MSPD : 12 years of SXRPD on Operando Batteries at ALBA, MSPD2 to come

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The Material Science and Powder Diffraction beamline (BL04-MSPD) [1] has acquired sound expertise in performing Synchrotron X-ray Powder Diffraction (SXRPD) experiments on Operando batteries. Since 2014, ~200 experiments of this type have been conducted on MSPD by users from all Europe, resulting in almost equal number of per review publications. The low noise and fast readout 1D position sensitive detector MYTHEN highly contributed to the success of such experiments. Throughout this period, data collection strategy and hardware (serial data collection [2], non-ambient temperature [3], current pulse discharge [4]), data visualization and synchronization with electrochemistry and data processing [5] have been continuously improved. Latest significant challenge is the impact of the intense synchrotron beam inhibiting the operation of the battery [6] leading in careful thinking of new data collection strategy, in particular since MSPD will move towards an undulator as insertion device hence higher flux density. So-called beam inhibition effect can be mitigated by selection of higher energies, serial data acquisition of multiple batteries and using a smaller beam but mesh mapping whilst (dis-)charging so to illuminate fresh points.

All the above will be touched essentially based on the beyond Li batteries master examples in which $Na_3V_2(PO_4)_2F_3$ and $Na_3V_2(PO_4)_3$ compounds are used as positive electrodes and sodium (des-)inserted. High angular resolution was initially applied to unambiguously confirm the orthorhombicity of $Na_3V_2(PO_4)_2F_3$ but tending to tetragonal when not fully “fluorized” [7]. Operando data collection resolved the multiple phases occurring when (des-)inserting 2 Na ions at various rates and/or grain coating for improving performances [8,9]. To be noted that batteries with $Na_3V_2(PO_4)_2F_3$ cathode material are now commercialized in portable devices. The so called NASICON $Na_3V_2(PO_4)_3$ positive cathode has been studied on MSPD by SXRPD on Operando batteries at variable temperatures using either ALBA designed temperature cells [4] or developed at LRCS, Amiens [10]. Finally, seconds order pattern acquisition appeared necessary in the case of blended electrodes (NMC-LFP-LMO) to decoupled the active role of each material whilst discharging (Li insertion here), the latter being performed by sending high intensity current pulses followed by long relaxation.

Beside diffraction, hard Xray spectroscopy is generally used to follow the valence state of transition metal elements involved in the redox process of battery mechanism, the NOTOS beamline at ALBA allows collecting quasi simultaneously both XRD patterns and XANES/EXAFS spectra on Operando batteries. [11]. Multi modal and multi techniques in energy related material and catalysis has been established as a scientific priority in ALAB, for Operando batteries this encompass XRD, XAS, Xray Photoemission Spectroscopy, InfraRed spectroscopy and Transmission Electron Microscopy.

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