MS43-P15 Comparative analysis of *ex-situ* and *in-operando* X-ray diffraction experiments for lithium insertion materials

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A comparative study of *ex-situ* and *in-operando* X-ray diffraction experiments using the fast lithium ion conductor $Li_{0.18}Sr_{0.66}Ti_{0.5}Nb_{0.5}O_3$ 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 unit 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* diffraction may therefore enable to determine the strength of octahedral rotations in defect perovskites and allow correlations with the large variance of ionic conductivities in these materials.

References

[1] W. R. Brant, D. Li, Q. Gu & S. Schmid, *J. Power Sources* **302**, 126 – 134 (2016). Comparison of *ex-situ* and *operando* X-ray diffraction techniques for investigating lithium insertion defect perovskite $Li_{0.18}Sr_{0.66}Ti_{0.5}Nb_{0.5}O_3$.

[2] W. R. Brant, S. Schmid, A. Kuhn, J. Hester, M. Avdeev, M. Sale & Q. Gu, *ChemPhysChem*. **13**, 2293-2296 (2012). Rapid lithium insertion and location of mobile lithium in the defect perovskite $Li_{2y}Sr_{1-x-y}Ti_{1-2x}Nb_{2x}O_3$.

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

MS43-P16 PHOENIX: a tender energy beamline for in-situ X-ray studies

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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 um^2 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 $Ca(Mg)CO_3$ 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/phoenix

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[1] S. Pin et al., J. of Phys. Chem., 2013, 117, 8368-8376

[2] G. Nurk et al., J. Power Sources 2013, 240, 448-457

[3] J. Czapla-Masztafiak et al., Biophysical J. 2016, 110(6), 1304–1311

[4] M.W. Tew et al., J. Cat. 2011, 283(1), 45-54

[5] A. Vjunow et al., Journal of the Am. Chem. Soc. 2014, 136(23), 8296-8306

[6] E. Cato et al., Microchem. J. 2016, 126, 18-24

[7] M. Brown et al., J. Phys. Chem. Lett. 2012, 3, 231-235

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