

Fingerprinting Electronic-State Evolution during Battery Operations through Soft x-Ray Spectroscopy

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Batteries operate with evolving electronic states. The potential and kinetics of these electronic states define the transportation of the charges in either electrons or ions. The functionality of a battery is essentially realized by this controlled/guided motion of charges during the charge and discharge process. At present, extensive efforts have been paid to material synthesis and structural characterization, which have been highly appreciated. However, the evolution of electronic states in batteries remains elusive and largely unexplored.

In this work, we focus on the evolving electronic states in some of the Li-ion battery materials studied by soft x-ray spectroscopic tools and methodologies developed at the Advanced Light Source (ALS). Soft x-ray spectroscopy directly fingerprints the ion diffusion through the evolving electronic states. The revealed information is directly relevant to the charge dynamics during battery operations. The combined soft x-ray techniques provide the complete information on the valence and conduction states on the surface and in the bulk, with elemental, orbital and chemical-bond sensitivities.

We will first introduce various soft x-ray spectroscopic techniques with the focus on soft x-ray absorption spectroscopy (sXAS) and emission spectroscopy (sXES). These techniques are the most direct and sensitive probe of the chemical bonds and physical electronic states in battery materials. This is especially critical for studying transition-metal (TM) based cathodes, for which, soft x-ray spectroscopy reveals directly the TM-3d valence states through the dipole allowed 2p-3d transitions

(Fig.1), unlike the indirect measurements through hard x-ray techniques. Additionally, sXAS and sXES provide complementary information on the unoccupied and occupied states in the vicinity of the Fermi level (band gap), which are the most relevant states to the electronic property of the materials [1].

By virtue of the soft x-ray's sensitivity to the electronic state, we show that the bottom of conduction band of battery binder materials could be reliably accessed through sXAS. A comparative study provides valuable information on the electrical conductivity of polymers used in Li-ion battery anode, which helps both the fundamental understanding and practical optimization of the materials [2].

For TM-based cathode materials, we will discuss the spectroscopic fingerprints of the electronic state evolution during the battery operation through both *in-situ* and *ex-situ* measurements. The soft x-ray spectra provide abundant elemental-sensitive information on formal valency, local structure distortion, spin state evolution, TM-3d state configuration, and more importantly, phase transformation [3]. The contrast of the overall spectral lineshape between different cathode materials indicates the different types of phase transformation; while the contrast between *in-situ* and *ex-situ* spectra reveals intriguing charge dynamics in Li-ion battery electrodes, which is related to both the phase-transformation type and the mesoscale morphology of the electrodes.

[1] W. Yang et al., *J. Electron. Spectrosc. Relat. Phenom. (review)*, DOI: 10.1016/j.elspec.2013.03.008 (2013)

[2] G. Liu et al., *Advanced Materials* 23, 4679 (2011)

[3] X. Liu et al., *JACS* 134, 13708 (2012)

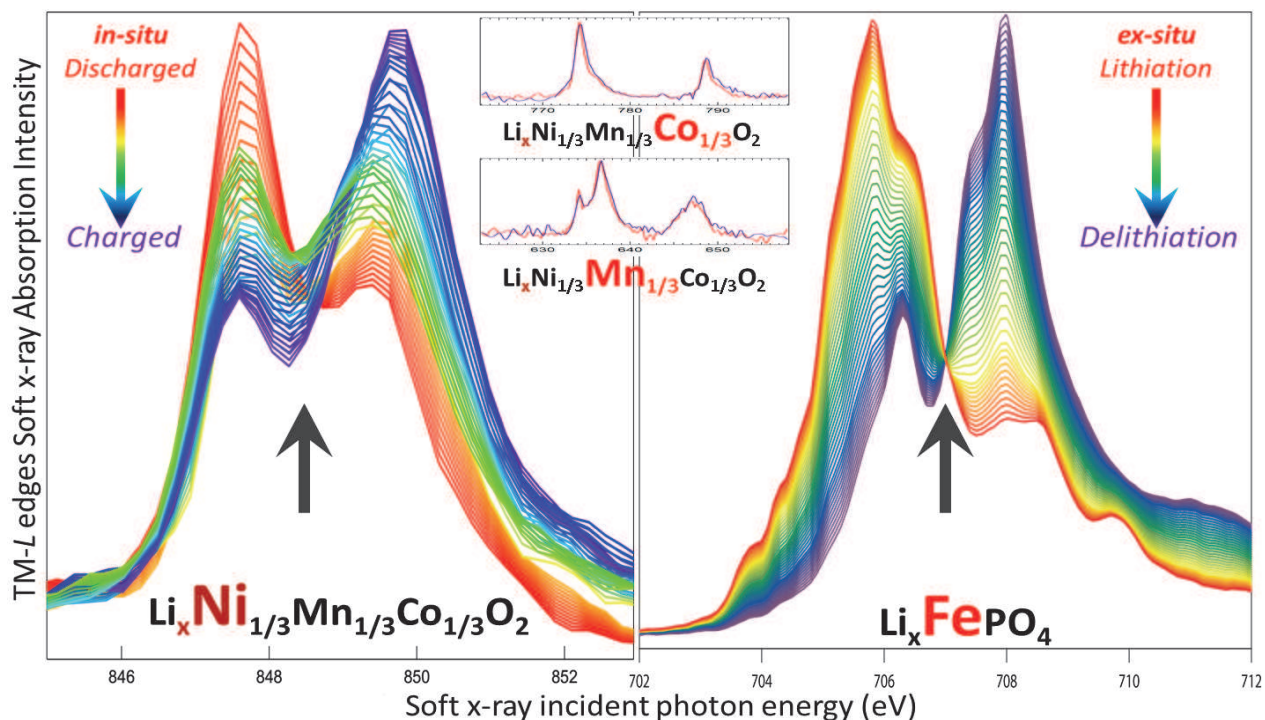


Fig.1 Elemental sensitive fingerprints of the transition-metal 3d state evolution during battery operation through soft x-ray spectroscopy. **(Left)** *in situ* and *operando* sXAS of Ni-L edges in the $\text{Li}_x\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ cathode collected in real-time with the electrochemical cycling between 3.5V (red) - 4.2V (dark purple). The spectral evolution indicates the valence change of Ni and the solid-solution type of phase transformation. On the contrary, inserts show there is no change with Co-L and Mn-L spectra within this electrochemical cycling range. **(Right)** *ex situ* sXAS of Fe-L edge in the Li_xFePO_4 cathode material at different (de)lithiation levels. The so-called isosbestic point (black arrow) provides spectroscopic indication on the dominating two-phase transformation [3], contrasting that of NMC compounds.