Time resolved in situ X-ray absorption spectroscopy

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QEXAFS = Quick scanning EXAFS
(“stepper motor QEXAFS”)

Conventional EXAFS scan: Step by step mode
measuring time $\approx$ 15 min

QEXAFS–scan: Motors are moving (quasi)continuously
EXAFS $\approx$ 5 s, XANES $\leq$ 1 s
0.002 – 0.05 s / data point

Standard EXAFS experiment with special software used

$\Rightarrow$ Fluorescence, e-yield detection, reflectivity possible,
wide energy range in one experiment ($\approx$ 15 keV)

$\Rightarrow$ Easy combination with VU-vis, Raman,… possible

BUT: Extremely stable monochromator necessary
$\Rightarrow$ crystals have to remain parallel within $<$ 0.5”!
Very fast scans using stepper motors: Pd foil (300 K)

QEXAFS in 0.81 s
0.002 s / data point

Energy range 700 eV
Si(311), channel cut,
$E_K = 24.348$ keV

QEXAFS at the K-edge of Ge powder

NSLS

Beamline X-11A, 16.6 s (0.02 s / data point)
Wide energy range: W L-edges

\[ \Delta E = 2900 \text{eV} \]

W powder (300 K), 40.8 s (0.02 s/point)

Growth of sputtered Cu films on a W substrate

In situ measurements, fluorescence detection using photo diodes
Corrosion of Mo in 1M KOH-solution


Corrosion sample cell

Electrolyte (1M KOH)

Mo electrode

X-rays

x

10 - 20 mm

⇒ Exact knowledge how Mo corrodes
(edge position, pre-edge peak ⇒ Mo⁶⁺, i.e. MoO₄²⁻)

Catalysts:

Small particles, big business


Activation of a CuO/ZnO/Al₂O₃ catalyst

In situ reduction in H₂ atmosphere
Time resolution: 50 ms
Simultaneous measurement of catalytic activity

⇒ Cu particle size can be determined directly!

(Piezo-QEXAFS, collaboration with Haldor-Topsoe A/S)
A novel fast monochromator: Drive system

**Goal:** Faster (ms), wide spectral range, continuous movement

Currently up to 40 Hz possible
⇒ 80 spectra / s
⇒ 12.5 ms / spectrum

Experiments at APS undulator 1-ID

Monochromator

Catalytic reactor
**CuO/ZnO-catalyst: Single scan, 50 ms**

\[ \Delta E = 1600 \text{ eV}! \]

Cu reference, measured *simultaneously*

Cu K

Zn K

Sample

**CuO/ZnO-catalyst: Reduction**

\[ \Delta t = 200 \text{ s} \]

Collaboration with J.-D. Grunwaldt and A. Baiker, ETH Zürich
CuO/ZnO-catalyst: Reduction

QEXAFS at SOLEIL

at SAMBA, a bending magnet beamline

Reference for the SOLEIL-data:
QEXAFS at SOLEIL (SAMBA BM-beamline)

Stack of Ni and Cu metal foils

(SOLEIL: 2.75 GeV storage ring near Paris)

First QEXAFS experiments at SOLEIL

Cu metal foil, XANES region
Noise of detector system is currently the limiting factor
**Discharge of new lithium battery materials:**

\[ \text{Li}_x \text{FePO}_4 \]

**Li}_x \text{FePO}_4\text{ cathode}

0.1 Hz, averaged over 75 spectra, lithiation speed C/3, starting with x=0.56.

Oxidation state changes from Fe$^{3+}$ to Fe$^{2+}$.

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This was **ONE edge**,

next: **TWO edges**!

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**Reference for the SOLEIL-data:**

J. Stötzel, V. Briois, E. Fonda, S. Belin, D. Lützenkirchen-Hecht and R. Frahm: *First QEXAFS Results at SOLEIL. 3rd SOLEIL User’s Meeting, École Polytechnique (Palaiseau, France), January 17-18, 2008*
Discharge of new lithium battery materials: \( \text{Li}_x\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2 \)

Measured at Ni K- and Mn K-edges alternately during discharge. 0.1 Hz, averaged over 20 spectra. Lithiation speed C/4.5, starting with \( x=0.414 \).

Oxidation state changes from Ni\(^{4+}\) over Ni\(^{3+}\) to Ni\(^{2+}\).

Discharge of new lithium battery materials: \( \text{Li}_x\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2 \)

Measured at Ni K- and Mn K-edges alternately during discharge. 0.1 Hz, averaged over 20 spectra. Lithiation speed C/4.5, starting with \( x=0.414 \).

Significant changes in the EXAFS.
Discharge of new lithium battery materials:

\[ \text{Li}_{x}\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2 \]

Measured at Ni K- and Mn K-edges alternately during discharge.
0.1 Hz, averaged over 20 spectra. Lithiation speed C/4.5, starting with \( x=0.414 \).

Oxidation state of Mn stays in a tetravalent state.

No significant changes in the EXAFS visible.
Tomographic absorption spectroscopy:

Entering the 3rd dimension

**XANES μ-tomography**
Collaboration with RWTH Aachen (B. Lengeler) and TU Dresden (C. Schroer)

- Monochromatic X-rays from oscillating monochromator
- Refractive lens
- Horizontal focal size: 6-10 µm
Sample below / above Cu K-edge

Sample in glass capillary, outer diameter 500 μm, inner diameter 400 μm.
Beam size: 10 μm x 10 μm

Reconstruction at different positions after several oxidation/reduction cycles:
What happens to the catalyst during catalysis?

All spectra can be decomposed into content of the Cu-oxides and Cu to answer this question!


Reconstructed spectra with references

Cu/ZnO catalyst: Cu distribution

Cu > Cu(I), 1.26 : 1

Average over whole cross section:
Cu : Cu(I) = 51 : 49

Cu < Cu(I), 1 : 1.8

⇒ Very detailed in situ observation of behaviour of real catalysts!
**Tomato root grown on a polluted (Zn, Pb) soil**

- Tomato root (diameter ~ 700µm)
- Low metal-ion concentration (<100 ppm):
  - ⇒ Fluorescence tomography, here: Zn K-edge

Below Zn K-edge

Above Zn K-edge

- Significant differences
- Zn concentrated in root bark

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