MEMO+

JÜLICH
FORSCHUNGSZENTRUM

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

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

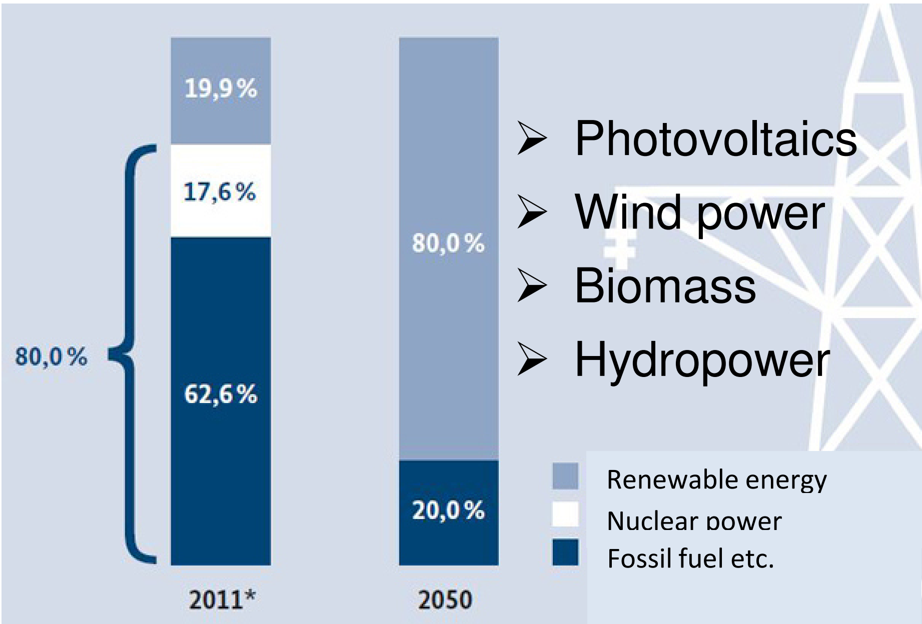
DKG-2015, Bayreuth, Germany

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



Statistisches Bundesamt, Feb. 2012

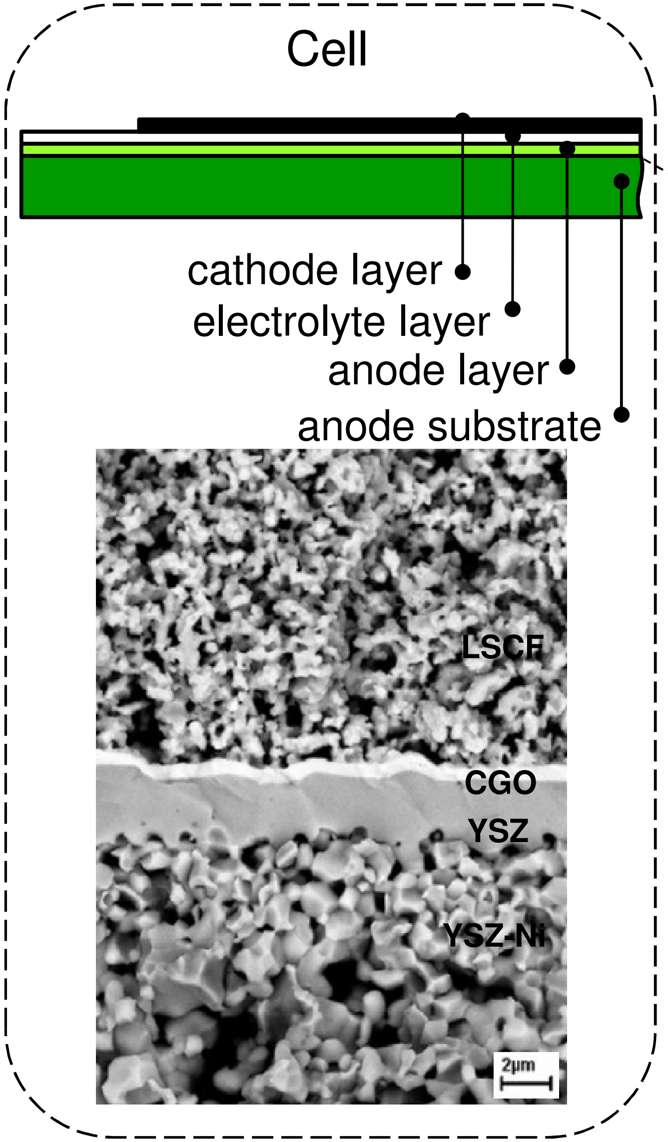
Storage concepts

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

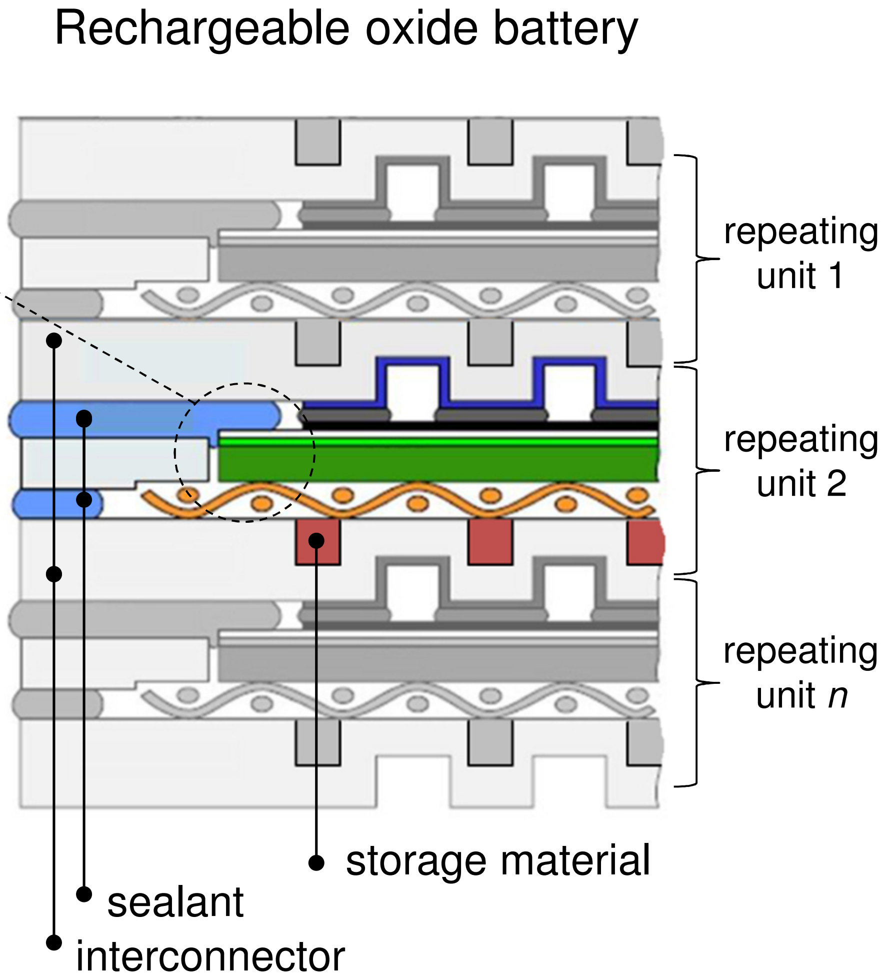
Renewable energy requires storage to be able to balance demand and supply

Mitglied der Helmholtz-Gemeinschaft

From Cell to ROB Battery

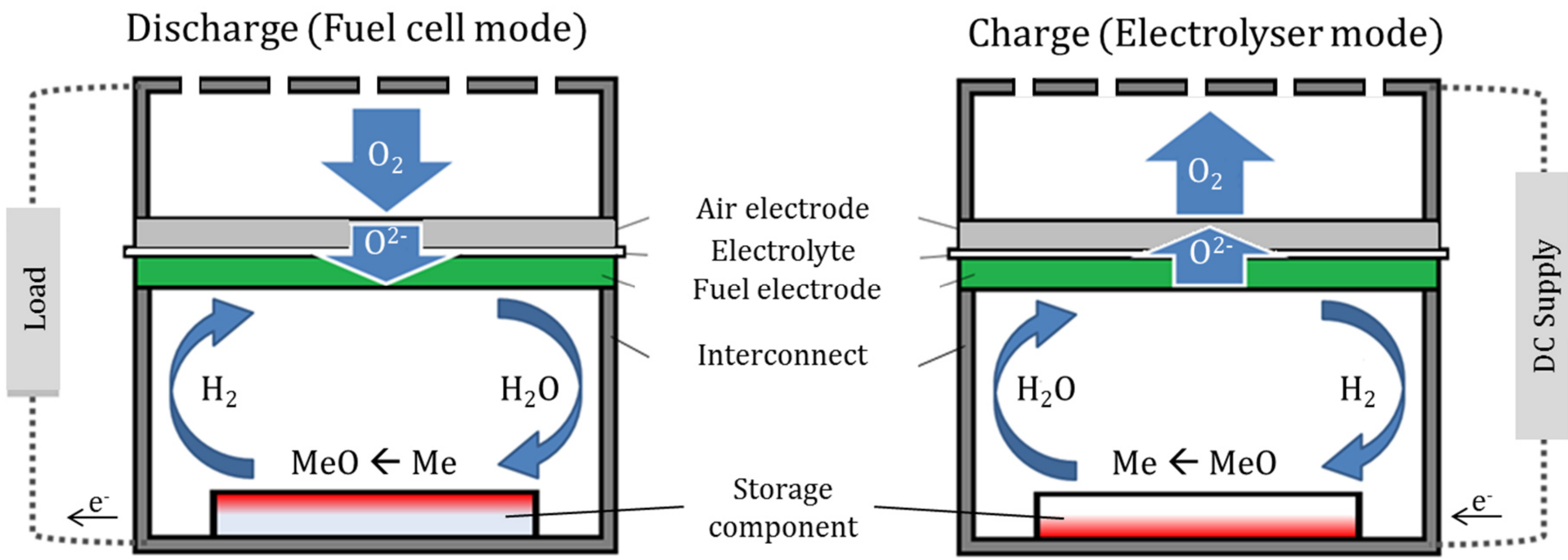


D. Roehrens et al., *International journal of hydrogen energy (2015)*



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

Rechargeable Oxide Battery (working principle)

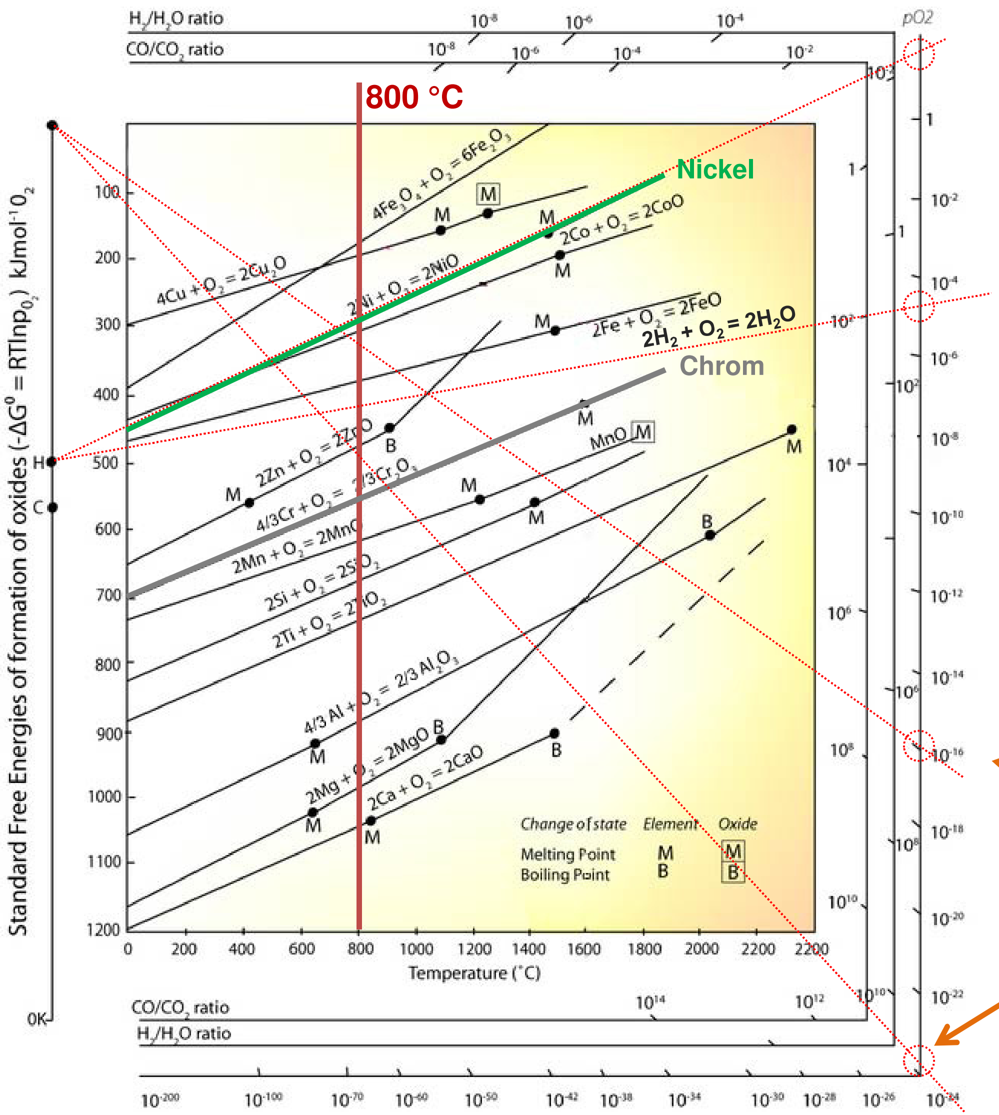


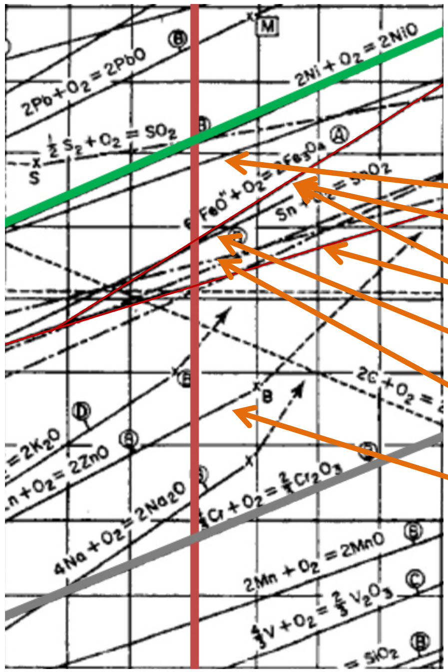
$$H_2 + O^{2-} \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} H_2O + 2e^- \quad \Leftrightarrow \quad Me + xH_2O \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} MeO_x + xH_2$$

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

Mitglied der Helmholtz-Gemeinschaft

Storage: Materials and Limits





Oxidation of Nickel
$p_{O_2} < 10^{-16}$ bar

Decomposition of interconnect oxide scale: $p_{O_2} \approx 10^{-24}$ bar

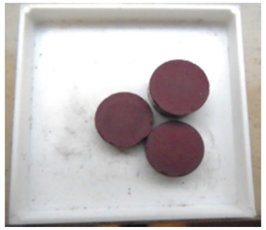
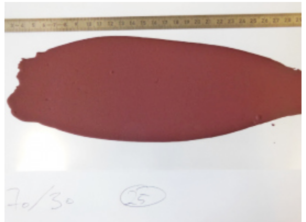
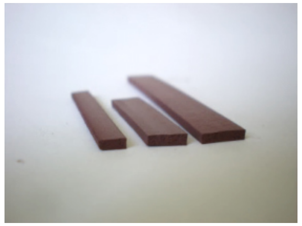
Among other metals iron shows required properties for O_2 storage and its release

Mitglied der Helmholtz-Gemeinschaft

Research Approach

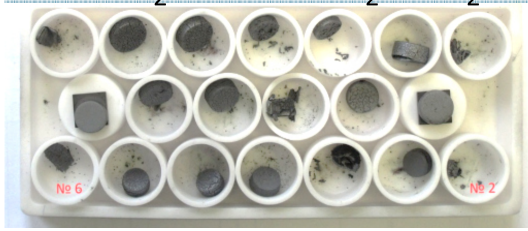
Manufacturing of storage material

pressing | tape casting | extrusion

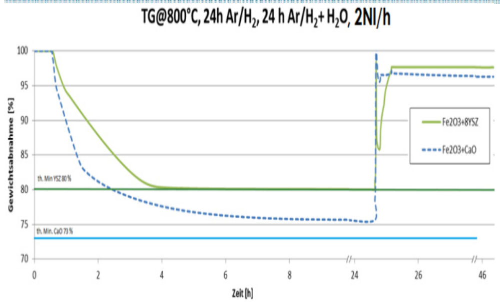




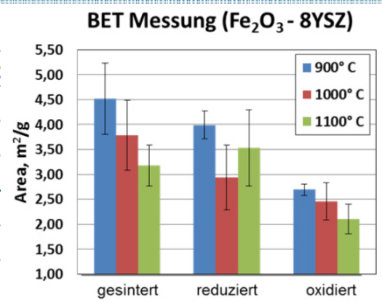
Redox cycling in furnace

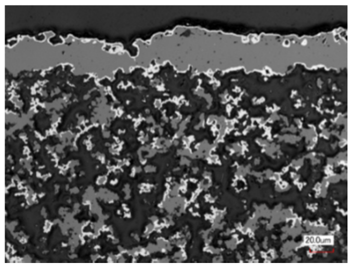
Ar-2%H_2 ↔ Ar-2%H_2-7%H_2O



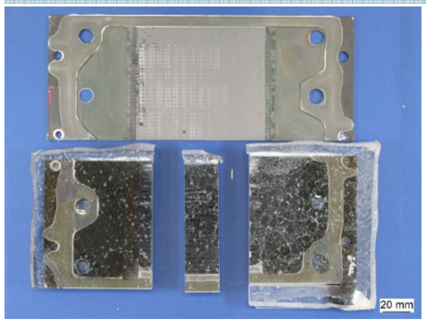
Investigations (morphology, porosity, kinetics)

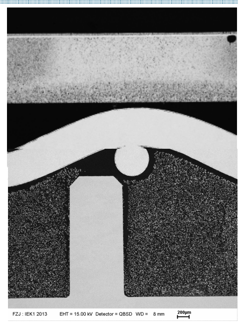




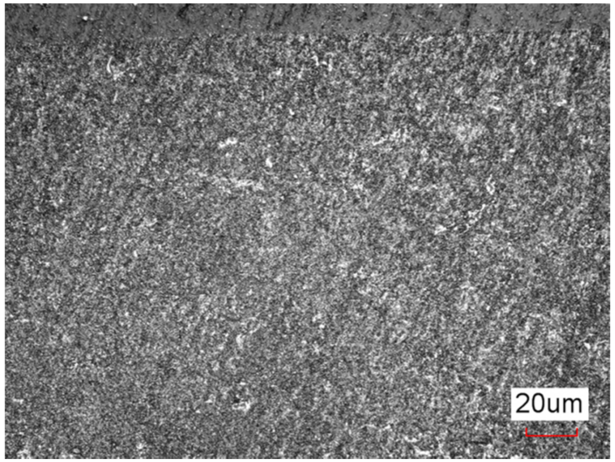


Battery test

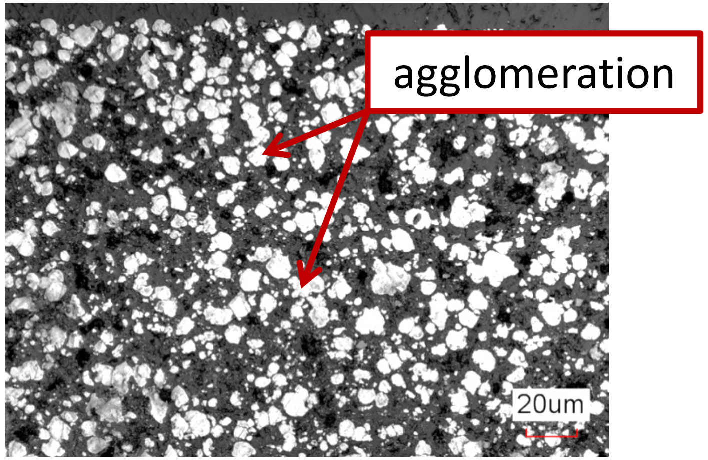




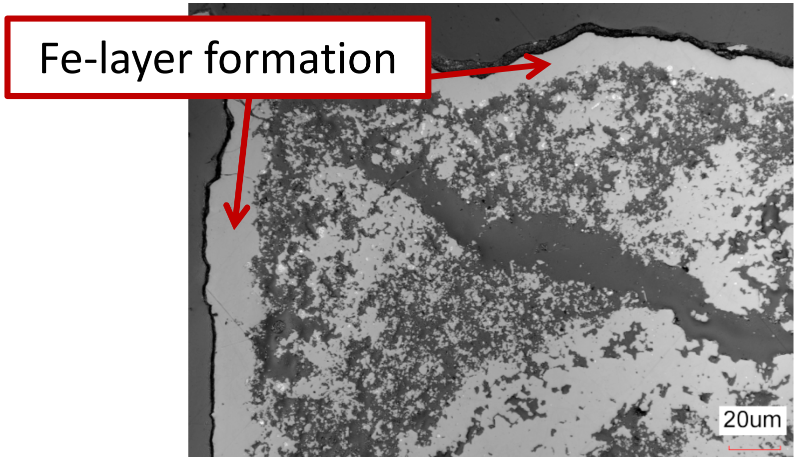
Pure Iron Oxide (without support matrix)



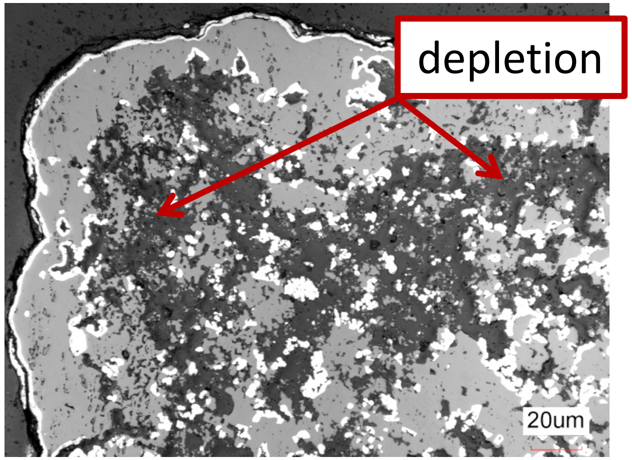
As sintered (900 °C, 5K/min, 3h, air)



Reduced in Ar+2%H_2 @800 °C for 10 h (1.half cycle)



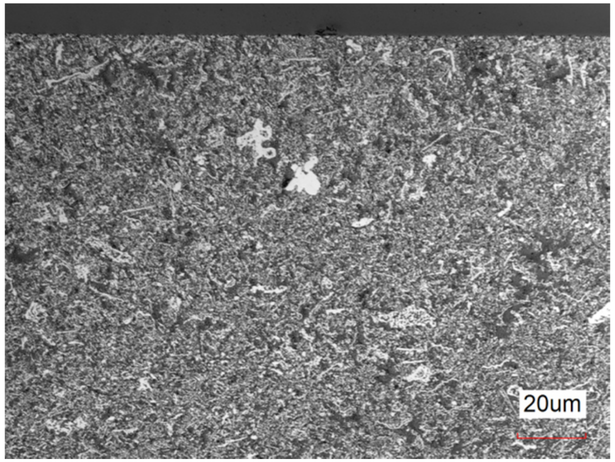
Oxidised in Ar+2%H_2+7%H_2O @800 °C (10. half cycle)



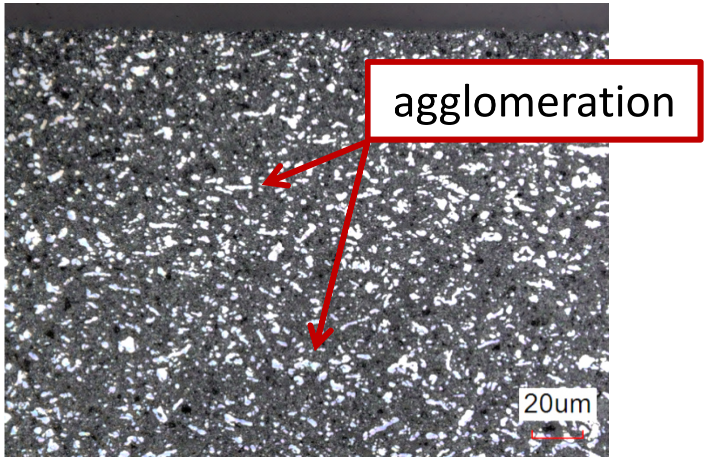
Reduced in Ar+2%H_2 @800 °C for 10 h (11.half cycle)

Iron-layer formation and agglomeration → rapid degradation

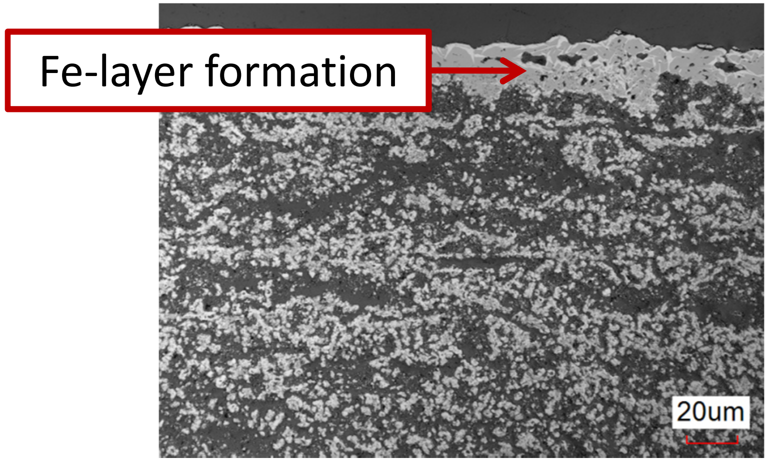
Iron Oxide with 8YSZ (inert matrix)



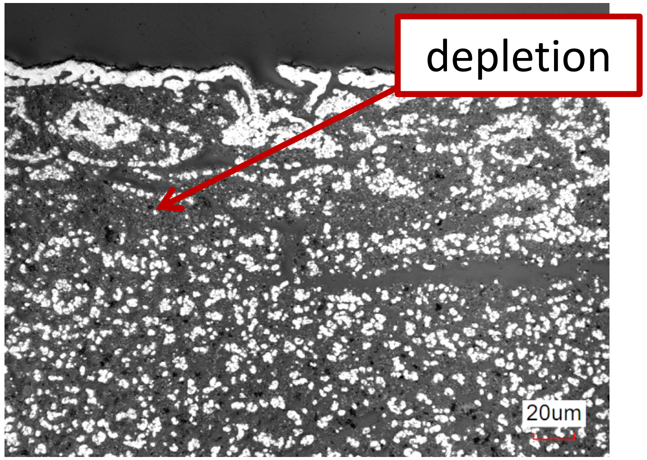
As sintered (900 °C, 5K/min, 3h, air)



Reduced in Ar+2%H_2 @800 °C for 10 h (1.half cycle)



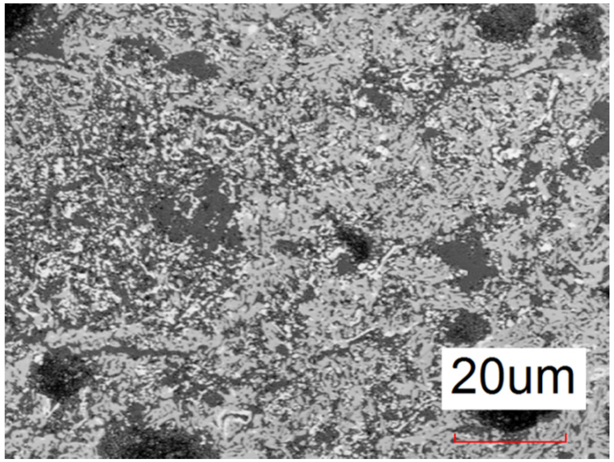
Oxidised in Ar+2%H_2+7%H_2O @800 °C (10. half cycle)



Reduced in Ar+2%H_2 @800 °C for 10 h (11.half cycle)

Less extensive iron-layer formation and agglomeration → slower degradation

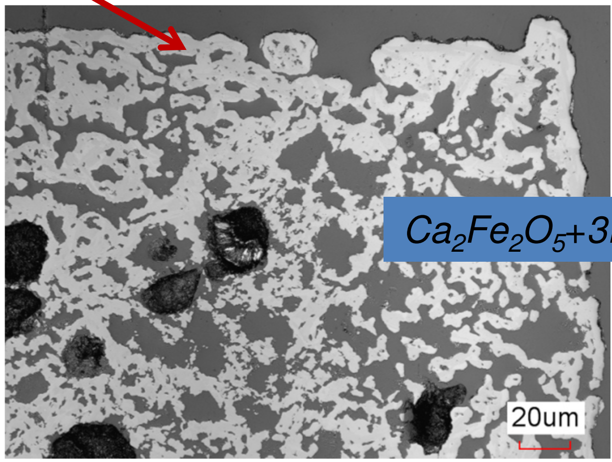
Iron Oxide with CaO (reactive matrix)



As sintered (900 °C, 5K/min, 3h, air)

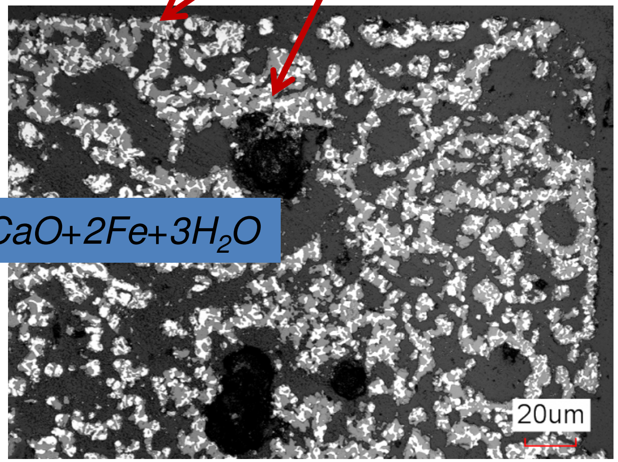
layer formation

layer decomposition



Oxidised in Ar+2%H_2+7%H_2O @800 °C (10. half cycle)

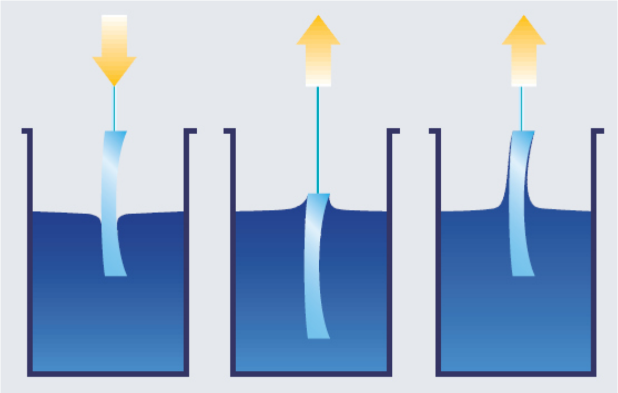
$Ca_2Fe_2O_5+3H_2 \leftrightarrow 2CaO+2Fe+3H_2O$



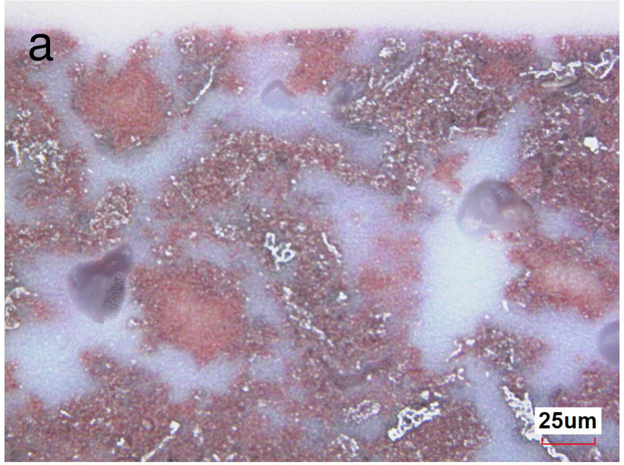
Reduced in Ar+2%H_2 @800 °C for 10 h (11.half cycle)

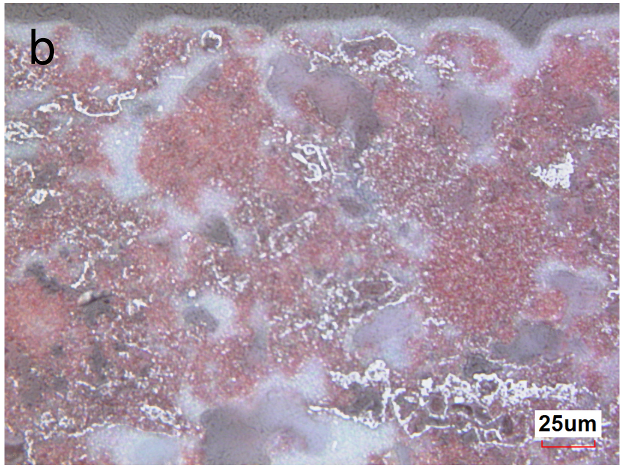
Possible prevention of sintering effect and outer layer formation

Dip-Coated Storage (green state)



http://bimas.lt/akys/literatura.pdf

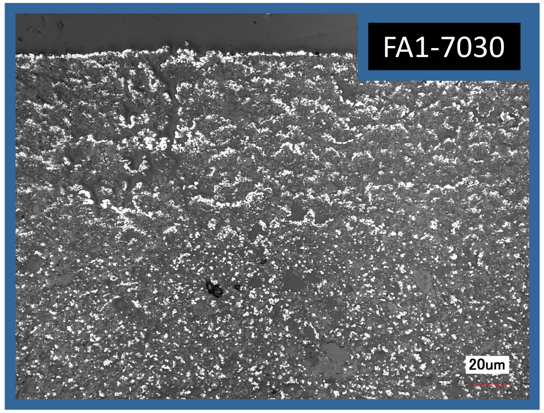


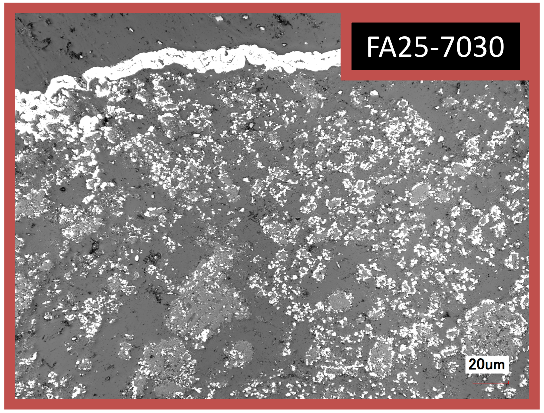


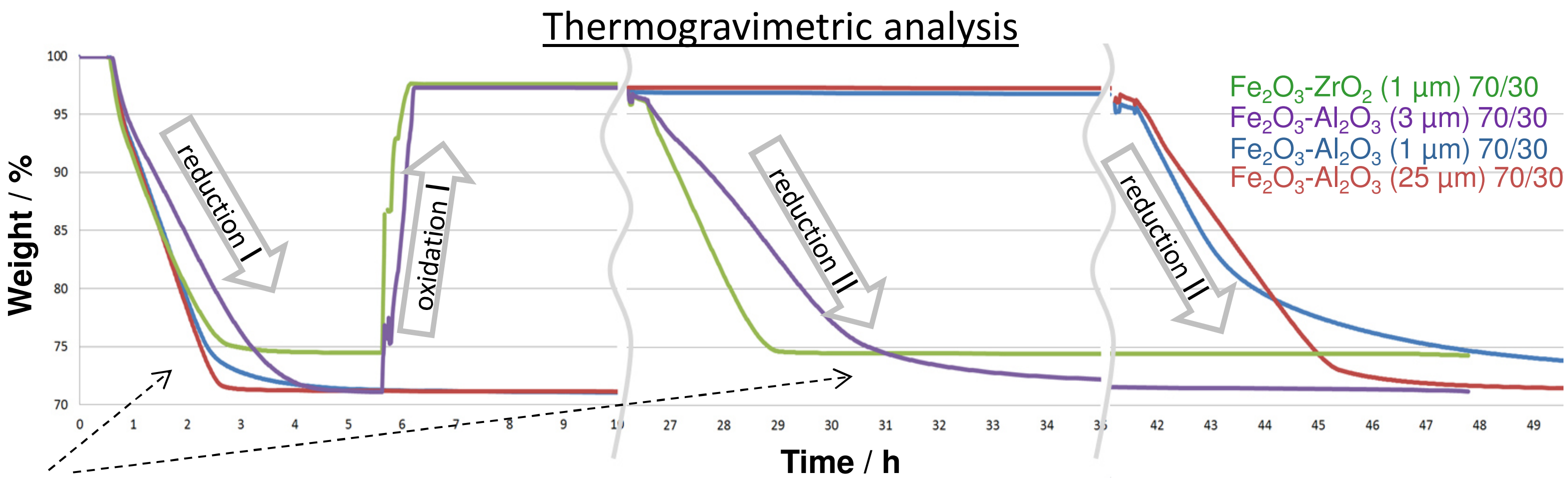
Fe_2O_3/8YSZ (≤ 1 µm) 70/30 vol% non-sintered specimens after dip-coating in: **(a)** viscous and **(b)** dilute (50% solvent) 8YSZ (d_{50}~150nm) slurry

Additional filling of voids by inert porous material might sufficiantly reduce a drastic iron migration towards the surface

Tape-Cast Storage Fe_2O_3/Al_2O_3 (x µm) (effect of particle size)



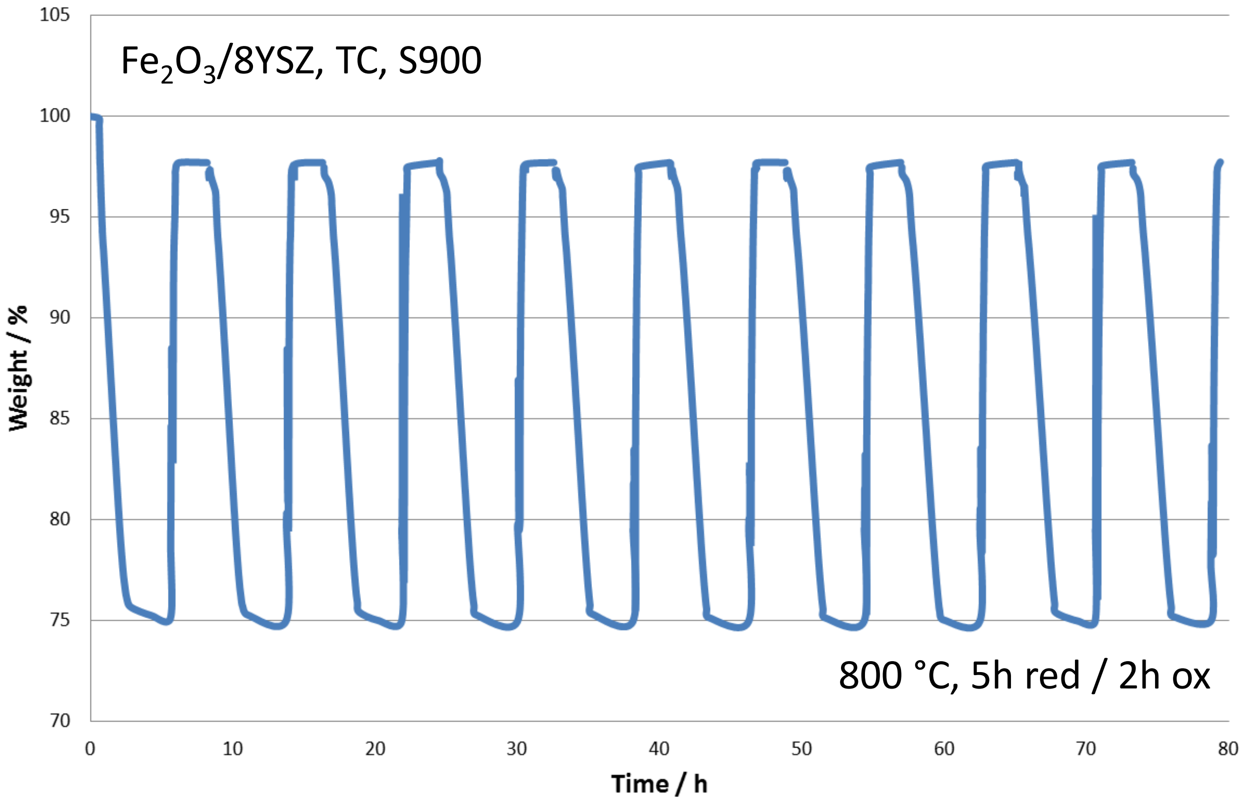


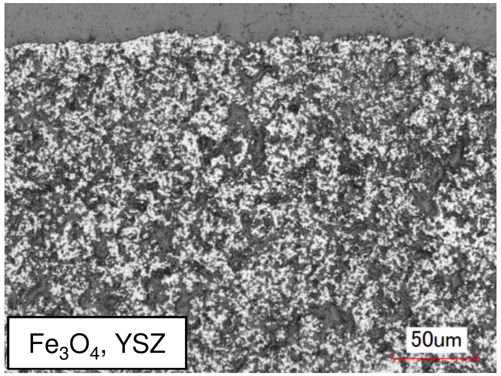


The more rapidly material gets reduced, the faster battery charging is expected

Mitglied der Helmholtz-Gemeinschaft

Redox Cycling in TG-facility (10 cycles) (trend of degradation)



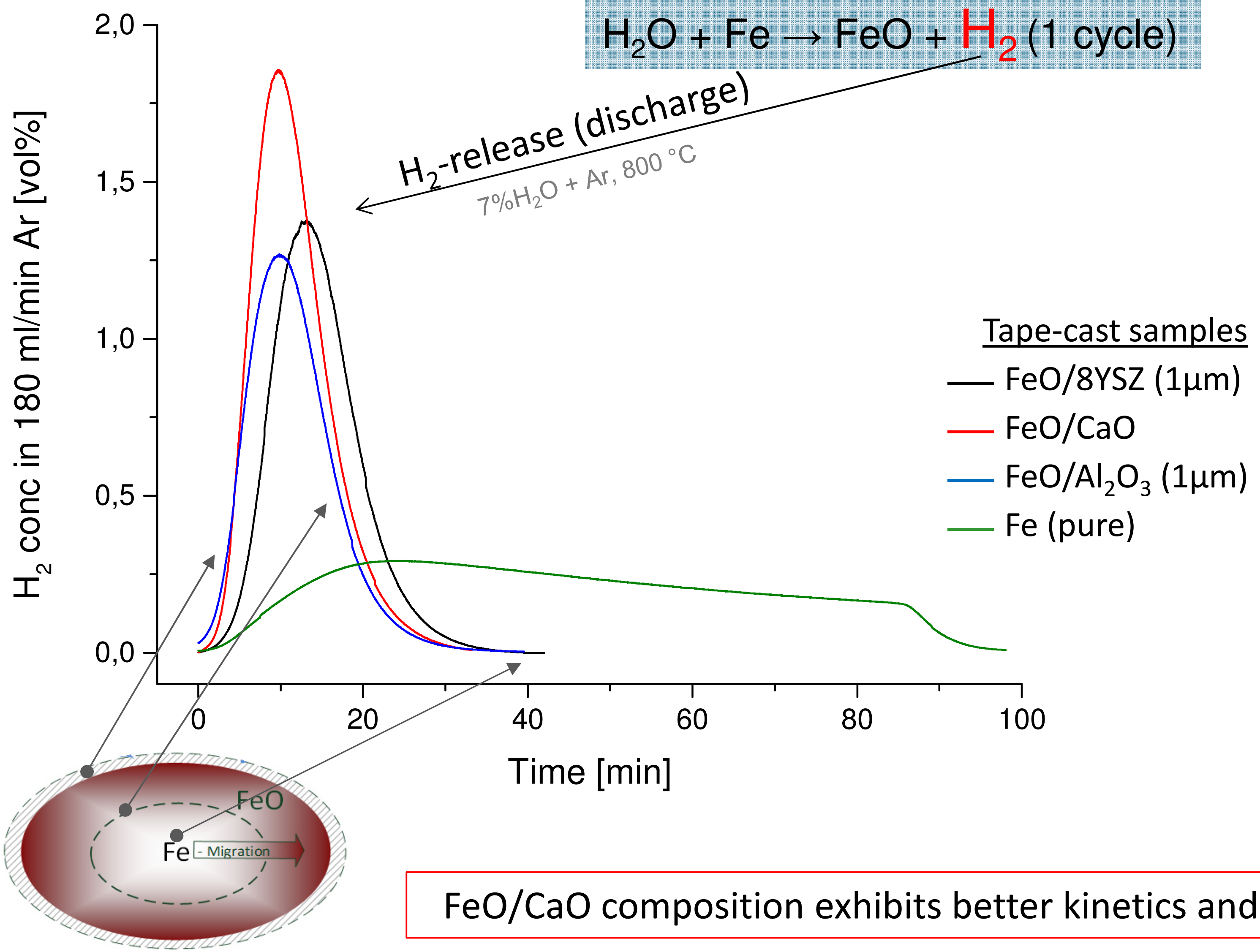


After 10 cycles the TG-results show no storage digradation. To reveal a “start point“ of degradation the number of cycles and their duration have to be changed.

Mitglied der Helmholtz-Gemeinschaft

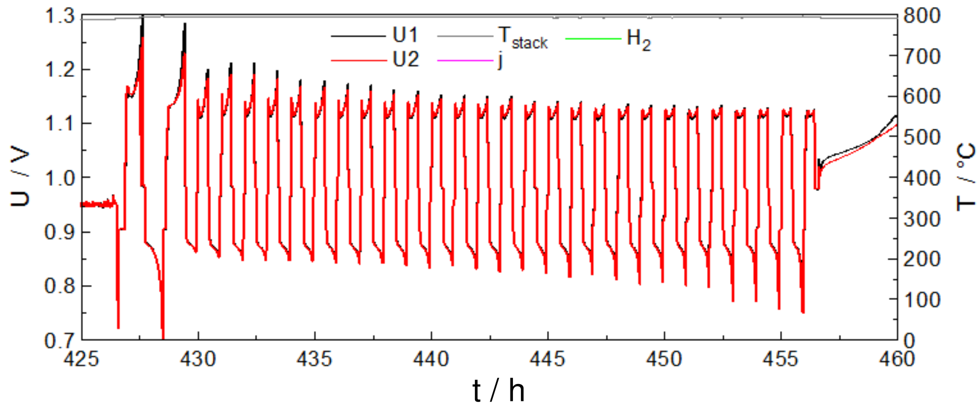
Combination of Thermogravimetry and Mass Spectrometry (TG-MS)

$H_2O + Fe \rightarrow FeO + H_2$ (1 cycle)

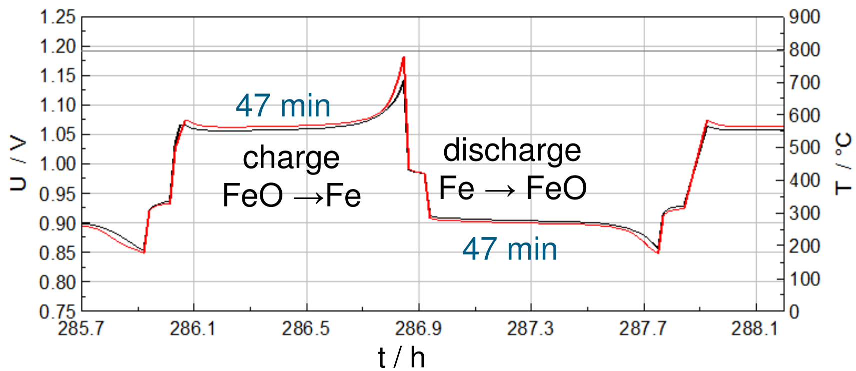


FeO/CaO composition exhibits better kinetics and O_2-storage

Battery Testing (storage material Fe_2O_3/8YSZ, S900, TC)



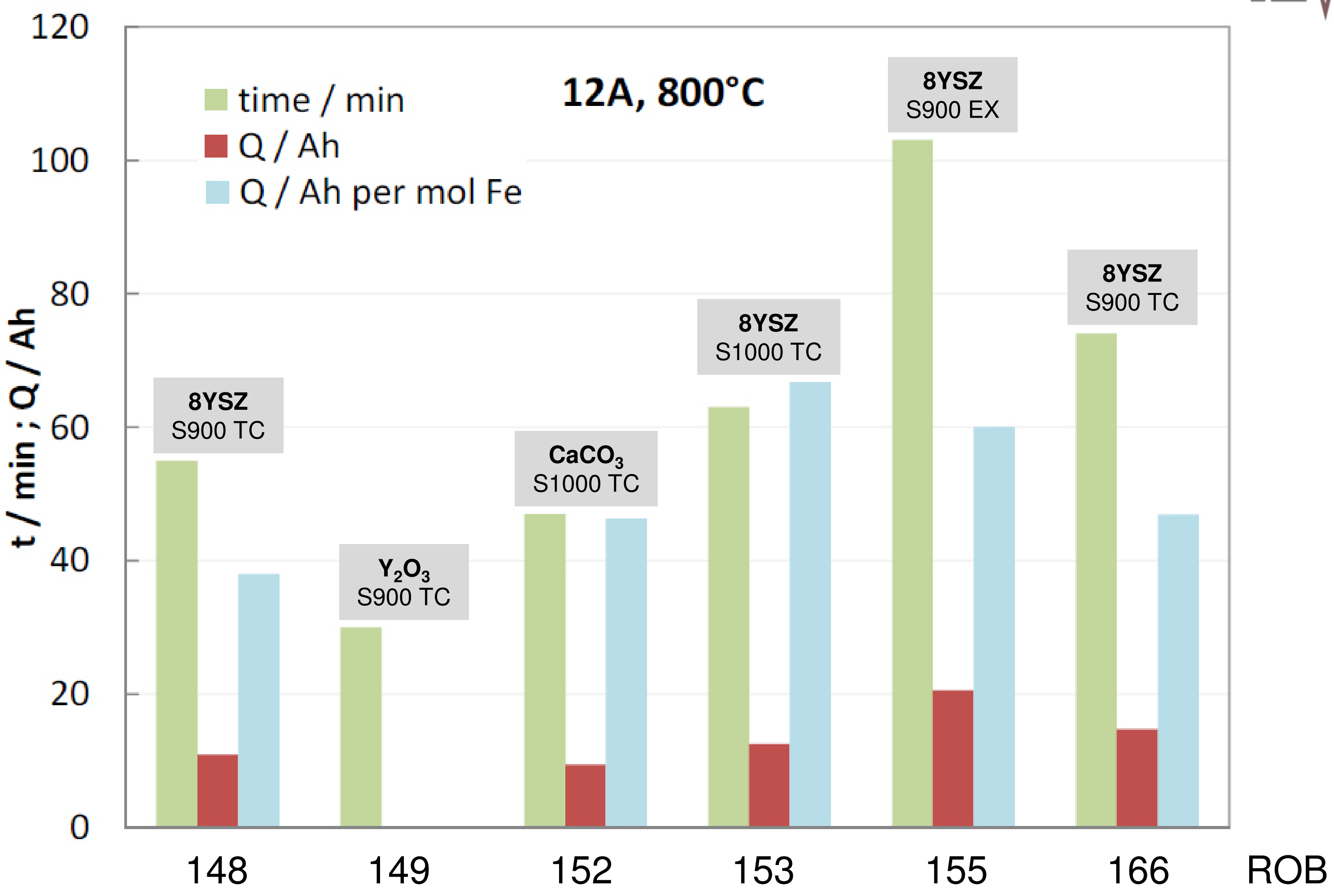
Results of a two-cell stack with tape-cast storage components made of Fe_2O_3 and 8YSZ sintered at 1000°, operated at 150 mA/cm²



47 min / half cycle, 150 mA/cm², 0.8-1.2 V/cell, storage usage ~70-80 %

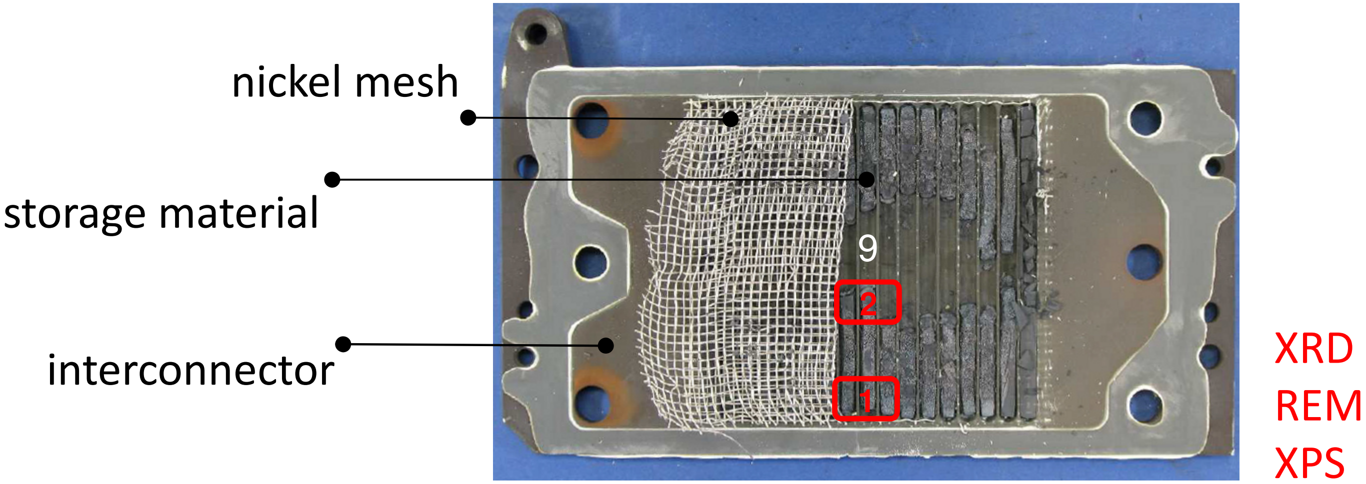
Mitglied der Helmholtz-Gemeinschaft

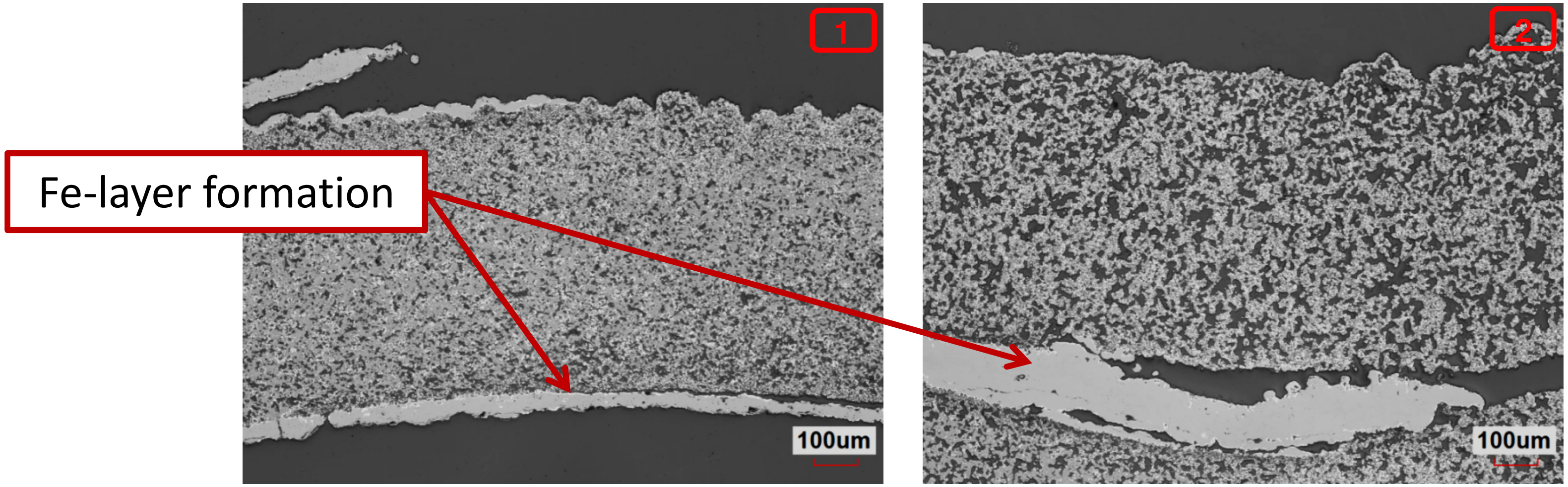
Battery Overview



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)





Cross-section of storage Fe/8YSZ (channel 9, edge) *Cross-section of storage Fe/8YSZ (channel 9, centre)*

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

JÜLICH
FORSCHUNGSZENTRUM

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:

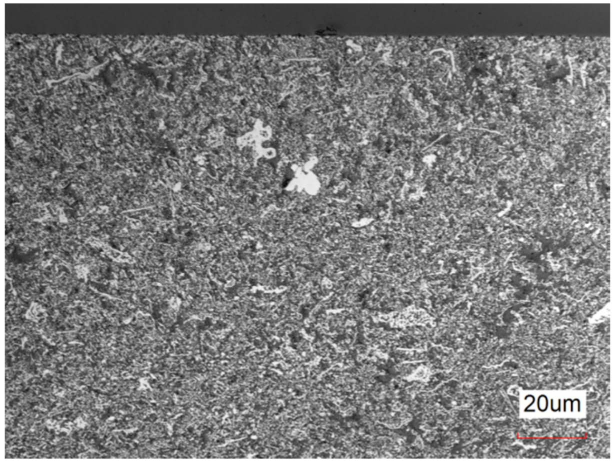
“Elektrochemische Metall-Metalloxid-Hochtemperaturspeicher für zentrale und dezentrale stationäre Anwendungen (MeMO)” (№ 03EK3017)

Bundesministerium
für Bildung
und Forschung

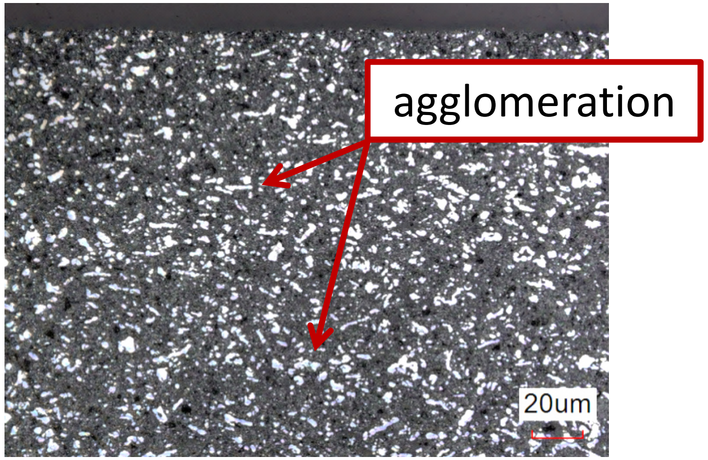
APPENDIX

Fe_2O_3/8YSZ 70/30 vol%

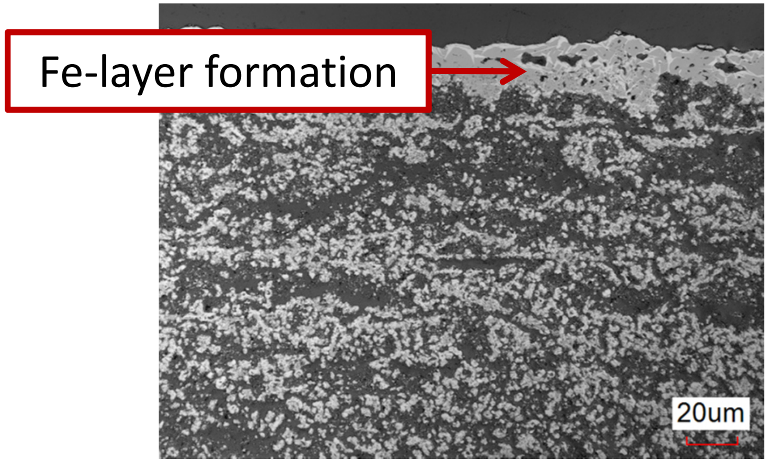
JÜLICH FORSCHUNGSZENTRUM



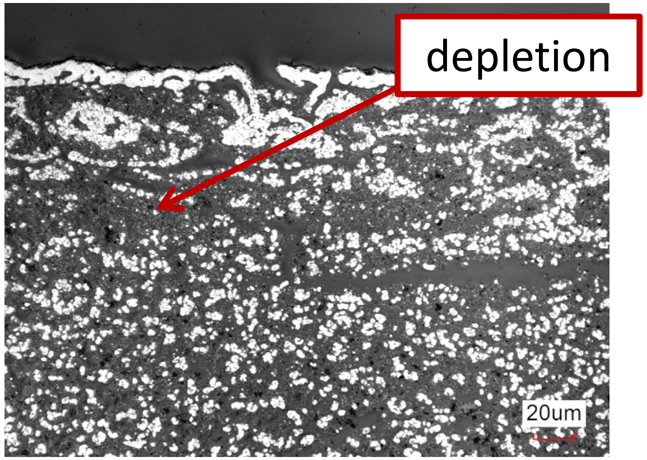
As sintered (900 °C, 5K/min, 3h, air)



Reduced in Ar+2%H_2 @800 °C for 10 h (1.half cycle)



Oxidised in Ar+2%H_2+7%H_2O @800 °C (10. half cycle)



Reduced in Ar+2%H_2 @800 °C for 10 h (11.half cycle)

Mitglied der Helmholtz-Gemeinschaft