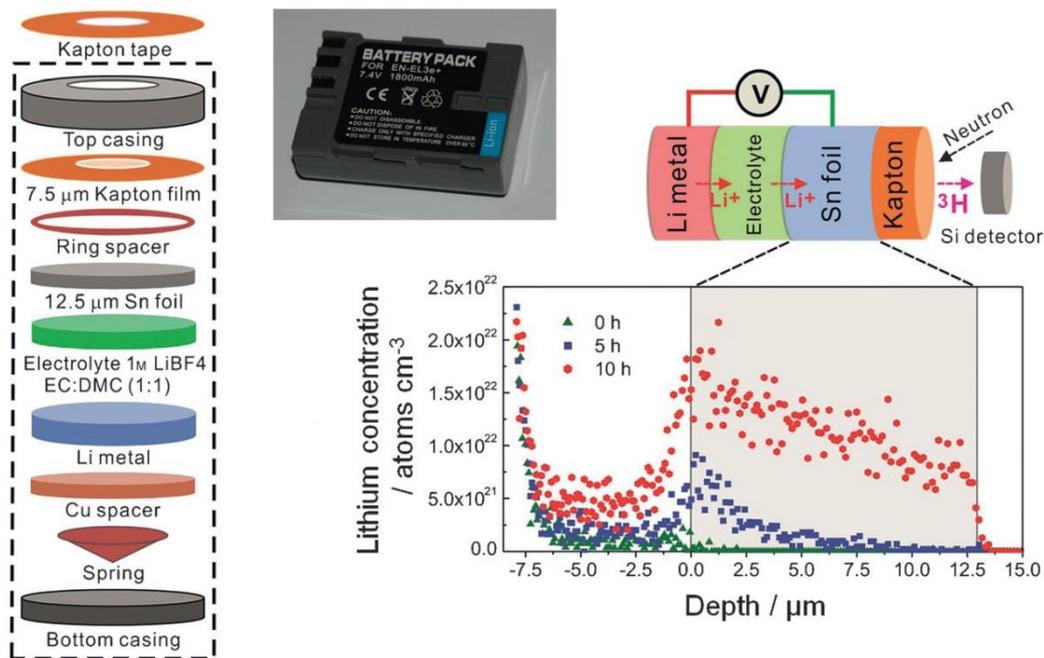




Depth profiling Lithium-ion batteries with neutrons

Rechargeable lithium-ion batteries are part of everyday life, with widespread use in consumer electronics such as mobile phones or laptop computers. They are based on the migration of lithium ions between a positive electrode (cathode), which is a lithium-containing material, and a negative electrode (anode), normally a porous material, through an electrolyte. Lithium transport during charge and discharge of the batteries is fundamental for their efficiency, capacity, and durability.

Real-time in-situ visualization and quantification of the changing lithium distribution in the batteries during charging and discharging is extremely useful information to assist their development, and in particular to improve the understanding of the mechanisms which limit charge and discharge rates. And currently there is one single technique that can deliver such a challenging feat: Neutron Depth Profiling (NDP).



Left: schematic Li-ion test battery. Right: Three snapshots of the in situ NDP spectra showing Li transport during charging/discharging a battery. EC=ethylene carbonate, DMC=dimethyl carbonate.

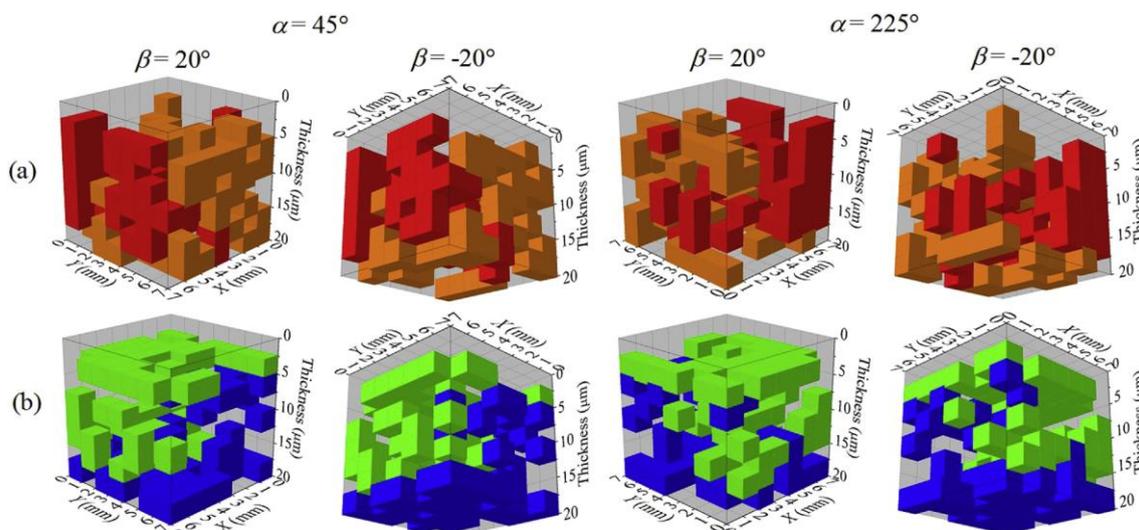
Figure credit: Adapted from [Danny X. Liu et al., 2014](#).

NDP has long been used to depth profile lithium in diverse materials. Dr. Jos Oudenhoven and co-workers from the Eindhoven University of Technology in the Netherlands performed in-situ NDP on thin film solid state micro-batteries, observing the evolution of the lithium concentration profile at a few moments in time ([Oudenhoven et al., 2011](#)). Prof. Anne C. Co and her co-workers from the Ohio State University, US, did real-time in-situ quantification of Li transport in a Li-ion cell, collecting one NDP spectrum every 5 minutes during charge and discharge ([Danny X. Liu et al., 2014](#)). This provided previously unattainable information on rates and losses of lithium incorporation in different parts of the battery, and established



operando NDP as an invaluable technique for the understanding of Li transport in Li-ion batteries.

One of the problems subsequently addressed was the reduction of battery weight. The current in the anode is conventionally collected by a copper film, which is heavy and expensive. Aluminum is much lighter and also cheaper. So far, a reaction of aluminum with lithium, that removes the lithium ions from the anode, has prevented its use in Li-ion batteries. The viability of Al as the anode current collector in a lithium-ion cell was demonstrated with operando NDP in a cell where the aluminum was covered with a protective 500 nm thick Sn layer ([Danny X. Liu et al., 2015](#)). The Sn acted as a protective layer by incorporating some lithium, which did not react with the aluminum.



3D reconstructions of high and low regions of Li concentration in two LiFePO_4 electrodes: (a) LFP1, high lithium regions in red and low lithium regions spots in yellow; (b) LFP5k, high lithium regions in green and low lithium regions in blue. α is the azimuthal angle and β is the tilt angle.

Figure credit: [Yuping He et al., 2015](#).

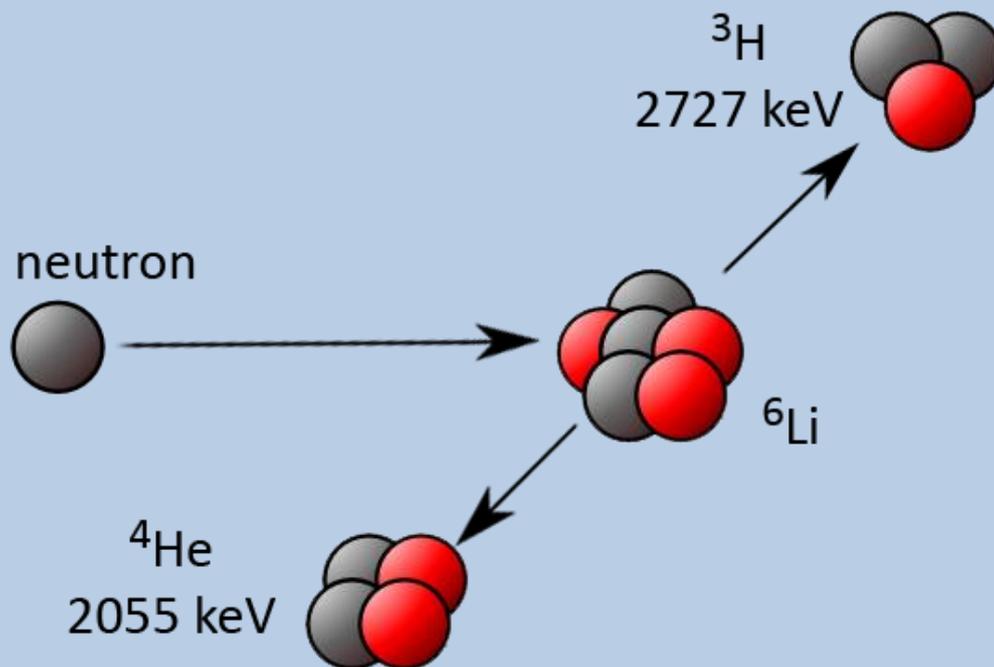
Yuping He from the Binghamton University, US, and co-workers, directed the neutron beam with a $1 \times 1 \text{ mm}^2$ aperture over the surface of a Li-ion cell with LiFePO_4 electrode, measuring the Li depth profile for each pixel ([Yuping He et al., 2015](#)). Putting all depth profiles together, the result is the 3D lithium distribution for the entire sample. They compared electrodes with only one and with 5000 charge/discharge cycles (LFP1 and LFP5k in the figure). After 5000 cycles, the Li concentration decreased by about 40%, while the lateral inhomogeneity increased significantly. This is a direct observation of one cause of degradation and failure of the battery.

What is Neutron Depth Profiling?

Neutron depth profiling measures the concentration of a few specific elements as a function of depth, to depths up to some tens of micrometers.

When a beam of thermal neutrons crosses a sample, a sample nucleus at a certain depth may capture a neutron, emitting charged particles as reaction products. The emitted particles have a well-defined initial energy, but lose energy as they cross the sample towards the detector. The deeper the capture reaction took place, the less energy they have when they are detected. The measured yield of particles at a given energy of detection is a measurement of the concentration of the species at the corresponding depth of origin.

For instance, lithium is detected via the reaction $n + {}^6\text{Li} \rightarrow {}^4\text{He} (2055 \text{ keV}) + {}^3\text{H} (2727 \text{ keV})$, where the kinetic energy of each reaction product is indicated. Either the alpha particle (${}^4\text{He}$) or the tritium (${}^3\text{H}$) can be detected. The alpha particle loses energy quickly as it crosses the sample, and therefore it probes a shallower region of the sample than the tritium. For thick samples the tritium signal is normally used. For thinner samples the alpha particle signal has the advantage of a better depth resolution.



Other techniques

Heavy Ion Elastic Recoil Detection Analysis (HI-ERDA) is highly sensitive to light elements including lithium, and depth profiles with resolution of a few nanometers can be achieved. However, the probed depth is usually a fraction of micrometer, limiting the type of samples that can be studied.

Particle Induced Gamma-ray Emission (PIGE) is also highly sensitive to lithium, but without depth profiling, that is, it can be used to determine total concentrations over the probed depth. However, it can be combined with a scanning microbeam to obtain 2D maps of lithium distribution (see e.g. [K. Mima et al., 2012](#), [A. Habrioux et al., 2012](#)).