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Neutron Imaging Methods for the Investigation of Energy Related Materials
Fuel Cells, Battery, Hydrogen Storage and Nuclear Fuel
10 years ago: a conference about nuclear energy would be expected

today: most talks related to alternative (renewable) energy research

however: there is a potential in neutron research for nuclear materials too …
Outline

1. Introduction

2. THE METOD OF NEUTRON IMAGING

3. FACILITIES AT PSI

4. APPLICATIONS IN THE ENERGY FIELD
   • *Electric Fuel Cell Research*
   • *Li-Ion Batteries*
   • *Hydrogen Storage*
   • *Nuclear Fuel Inspection*

5. Discussion

6. Conclusion & outlook
Introduction: the problems to be solved

• To provide non-destructive and non-invasive tools for material tests and performance optimization

• Neutrons have properties in this respect which can be used alternatively and complementarily to the more established X-ray methods

• As a guide line for neutron studies: heavy elements are transparent, light elements deliver relatively high contrast
Comparison N ↔ X (example: hard-disk drive)
Principle of neutron imaging

\[ I = I_0 \cdot e^{-\Sigma \cdot d} \]

- \( I_0 \) = initial beam intensity
- \( I \) = beam intensity behind the sample
- \( d \) = sample thickness in beam direction
- \( \Sigma \) = attenuation coefficient of the material

\( \rightarrow \) quantification of the involved materials
Spallation neutron source SINQ @ PSI

- In operation since 1997
- Driven by 590 MeV protons on a Pb target
- Intensity about 1.2 mA, corresponding to 1 MW thermal power
- Installations for research with thermal and cold neutrons

Still the world’s strongest stationary spallation source
SINQ – Layout, Imaging Beam Lines
ICON-beam line @ SINQ

- Space for Selector or Chopper
- Micro-Tomography-Position
- Beam limiters
- Position for large objects
- Variable apertures 1 … 80 mm, Be filter
<table>
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<th>ICON</th>
<th>NEUTRA</th>
<th>BOA</th>
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<td>cold neutrons</td>
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<td>higher contrast</td>
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<td>variable aperture, Bi-</td>
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<td>polarized neutrons</td>
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<td>micro-tomography-setup</td>
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<td>UNDER CONSTRUCTION</td>
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<td>tilted detector option</td>
<td>X-TRA option (320 kV tube, high current)</td>
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<td>fuel cell infra-structure</td>
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Detector options with CCDs

FOV and pixel size for the detector systems at PSI's neutron imaging facilities
Micro-Tomographie-Setup an ICON

Specifications
• FOV: 2.7cm * 2.7cm
• Pixel size: 13µm
• CCD with 2048*2048 pixels
• Scintillator 10 µm thick
• L/D>1000
Example for neutron micro-tomography

5 mm
APPLICATIONS IN THE ENERGY FIELD

- Polymer-Electrolyte-Membrane (PEM) fuel cell,
- Lithium-Ion batteries
- Hydrogen storage in several metallic structures
- Study of nuclear fuel and its cladding

→ Results for these topics ←
← approaches and offer to partners →
PEM Fuel Cell - Principle

\[ \text{H}_2 + \text{O}_2 \rightarrow \text{H}_2\text{O} \]
The membrane needs humidification to provide proton conductivity.

**Anode:**
\[ \text{H}_2 \rightarrow 2 \text{H}^+ + 2 \text{e}^- \]

**Cathode:**
\[ \frac{1}{2} \text{O}_2 + 2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{H}_2\text{O} \]

Condensed water can disturb the access of gaseous reactants.

Source: P. Boillat, Electrochemistry, PSI
Through-plane option

- High frame rate possible (~30 Hz), depending on beam intensity
- Spatial resolution ~0.2 mm only
- Behavior at cathode or anode not distinguished
In-Plane measurements: water inside the membrane

- High detector resolution required
- Thickness of the cell in beam direction limited by neutron transmission
- High beam collimation needed
- Less neutron flux $\rightarrow$ lower frame rate
Differential Fuel Cell – for high resolution imaging

- Gas Diffusion Layer (GDL)
- Membrane with Electrode (MEA)
- Flow Field
- Gasket
- Neutron Beam

$I = 1 \text{ A/cm}^2$, $p = 2 \text{ bar abs.}$, $T = 70 \ ^\circ \text{C}$
Differential Fuel Cell – in reality

beam direction
In-Plane measurements; Detector improvement - Tilting

Beam → Cell → Detector → Radiogram

$d_{obj} = d_{det}$

Beam → Cell → Detector, tilted → Radiogram

$d_{obj}$

$d_{det}$
Resolution improvement - Results

Investigation of a 150µm wide absorber stripe

Source: P. Boillat, Electrochemistry, PSI
Cell performance and water management

Membrane

Gas diffusion layers (GDL)

Anode

(a)

Rib

Channel

Cathode

(b)

(c)

(d) 550

Dry

Excess water

Voltage [mV]

500

450

400

Average water content [a.u.]
current topics of Fuel Cell Research using Neutrons

- Simultaneous neutron imaging of 6 cells
- Start-up behavior of PEM-FC and operation under sub-zero conditions
2002 – 2008: Through-plane

100 µm pixel
200 µm FWHM
2008 – 2012: High resolution In-plane

2.35 μm pixel
< 10 μm FWHM
2012: In-plane, but with 6 cells!

6 μm pixel
25 μm FWHM
Motivation

2012: In-plane, with 6 cells ... but why?

- Efficient use of beam time
- Improved repeatability
  - Identical conditions for all cells
  - Study of design parameters
Testing different designs

2D

1D

μ-interdigitated
Motivation

- Testing different compression rates

![Comparison of compression rates at 60%, 30%, and 5%](image-url)
Motivation

➢ Testing different materials

MPL = Micro Porous Layer
Motivation

- Imaging

- Impedance spectroscopy

-Im(Z)  -Im(Z)  -Im(Z)  -Im(Z)

Re(Z)  Re(Z)  Re(Z)  Re(Z)
Motivation

- Imaging

Set-up

How?

- Printed circuit board
- Spring contacts
- Cooling gas
- Heating liquid
- Out (MFCs)
- In
- By-pass
- Out (MFCs)
- In
- By-pass
- Printed circuit board
Set-up

How?
Results

Influence of the MPL: voltage

T = 70°C, RH = 100%/100%
Results

Influence of the MPL: water distribution

- Temperature: T = 70°C
- Relative Humidity: RH = 100%/100%
- Current Density: i = 0.5 A/cm²

The graph shows the water content (% vol tot) across different positions in the membrane [µm] with and without MPL on both sides. The graph compares the water distribution for different scenarios:

- **No MPL**
- **MPL both sides**
- **MPL anode**
- **MPL cathode**
Mass transport losses... 

... may originate from water accumulation in MEA region.
Neutron imaging of isothermal sub-zero degree Celsius cold-starts of a polymer electrolyte fuel cell (PEFC)
Motivation

Voltage

Current

Time

$\Delta t_{\text{work}}$

$\text{H}_2\text{O}_2$ $\rightarrow$ $\text{H}_2$ $\rightarrow$ $\text{O}_2$ $\rightarrow$ $\text{H}_2\text{O}$
**Procedure**

- **RH**: 30% for 30 minutes.
- **T**: 25°C for 10 minutes, then drop to -10°C for 15 minutes.
- **U**: 0.9 V for 35 minutes, then reduce to 0.1 A/cm² for 20s.
- **i**: 2 to 117 minutes, then 15 minutes.
Isothermal Sub Zero Startup

Anode Cathode

Startup at -10°C, 0.2 A/cm²

Total time: 20 minutes
Results: Isothermal Sub Zero Startup

Startup at -10 °C, 0.2 A/cm²

- Anode
- Cathode
- Membrane & Catalyst
- GDL

Graph showing:
- Water content [% vol tot]
- Voltage [V]
- Current density [A/cm²]

Lines representing:
- Water in GDL
- Water in Membrane/CL
- Current density
- Voltage
Fuel Cell Research using Neutron Imaging

- Established as powerful non-invasive method
- Direct water quantification
- Through plane and in-plane observation possible
- Coupled with in-situ electrical scanning (voltage, current density)
- High flexibility in spatial and time resolution
Li-Ion battery research

- Li-Ion migration during charging/discharging processes visible with neutron imaging methods? (ongoing)

- Gas production during operation and its influence onto the cell performance

work done:

The migration process within Li-Ion batteries

might it be possible to visualize the transfer with neutrons?

Specific approach:

Li-6: tot. CS=944 barn
Li-7: tot. CS=1.1 barn

→ Doping of the agents
Li-Ion battery development and performance improvement

TEST DEVICE

1. Teflon bolts
2. Polypropylene sealing ring
3. Aluminum cell covers
4. Current collector plates
5. Electrodes
6. Gel-type electrolyte
7. Gas space

Data from:
Gas production in relation to the charging process

- lateral distribution of gas bubbles visible
- formation of growing gas channels
- PC (propylene carbonate) electrolytes show the evolution of large amounts of gas, resulting in an unfavorable distribution of the local current density and reduction of the cell charge capacity.
- GBL-based gel-type electrolytes show a usable electrochemical behavior and the evolution of only very small amounts of gas.
Hydrogen storage in metal hydrides

- Processes are reversibly
- For gas release high temperature required
- Efficiency still topic for investigations
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**Legend**

\[
\text{Attenuation coefficient [cm}^{-1}\text{]} = \frac{\sigma_{\text{total}} \times \text{sp.gr.}}{\text{at.wt.}} \times 0.6023
\]


Verification of the hydrogen accumulation

Simplified setup for non-invasive hydrogen determination

- in-situ determination of loading/reloading processes
- direct quantification of the hydrogen amount
- high spatial and time resolution
- 2D and also 3D investigations possible
Investigation of nuclear fuel

U-235 and U-238 can be distinguished easily:

\[
\text{tot. CS (U-235)} = 700 \text{ barn} \\
\text{tot. CS (U238)} = 12.17 \text{ barn}
\]

- non-invasive determination of the enrichment
- observation of the pellet integrity
- status of the fuel burnup
Investigation of nuclear fuel cladding

• In the long-term operation of NPPs a hydrogen accumulation in the Zr based cladding can happen.

• A final consequence of this hydrate clustering might be cladding failure and fission product release.

• Neutron imaging is a useful tool for the visualization and quantification of the amount of locally fixed hydrogen.
Investigation of nuclear fuel and its cladding

broken fuel rod (caused by H load?)

special setup (NEURAP) required
Hydrogen Quantification in the cladding

![Graph showing ppm(H) vs. Position x (mm)]
Conclusions

• It has been shown that neutron imaging can contribute to analyze energy relevant samples and to optimize related processes

• High resolution in time and space is provided together with the specific contrast in the neutron transmission

• The quantitative data obtained from the images can be compared to model considerations

• Further progress will be obtained by energy-selective imaging, phases contrast imaging and the use of polarized neutrons
The facilities at PSI are prepared to host further such studies on demand