Implementation of Developed Storage Material for First Prototypes of High-Temperature Rechargeable Oxide Batteries (ROB)

O.A. Tokariey, C.M. Berger, P. Orzessek, W. Braun, Q. Fang, W.J. Quadakkers, L. Blum, N.H. Menzler, O. Guillon

DKG-2015, Bayreuth, Germany
Outline

• Motivation and ROB advantages
• Working principle of the battery
• Storage material and its selection
• Battery test
• Conclusions
• Outlook
Motivation

German national energy concept of power generation – plan for 2050

- Photovoltaics
- Wind power
- Biomass
- Hydropower

Storage concepts

- Pumped-storage hydroelectricity
- Electrolysis
- Electrolysis + Methanation
- Rechargeable batteries

Renewable energy requires storage to be able to balance demand and supply
From Cell to ROB Battery

Cell

- cathode layer
- electrolyte layer
- anode layer
- anode substrate

Rechargeable oxide battery

- repeating unit 1
- repeating unit 2
- repeating unit n

- sealant
- interconnector
- storage material

Requirements: evenness, thickness uniformity, reproducibility, homogeneity, gas tightness, stackability

D. Roehrens et al., International journal of hydrogen energy (2015)
Rechargeable Oxide Battery
(working principle)

State of the storage is responsible for such characteristics: oxygen capacity, structural stability, rate capacity, metal utilization and cycle life

\[
\begin{align*}
\text{discharge:} \quad H_2 + O^{2-} & \rightleftharpoons H_2O + 2e^- \\
\text{charge:} \quad Me + xH_2O & \rightleftharpoons MeO_x + xH_2
\end{align*}
\]
Among other metals iron shows required properties for O$_2$ storage and its release.
Research Approach

Manufacturing of storage material
- pressing
- tape casting
- extrusion

Redox cycling in furnace
\[ \text{Ar-2}\%\text{H}_2 \leftrightarrow \text{Ar-2}\%\text{H}_2-7\%\text{H}_2\text{O} \]

Battery test

Investigations (morphology, porosity, kinetics)
Pure Iron Oxide (without support matrix)

Iron-layer formation and agglomeration → rapid degradation
Iron Oxide with 8YSZ (inert matrix)

As sintered (900 °C, 5K/min, 3h, air)

Reduced in Ar+2%H₂ @800 °C for 10 h (1. half cycle)

Oxidised in Ar+2%H₂+7%H₂O @800 °C (10. half cycle)

Reduced in Ar+2%H₂ @800 °C for 10 h (11. half cycle)

Less extensive iron-layer formation and agglomeration → slower degradation
Iron Oxide with CaO (reactive matrix)

Layer formation:
- Oxidised in Ar+2%H₂+7%H₂O @800 °C (10. half cycle)
- Reduced in Ar+2%H₂+7%H₂O @800 °C (11. half cycle)

Layer decomposition:
- Ca₂Fe₂O₅+3H₂ ↔ 2CaO+2Fe+3H₂O

Possible prevention of sintering effect and outer layer formation.
Dip-Coated Storage (green state)

Fe$_2$O$_3$/8YSZ (≤ 1 µm) 70/30 vol% non-sintered specimens after dip-coating in: (a) viscous and (b) dilute (50% solvent) 8YSZ ($d_{50}\sim 150$nm) slurry

Additional filling of voids by inert porous material might sufficiently reduce a drastic iron migration towards the surface
Tape-Cast Storage Fe$_2$O$_3$/Al$_2$O$_3$ (x µm) (effect of particle size)

The more rapidly material gets reduced, the faster battery charging is expected.
Redox Cycling in TG-facility (10 cycles) (trend of degradation)

After 10 cycles the TG-results show no storage degradation. To reveal a “start point” of degradation the number of cycles and their duration have to be changed.
Combination of Thermogravimetry and Mass Spectrometry (TG-MS)

\[
\text{H}_2\text{O} + \text{Fe} \rightarrow \text{FeO} + \text{H}_2 \quad (1 \text{ cycle})
\]

H$_2$-release (discharge)

7\%H$_2$O + Ar, 800 °C

Tape-cast samples
- FeO/8YSZ (1μm)
- FeO/CaO
- FeO/Al$_2$O$_3$ (1μm)
- Fe (pure)

FeO/CaO composition exhibits better kinetics and O$_2$-storage
Battery Testing (storage material Fe$_2$O$_3$/8YSZ, S900, TC)

Results of a two-cell stack with tape-cast storage components made of Fe$_2$O$_3$ and 8YSZ sintered at 1000°, operated at 150 mA/cm$^2$

47 min / half cycle, 150 mA/cm$^2$, 0.8-1.2 V/cell, storage usage ~70-80 %
The calculated storage capacity of ROB-153 is ~ 70 Ah for 1 mol Fe, which shows better battery performance among others. Amount of storage influences the capacity.
Battery Post-Test Analysis (ROB 153 after 260 cycles)

Different storage structures might be related to non-uniform temperature and gas consumption (inflow), which might lead to non-uniform power generation.
Conclusions

• The working principle of the rechargeable oxide battery (ROB) was proven
• Stability of the storage material can be increased by adding oxide matrices
• Thermogravimetry, mass-spectrometry, porosimetry and microscopic investigations after laboratory redox cycling, as the tools to qualitatively understand/predict behaviour of the storage under battery conditions
Outlook

• Improvement of the battery efficiency by advanced storage concept, lower operating temperature (600°C) as well as optimised battery design

• Investigation and scientific explanation of the model, which might reveal the degradation mechanism of storage material

• Experimental modelling of storage behaviour avoiding expensive battery operation
Acknowledgements

The authors would like to acknowledge all colleagues who contributed to this research at JÜLICH and the German Federal Ministry of Education and Research for providing financial support within the project:

“Elektrochemische Metall-Metalloxid-Hochtemperatur-Speicher für zentrale und dezentrale stationäre Anwendungen (MeMO)” (№ 03EK3017)
APPENDIX
Fe$_2$O$_3$/8YSZ 70/30 vol%