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
• Cell manufacturing
• Cell characterization
• Degradation measurements
• Conclusion and Outlook
Storage of Electricity from Renewable Energy Sources

- Need for energy storage
  - Increasingly 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
Hydrogen as Storage Option

Source: LBST
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: CO₂ electrolysis
  → Co-electrolysis of H₂O/CO₂ 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 optimise 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
- Solid oxide fuel cell

Anode
- Screen printing

Electrolyte
- Cofiring of anode and electrolyte
- Transparent electrolyte

Cathode
- Current collector
- PVD-CGO
- Laser-cutting to dimensions up to 200 x 200 mm²

1200°C → 1100°C → 1400°C
Solid Oxide Electrolyser Cells: Planar Design

Materials

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

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)
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

- 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 In-situ Data Interpretation

Equivalent circuit model

- $L_1$: High frequency induction
- $P_0$: Ohmic resistance ($> 10^5$ Hz)
- $P_1$: Fuel electrode process A ($\sim 10^4$ Hz)
- $P_2$: Fuel electrode process B ($\sim 10^3$ Hz)
- $P_3$: Oxygen electrode process ($\sim 10^2$ Hz)
- $P_4$: Fuel electrode mass transport ($\sim 10^1$ 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

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 humidities
- 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

- Probably Sr-segregation
  - High resolution XPS
- Contamination?
- Possibly some sintering

Reference 1000 h @ OCV
1000 h @ 1.5 A/cm²
Summary

- 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 significant for degradation and dependent on current density
- Lower frequency fuel electrode process is stable after initial activation independent of current density
- No degradation in mass transport limitation
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Thank you for your attention