Neutron diffraction reveals insights into degradation mechanisms in Co-free batteries

Neelima Paul

Heinz Maier-Leibnitz Zentrum (MLZ), Technische Universität München, 85747 Garching, Germany

Neelima.Paul@frm2.tum.de

Lithium-ion batteries are currently the most popular energy storage device. Here, Li-ions are exchanged between the cathode and the anode, and electrical energy is generated by conversion from chemical energy. However, most cathodes contain the toxic cobalt, which is often mined under environmentally unfriendly conditions and whose price fluctuates widely. Cobalt-free lithium spinels are a cheaper, robust and safer alternative. Another good alternative is a lithium iron phosphate cathode, which offers in addition a longer lifespan. Yet another upcoming complementary battery technology are Na-ion batteries, which are more available, sustainable and cost-effective compared to Li-ion batteries. However, in all these environment friendly batteries, there is still room for improvement to ensure, for example, longer driving ranges or shorter charging times in transportation.

In this regard, it becomes important to understand fundamental *structure-property relationships* which lead to capacity fade, in order to design batteries with improved electrodes and thereby performance enhancement. *Neutron diffraction* offers crucial information in this regard, particularly due to its unique properties such as its sensitivity for quantification of light elements such as Li, lithiated graphite, and ability to detect superstructure reflections in battery electrodes.

With help of three examples, this presentation will reveal how investigations with neutrons diffraction offer insights on different aging contributors such as loss of electrochemically active Li, active material degradations etc. For each of these cases, it will be shown how optimization of electrode design with feedback from obtained neutron data can lead to enhanced cell performance by positively affecting key parameters such as lifetime, charging rate, energy density.

In lithium iron phosphate batteries, using anodes containing mesocarbon microbeads instead of needle coke graphite, faster charging capabilities and a longer lifetime were achieved [1]; by using Co-free Li spinel cathodes and extending the operating voltage limits, both reductions in costs and increase in energy densities compared to conventional cathodes were possible [2]; charge ordering arising from transition metal superstructure ordering was identified as one of the main contributors to Na+/vacancy orderings in $Na_xNi_{1/3}Mn_{2/3}O_2$cathode materials for sodium-ion batteries, whereas with P2-$Na_xMn_{3/4}Ni_{1/4}O_2$, these transition metal superstructures were partially disrupted resulting in smoother electrochemical voltage profiles [3].

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