3D *Operando* Monitoring of Lithiation Spatial Composition in NMC Cathode Electrode by X-ray Nano-CT & XANES Techniques

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Over the last decades, with increasing energy demand along with the shift towards greener energy solutions, Li-ion batteries have gained attraction for energy storage applications.[1] Due to the high complexity in the hierarchical architecture of composite electrodes, it is extremely challenging to ensure a homogenous electrode structure. The non-uniform distribution of phases, leading to microstructural heterogeneities, has been shown to induce a non-uniform electrochemical behavior, which can deteriorate the performance, and cause macroscopic failures.[2,3] Therefore, the identification of these microstructural heterogeneities and understanding their effects on the dynamics of (de)lithiation is crucial to improve electrode design.

Lithium compositional distributions in composite electrodes can also be investigated using various techniques such as Raman microscopy,[4] X-ray diffraction (XRD),[5] or 2D X-ray absorption near-edge structure spectroscopy (XANES).[6] However, these methods have been restricted to low spatial resolution or spatially integrated signal along the depth direction. These methods hence cannot accurately capture the spatial distributions and can lead to a limited interpretation of the mechanism. Recently, Finegan *et al.*[7] used *Operando* X-ray diffraction-computed tomography (XRD-CT) for characterizing, in 3D, the dynamic crystallographic structure between and within LMO particles during electrochemical operation.

Several works have combined XANES and X-ray tomography to generate a rich data set that allows a direct correlation of the chemical information and the microstructure. Meirer *et al.*[8] used 3D XANES to probe the conversion of NiO to Ni metal in a partly reduced electrode. They found significant inhomogeneities in terms of chemical states across particles as well as evidence of fracturing caused by volume expansion during the reaction. More recently, Wang *et al.*[9] collected a 46-point spectrum across the iron K-edge of a $LiFePO_4$ cathode particle and developed a run-out correction system to enable automated tomography.

Here, we perform XANES coupled with transmission X-ray computed tomography (TXM-CT) at nanoscale in *Operando* mode to investigate $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ (NMC) positive electrodes[12]. The ability to probe battery materials in an *operando* mode provides significant advantages over *ex situ* approaches and allow characterizing the microstructure evolution while capturing the electrochemical reaction kinetics inside electrode and active materials (AM). In this work, we demonstrate that *Operando* XANES-TXM nanoCT allows access to the Li distribution (local Li concentration) at nanoscale within the LiB electrodes during the operation. We also proposed a method that relies on just

three energy levels located at pre-edge, edge, post-edge for minimization of radiation damage to the sample. Also, a specific electrochemical cell and a sample preparation process were introduced, which make the use of electrodes typical to those used in real-life applications possible.

Our experimental results unveil the non-uniformity of the Li repartition throughout the LiB porous electrodes during operation [10]. As a result, there are regions being more active than the others as well as preference spots on the particle surface where the reactions are more likely to occur. The Li repartition across the electrode depth is adequately uniform, which indicates a negligible effect from porous electrode. This is expected as we used EC:DMC solvent-based electrolyte at 1.2 M which reduces the limitation from ionic transport in liquid phase within the porous electrode. Thus, we can conclude that mass transport in the electrolyte is not rate limiting factor in this electrode under the applied cycling conditions. In addition, some of the reconstructed slices also revealed that the lithiation process could also happen from internal pores of the AM particles. This observation also implies that the electrolyte along with the carbon conductive can penetrate some internal pores through the AM grain boundaries and allow the (de)lithiation process to occur from the inside of the NMC secondary particles.

Finally, we expect that our analysis technique will provide a direct method to unveil the effects of the electrode microstructure on its electrochemical performance [11,13]. This multiscale insight can shed light to the optimization of the electrode design to improve the electrode performance.
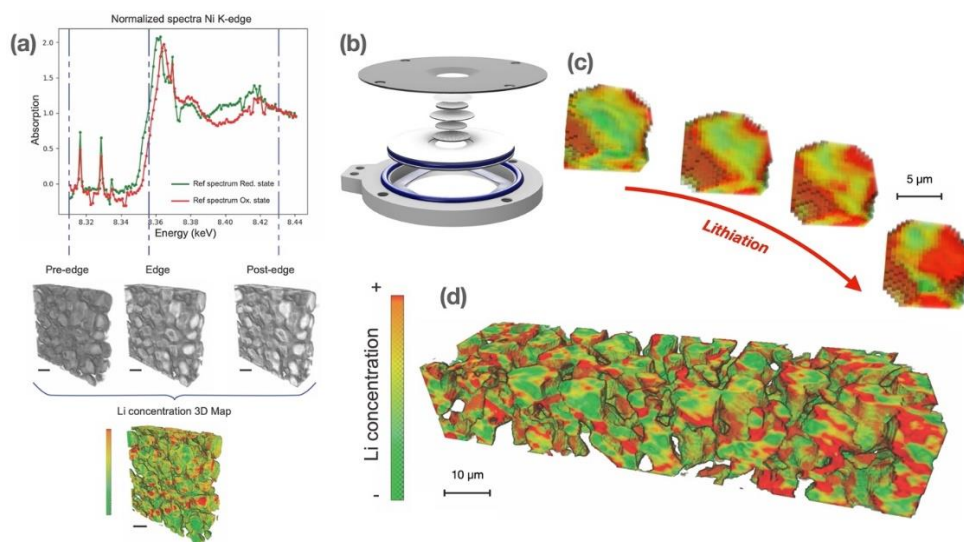
Figure

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