Comparative analysis of ex-situ and in-operando X-ray diffraction experiments for lithium insertion materials

Siegbert Schmid1, William R. Brant1,2

email: siegbert.schmid@sydney.edu.au

A comparative study of ex-situ and in-operando X-ray diffraction experiments using the fast lithium ion conductor Li0.18Sr0.66Ti0.48Nb0.5O3-y will be presented. Ex-situ analysis of synchrotron X-ray diffraction data suggests that a single phase material exists for all discharges to as low as 0.422 V. For samples with higher lithium content, it is possible to determine the lithium position from the X-ray data. However, in-operando X-ray diffraction reveals a kinetically driven two phase region on cycling below 1 V. Monitoring the change in unit cell dimension during electrochemical cycling showed a reduction in the rate of cell expansion part way through the first discharge and during the second discharge, caused by a drop in lithium diffusion into the bulk material for higher lithium contents. A more significant change is a jump in the unit cell expansion once the lithium content exceeds one lithium ion per vacant site, caused by damping of octahedral rotations. This provides a link between lithium content and octahedral rotations. Using in-operando X-ray diffraction may therefore enable to determine the strength of octahedral rotations.

References
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Keywords: lithium insertion, X-ray diffraction, in-operando

PHOENIX: a tender energy beamline for in-situ X-ray studies

Camelia N. Borca1, Reto Wetter1, Christophe Frisch1, Katja Henzler1, Jacinta Xto1, Markus Janousch1, Thomas Huthwelker1

email: camelia.borca@psi.ch

The PHOENIX beamline at the Swiss Light Source is specially designed for in-situ experiments covering an energy range of 400 to 8000 eV. This energy range provides opportunity to study light elements (e.g. O, Na, Mg, Al, S, Cl … Fe) using X-ray absorption spectroscopy (XAS). The high photon flux delivered by an elliptical undulator can be focused to 2.5 μm2 using X-ray mirrors. Topics addressed by users include environmental [1] and energy research [2], biology [3] and catalysis [4-5], as well as art preservation [6]. Experiments can be performed in two flexible vacuum end-stations, providing ample opportunity for in situ studies.

For the in-house research we focus on in situ studies of aqueous carbonate nucleation using a variety of liquid cells with precise control of the pH value, temperature and saturation index. For fast XAS measurements (ms and above) we use liquid jets [7] and for slow measurements (min to hrs) we have developed in-situ titration cells as well as flow-through cells which allow simultaneous XAS and XRD measurements. The first results obtained on CaCO3 and Ca(Mg)CO3 nucleation and growth in aqueous environments will be presented. The measured XAS spectral features contain information on the local order around Mg/Ca atoms, while the XRD spectra unveils the phase transformation in time of the pure and Mg doped Ca carbonates.

For further information about the beamline: https://www.psi.ch/sls/phoenix/philox

Contact: thomas.huthwelker@psi.ch, camelia.borca@psi.ch

References

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