Study of Detailed Degradation Behavior of Solid Oxide Electrolyzer Cells (SOEC)

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Outline

• Introduction: Need for energy storage
  Principle of solid oxide electrolysis

• Motivation and concept

• Cell manufacturing and characterization

• Degradation study and results from post-mortem analyses

• Conclusion
Storage of Electricity from Renewable Energy Sources

- Need for energy storage
  - Increasing fluctuating power generation
  - Mobile applications

- Electrical energy difficult to store
  - Conversion to chemical energy

- Water electrolysis: \( \text{H}_2\text{O} + W_{\text{el}} \rightarrow \text{H}_2 + \frac{1}{2} \text{O}_2 \)

- Solid oxide electrolysis is one possible conversion technology
Principle of Solid Oxide Electrolysis

Advantages:

- High temperature (600 - 900° C)
  - Fast reaction kinetics
  - Low overvoltage
  - High efficiency & high current densities
- No noble metals as catalysts
- Fuel versatility: CO$_2$ electrolysis
  → Co-electrolysis of H$_2$O/CO$_2$ possible
  → Syn-gas production
  → External (or internal) hydrocarbon formation

Problem:
Low longevity - Degradation
Present Work – Motivation and Concept

Systematic study: operating parameter → degradation

- Temperature (T)
- Fuel gas humidity (AH)
- Current density (i)

Experimental concept:

- Degradation experiments for 1000 h
- Test rig – quadruple cell measurement
  - Identical temperature, gas supply (and also incidents)
  - Four different current densities simultaneously
- Fuel electrode supported cells from FZ Jülich and CeramTec
  - Ni-8YSZ support | Ni-8YSZ | 8YSZ | CGO | LSCF
Objectives

- To gain fundamental understanding of degradation processes
  - Distinguish between degradation processes
  - Identify degradation mechanisms
  - Correlate them with operating parameters

- To optimize cells for electrolysis operation

- To adapt operating parameters for low degradation
Manufacturing Steps of SOFC Anode-Supported Cells

- **Substrate**
  - Warm pressing with Coat Mix® powder or tape casting
  - **1200° C**

- **Anode**
  - Screen printing
  - **1100° C**

- **Electrolyte**
  - Cofiring of anode and electrolyte
  - **1400° C**

- **Cathode**
  - Current collector
  - Transparent electrolyte
  - **PVD-CGO**

- **Solid oxide fuel cell**
  - Laser-cutting to dimensions up to 200 x 200 mm²
Solid Oxide Electrolyser Cells: Planar Design

Materials

Anode: \((\text{La,Sr})(\text{Fe,Co})\text{O}_3\)

Diffusion barrier: CGO – 1-5 µm

Electrolyte: 8YSZ – 5-10 µm

Cathode: Ni/YSZ

Cathode Substrate: Ni/YSZ
I-V Curves at 750 °C as a Function of Steam Content
(Flow rates: 2 l/min H₂/H₂O, 3 l/min air)
I-V Curves at 800 °C as a Function of Steam Content
(Flow rates: 2 l/min H₂/H₂O, 3 l/min air)

Cell Voltage / V

Current density / A*cm²

-1.5 -1 -0.5 0 0.5 1 1.5

-0.5 0 0.5 1 1.5 2

800°C - 7%AH
800°C - 40%AH
800°C - 60%AH
800°C - 80%AH
Degradation Experiment and Impedance Data Interpretation

- 4 cells measured simultaneously at different current densities
- Linear degradation after initial phase
- Be careful with interpretation of voltage degradation rate
Degradation Experiment and Impedance Data Interpretation

$ASR(t) = \frac{U(t) - OCV}{i(t)}$

- Degradation rate at 1.5 A/cm² only 13 % higher than at 1.0 A/cm²
- Degradation rate at 0.5 A/cm² significantly lower
- ASR degradation rate about 30% compared to 3% voltage degradation (per 1000 h @ 0.5 A/cm²)
Degradation Experiment and Impedance Data Interpretation
Method 1: DRT-Analysis with parameter variation

Impedance - Spectra

Levenberg-Marquardt algorithm

DRT-Spectra

Information for improved CNLS fitting

Fuel electrode: 2 slpm 80% H2O, 20% H2
Oxygen electrode: 2 slpm Air
T = 800°C
Degradation Experiment and Impedance Data Interpretation
Method 2: Physico-chemical modelling

5 rate limiting processes:

- Ohmic contributions
- First Fuel Electrode (FE) Process: $1-2\cdot10^4$ Hz
  Charge transfer reaction at TPB coupled with ionic transport in porous electrode geometry
- Second Fuel Electrode (FE) Process: approx. $1\cdot10^3$ Hz
  Charge transfer coupled at TPB
- Oxygen Electrode Process: $1-2\cdot10^2$ Hz
- Mass transport limitation: $1-2\cdot10^1$ Hz
  Diffusion through FE-support along with gas conversion

→ Both methods are in good agreement!
Degradation Experiment and In-situ Data Interpretation

Equivalent circuit model

- **L₁**: High frequency induction
- **P₀**: Ohmic resistance (> $10^5$ Hz)
- **P₁**: Fuel electrode process A (~ $10^4$ Hz)
- **P₂**: Fuel electrode process B (~ $10^3$ Hz)
- **P₃**: Oxygen electrode process (~ $10^2$ Hz)
- **P₄**: Fuel electrode mass transport (~ $10^1$ Hz)
Influence of Current Density on Degradation

- Ohmic resistance contributes more than 50% of total ASR.
- Degradation of ohmic resistance is most severe.
- Oxygen electrode has small ASR but high contribution to degradation.
- Fuel electrode process 1 degrades while process 2 improves performance.
Influence of Current Density on Degradation

P_0: Ohmic resistance
- Obvious correlation with current density
- Linear degradation with time
Influence of Current Density on Degradation

P_1: Fuel electrode process 1

- Also obvious correlation with current density
- Degradation initially fast but slowing down with time
Influence of Current Density on Degradation

P_2: Fuel electrode process 2
- Offset of 1.0 A/cm² curve is likely artifact (compare process 3)
- Degradation independent of current density
- Initial improvement of performance
- Very stable after initial change
Influence of Current Density on Degradation

**P_3: Oxygen electrode process**
- Shift shown by 1.0 A/cm² curve is likely artifact (compare process 2)
- Initially stable → afterwards linear degradation
- Degradation independent of current density
Influence of Current Density on Degradation

P_4: Fuel electrode mass transport
- Very little degradation
- Independent of current density
Influence of Current Density on Degradation

Degradation after 1000 h
- Ohmic resistance: strong dependence on current density
  Dependence possibly exponential
Influence of Current Density on Degradation

Degradation after 1000 h

- Fuel electrode process 1: clear linear dependence on current density
- Other three processes: no current dependency
Humidification

Ohmic resistance ($R_0$):
- Dependent on current density

Fuel electrode polarization ($R_{1+2}$):
- Lower degradation rate at higher humidities…
- … but higher degradation dependence on current density
Humidification

Oxygen electrode polarization (R_3):
- Humidity has very little influence

Fuel electrode polarization (R_4):
- Generally small degradation
- Lower at higher humidity
- No obvious trend
Post-mortem Analysis – Electrolyte

Reference

1000 h @ OCV

1000 h @ 1.5 A/cm²

Ohmic resistance:
- Weakening of YSZ|CGO|LSCF interface → probably formation of cracks
- Visible cracks probably formed during sample preparation along weakened microstructure
Post-mortem Analysis – Oxygen Electrode

Reference 1000 h @ OCV 1000 h @ 1.5 A/cm²
Post-mortem Analysis – Oxygen Electrode

- Formation of a new crystalline compound
- Higher polarization \(\rightarrow\) change more pronounced
- More detailed analyses necessary for reliable information on new phase
Post-mortem Analysis – Oxygen Electrode

oxide/metal species
Post-mortem Analysis – Fuel Electrode

Percolation
- Ni almost completely percolated
- Ni can be separated from percolation network in cross section
EDX measurement: no Ni depletion

1000 h @ 1.5 A/cm², 850°C and 80% MH
Conclusion

- Correlation between degradation and current density has been investigated
- Ohmic resistance dominates degradation and increases with current density
- Oxygen electrode contributes significantly to degradation and is independent of current density
- Higher frequency fuel electrode process is significant for degradation and dependent of current density
- Lower frequency fuel electrode process is stable after initial activation and independent of current density
- No degradation in mass transport limitation
- Results of post-mortem analyses give further information and must be further evaluated
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Thank you for your attention