

Decoupling cationic–anionic redox processes in Li-rich cathodes using operando XAS

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The $\text{Li}_{1+x}\text{M}_{1-x}\text{O}_y$ (M=3d/4d/5d transition-metal) compounds constitute a unique playground for high capacity positive electrodes in Li-ion batteries. In addition to the charge-transfer occurring at the M cationic site, the anionic oxygen redox activity is triggered by the presence of non-bonding O 2p states close to the Fermi level [1]. Since the electronic and atomic structures are closely related, extra-capacity is strongly dependent on the structural and compositional parameters of the materials, such as M/O stoichiometry, Li–M cationic disorder and M–O covalence. In case of 3d-based Li-rich NMC, the large extra-capacity is partially associated to the release of oxygen, limiting its practical applications [2]. Theoretical calculations suggest that 4d and 5d based compounds with higher a covalence of the M–O bonds are more stable against surface O_2 release than Li-rich NMC and are more conducive for reversible anionic redox [3]. However, there is no clear consensus on the role of anionic redox toward application-wise important properties (i.e., voltage hysteresis, kinetics, and structural stability) in these Li-rich cathodes and further studies in operando conditions are mandatory to shed light on these issues.

We have investigated the charge compensation mechanism and local structural evolution in two Li-rich layered oxides, i.e. $\text{Li}_2\text{Ru}_{0.75}\text{Sn}_{0.25}\text{O}_3$ (LRSO) and Li_3IrO_4 (LIO), using X-ray absorption spectroscopy in operando conditions. A chemometric approach based on Principal Component Analysis (PCA) and Multi-variated Curve Resolution–Alternating Least-Square (MCR-ALS) method was used to extract and reconstruct the orthogonal components that are able to describe the whole XAS dataset [4].

In the case of LRSO [5], we demonstrate a spectroscopy-driven visualization of electrochemical reaction paths, which enabled us to neatly decouple the individual cationic-anionic redox contribution during cycling. We hence establish the redox and structural origins of all dQ/dV features and demonstrate the vital role of anionic redox in hysteresis and kinetics.

For the newly synthesized LIO [6], the O/M parameter delineates the boundary between the material's maximum capacity and its stability. In fact, the LIO compound pushes the anionic redox to its limit with three Li extracted from Li_3IrO_4 on oxidation without participation of Ir in the redox process. This exacerbated capacity does not come without a cost, since a loss of O_2 and a complete amorphization of the material is observed at the end of charge. However, a reversible capacity of nearly 3.5 e^- per transition metal is obtained by limiting the first delithiation to $x=1$ in Li_xIrO_4 , with a larger degree of redox participation of Ir and O in the lower and higher voltage region, respectively.

These fundamental insights about anionic-redox-based electrochemical energy storage are crucial for the design of new high energy-density batteries and the improvement of the existing ones.

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