"In-operando" neutron scattering studies on commercial Li-ion batteries

A. Senyshyn, M.J. Mühlbauer, O. Dolotko, H. Ehrenberg

Energy Challenges Germany 2050
28 June 2012
Why Lithium?

Acceleration

Energy density, Wh/kg

Distance

10^4

10^3

10^2

10^1

10^0

10^{-1}

10^{-2}

10^{-3}

Power density, W/kg

Electrolytic capacitor

Double-layer capacitor

Lead (Pb) battery

Nickel-cadmium (Ni-Cd) battery

Nickel metal hydride (NiMH) battery

Li-ion battery

Fuel cells

28 June 2012
Major challenges of Li-ion battery technology

1. Specific energy – amount of energy per unit mass (C/3, 150Wh/kg);
2. Energy density – amount of energy per unit volume (C/3, 230Wh/l);
3. Calendar life – (10 ÷ 15 years);
4. Operating temperature range – (-40°C ÷ 50°C);
5. Selling price – (150$/kWh);
6. Safety – serious hazards have been reported.

Ways to improve:

1. Use of new materials;
2. Optimisation of the battery design and processing;
3. Understanding of the fatigue processes;
4. Enhancement of thermal stability;

Studies of the battery „in-operando“. New non-destructive technique of studies is needed.
Advantages of neutron scattering

The energy of thermal neutrons is in range of meV

Neutrons weakly perturb the experimental system, i.e. non-destructive.

Neutrons are highly penetrating into the matter

Studies of bulk processes under realistic conditions (in complex environments).

Neutrons interact with nucleous.

Neutrons can localize light atoms (e.g. hydrogen, lithium) in the presence of heavier ones and to distinguish neighboring elements from Periodic Table and isotopes.

The wavelength of thermal neutrons is similar to interatomic spacings.

Details of the crystal structure.
Radiography: a principle (μm resolution)

- Collimated neutron beam
- Pinhole diaphragm
- Sample

© F. Piegsa, PSI
ANTARES - Neutron radiography and tomography

Collimation ratio L/D=800,

Field of view 100x100 mm$^2$ ~ 100 µm pixel resolution

Cylindrical cells (18650-type, 2600 mAh, 3.0-4.2 V window); Electrodes: LiCoO$_2$, graphite
Tomography: a principle

Inverse Radon transformation; filtered back projection algorithm; number of projections 600;

Assignment of Absorption Levels to a chosen color scheme
Tomography reconstruction on 18650-type battery

Photo 3D model Sketch

Cylindrical lithium-ion battery

Neutron absorption

high

low

Energy Challenges Germany 2050

28 June 2012
Tomography reconstruction on 18650-type battery

Polychromatic beam

Monochromatic beam*

*\( \lambda = 1.5482 \text{ Å} \)
Diffraction from crystalline materials (pm resolution)

High resolution neutron powder diffractometer SPODI at FRM-II
Transmission mode, Take-off 155°
Information content of a powder pattern

- Background
  - Sample
  - Scattering from sample holder, air etc.

- Reflections
  - Position
  - Intensity
  - Profile (FWHM, peak shape)
    - Instrument function
    - Sample broadening

- Incoherent scattering:
  - a) Compton scattering
  - b) TDS

- Amorphous fraction
  - (local order/disorder)

- Lattice parameters
  - Space group

- Crystal structure:
  - Atomic positions
  - Temperature factor
  - Occupancy (Disorder)

- Qualitative phase analysis

Real structure:
- Stress,
- Strain
- Crystallite size
- Domain size,...

© R. Dinnebier, MPI FKF
Rietveld refinement of typical diffraction pattern for 18650 Li-ion battery

Beam dimensions: 40x15 mm²
Profile function: Pseudo-Voight (TCH)
Contributions
- Cathode material LiCoO₂;
- Anode material (graphite and Li-intercalated carbons);
- Steel housing + centre pin;
- Copper and aluminum current collectors;

Fatigue of battery: introduction

Two batches of Li-ion cells purposefully cycled (CCCV, 1C) at 25°C and 50°C for 200, 400, 600, 800 and 1000 times
Fatigue of battery: crystal structure

Possible reasons: Li-plating (dendrite growth), microcracks formation in electrodes; oxidation processes and phase transformations; SEI growth/electrolyte decomposition

Effect on Li-concentration

By the fatigue introduced the system looses free (transport) lithium; Lithium loss correlate to the reduction of discharge capacity;
Evolution of diffraction data vs. Electrochemical treatment

(Cathode, SPODI, $\lambda=2.536$ Å)
Evolution of diffraction data vs. Electrochemical treatment

(Anode, SPODI, $\lambda=2.536$ Å)
Phase diagram of Li-intercalated carbons