions

Diagram showing the components and process of a SOEC model.
SOEC Model

- 11 spatially resolved layers
- Detailed material properties
- Detailed gas transport
- Charge transport
- Energy transport
- Electrochemistry: thermodynamically consistent elementary kinetics
- Model for a commercial electrolyte-supported cell from Sunfire

\[ \xi^i = \phi \rho_{\text{mol}} x^i \]
\[ \psi^i = \frac{\rho_{\text{mol}}}{\mu} x^i K \nabla p + D_{\text{eff}}^i \rho_{\text{mol}} \nabla x^i \]

\[ \frac{\partial \xi^i}{\partial t} + \nabla \cdot \left( \psi^i - q^i \right) = 0 \]

\[ \frac{D_{\text{eff}}^i}{k_{\text{Knudsen}}} \left( \frac{
abla \Phi_{\text{ion}}}{\Phi_{\text{elec}} - \Phi_{\text{ion}}} \right) - q^i e^{2-} = 0 \]

\[ k^j = A T^e \exp \left( \frac{-\Delta g^j}{R T} \right) \]

\[ r_{\text{CTR},i} = k^j \prod_{i, \text{products}} \left( \frac{\alpha^i}{\sigma^i} \right)^{\gamma^j} \exp \left( \frac{(1 - \alpha) n F \Delta \phi}{R T} \right) \]

\[ q^i = \sum_j \frac{v^{ij} \sigma^i r^j}{\Gamma} \]
Elementary Kinetic Modeling

- Elementary kinetic modeling of co-electrolysis and RWGS on nickel:

\[
\begin{align*}
H_2(g) + 2(Ni) & \rightleftharpoons 2H(Ni) \\
O_2(g) + 2(Ni) & \rightleftharpoons 2O(Ni) \\
H_2O(g) + (Ni) & \rightleftharpoons H_2O(Ni) \\
CO_2(g) + (Ni) & \rightleftharpoons CO_2(Ni) \\
CO(g) + (Ni) & \rightleftharpoons CO(Ni) \\
CO_2(Ni) + (Ni) & \rightleftharpoons CO(Ni) + O(Ni) \\
OH(Ni) + (Ni) & \rightleftharpoons H(Ni) + O(Ni) \\
2OH(Ni) + (Ni) & \rightleftharpoons H_2O(Ni) + O(Ni) \\
H(Ni) + OH(Ni) & \rightleftharpoons H_2O(Ni) + (Ni) \\
O(Ni) + 2e^- & \rightleftharpoons (Ni) + O^2-(CGO)
\end{align*}
\]

\[
\frac{\partial \theta^i}{\partial t} = q^i \\
q^i = \sum_j \nu^{ij} \sigma^i r^j
\]

\[
r^j = k_f^j \prod_{i, \text{educts}} (\theta^i)^{v^{ij}} - k_r^j \prod_{i, \text{products}} (\theta^i)^{v^{ij}}
\]

\[
k_f^j = A T^n \exp\left(-\frac{E_{\text{act}}}{RT}\right) \\
k_r^j = k_f^j \exp\left(\frac{\Delta g^j}{RT}\right)
\]

\[
r^{CTR,j} = k_f^j \prod_{i, \text{educts}} (\theta^i)^{v^{ij}} \exp\left(\frac{(1 - \alpha)nF\Delta \phi}{RT}\right) \\
- k_r^j \prod_{i, \text{products}} (\theta^i)^{v^{ij}} \exp\left(\frac{\alpha nF\Delta \phi}{RT}\right)
\]

→ From elementary kinetic considerations the charge transfer step is the same, disregarding the fuel (H\textsubscript{2}O or CO\textsubscript{2})

[1]: Janardhanan & Deutschmann, JPS 62 (2006) 1192-1202
Model Validation

- Gas composition: 5% H₂, 63.7% H₂O, 31.3% CO₂
- H₂O/CO₂ ratio: 2.04

- Gas composition: 15.1% H₂, 63.7% H₂O, 21.2% CO₂
- H₂O/CO₂ ratio: 3.00

→ OCV decreases with higher CO₂ content of the gas
→ Efficiency decreases with decreasing temperature
Model Validation

**OCV:**

\[\text{H}_2\text{O}/\text{CO}_2 = 2\]
\[\text{H}_2\text{O}/\text{CO}_2 = 3\]

**0.6 A/cm\(^2\):**

\[\text{H}_2\text{O}/\text{CO}_2 = 2\]
\[\text{H}_2\text{O}/\text{CO}_2 = 3\]

→ H\(_2\)O (and H\(_2\)) improves the efficiency at OCV and under load
Model Validation

• Gas composition: 5% H<sub>2</sub>, 63.7% H<sub>2</sub>O, 31.3% CO<sub>2</sub> → H<sub>2</sub>O/CO<sub>2</sub> = 2.04

**OCV:**

- Peak at ~ 1Hz is temperature independent
- Peak at 10-100 Hz increases with decreasing temperature

→ At ~ 1Hz: Mass transport losses
→ 10-100 Hz: Kinetic losses due to charge transfer reaction
Model Validation

- Gas composition: 5% H₂, 63.7% H₂O, 31.3% CO₂ → H₂O/CO₂ = 2.04
- 0.6 A/cm² (0.5 A/cm² for 770°C):

  - Inductive peak becomes visible at ~ 0.1 Hz
  - Inductive peak increases with decreasing temperature

→ Where does induction come from?
Impedance Analysis

- Simulation of impedance spectra at OCV, 0.48 and 1 A/cm², H₂O/CO₂ = 3.00:

- Electrolyte ion conductivity increases with temperature

→ Inductance at a given current density depends on \( \frac{\partial T}{\partial i} \), i.e. \( \frac{\partial \sigma}{\partial i} \)
Model Predictions

- Fuel utilization of $\text{H}_2\text{O}$ and $\text{CO}_2$: $FU^i = \frac{m^i_{\text{in}} - m^i_{\text{out}}}{m^i_{\text{in}}} \times 100\%$

RWGS:

$\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$

$\rightarrow$ At low current density the $\text{H}_2\text{O}$ utilization becomes negative due to RWGS
Model Predictions

- Ratio between H₂O- and CO₂-electrolysis from balance for O(Ni):

  \[ 
  \begin{align*}
  \text{H}_2\text{O:} & \quad \text{OH(Ni)} + (\text{Ni}) \rightleftharpoons \text{H(Ni)} + \text{O(Ni)} \\
  \text{CO}_2: & \quad \text{CO}_2(\text{Ni}) + (\text{Ni}) \rightleftharpoons \text{CO(Ni)} + \text{O(Ni)} \\
  \text{CTR:} & \quad \text{O(Ni)} + 2e^- \rightleftharpoons (\text{Ni}) + \text{O}^2^-(\text{CGO})
  \end{align*} \]

  If \( r_{\text{H}_2\text{O}} < 0 \) \( \Rightarrow \) RWGS:

  \[ \chi_{\text{CO}_2} = \frac{1}{V_{CL} \int_{\Omega_{CL}} \frac{r_{\text{CO}_2} + r_{\text{H}_2\text{O}}}{r_{\text{CTR}}} dV} \]

  If \( r_{\text{H}_2\text{O}} > 0 \) \( \Rightarrow \) WGS:

  \[ \chi_{\text{CO}_2} = \frac{1}{V_{CL} \int_{\Omega_{CL}} \frac{r_{\text{CO}_2}}{r_{\text{CTR}}} dV} \]

  \[ \chi_{\text{H}_2\text{O}} = 1 - \chi_{\text{CO}_2} \]

  \( \Rightarrow \) CO₂-electrolysis at low current, H₂O-electrolysis at high current
Summary

I. A detailed 2D non-isothermal transient SOEC model including thermodynamically consistent elementary kinetics has been developed and validated under various operating conditions.

II. Experimentally observed inductive phenomena are explained from physical theory: They are caused by an increase of ionic conductivity with current/temperature.

III. In co-electrolysis, mainly CO₂ is converted at low current and H₂O is converted at high current.
Thank you for your attention

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