Employing anionic redox chemistry to tune the electrochemical performance of Li-ion batteries

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Charge compensation for sulfide-type cathode materials for Li-ion batteries by redox chemistry of the sulfide sublattice is already know for decades. More recently, the remarkably high reversible capacity in specific Li-rich layered metal oxide cathode materials for Li-ion batteries has been associated with the contribution of anionic redox chemistry of the oxygen sublattice (i.e. oxidation of O^{2-} during lithium-ion extraction from the cathode material during charging of a battery), on top of cationic redox chemistry of redox-active transition metal ions.

In this lecture, the concepts of anionic redox chemistry in Li-rich layered oxide cathode materials for Li-ion batteries will be introduced. By the Mott-Hubbard vs. charge-transfer approach, the reversibility of the anionic redox of the oxygen sublattice will be correlated to the structural and chemical nature of Li-rich layered oxide cathode materials. It will be deduced that for 3d transition metal-containing Li-rich layered oxide cathode materials the anionic redox chemistry is to a lower extent reversible compared to their 4d and 5d transition metal-containing counterparts. Irreversible anionic redox chemistry implies the release of O_2, accompanied with a degradation of the initial layered structure to a spinel-type and eventually a rock salt-type structure, penalizing the energy density (i.e. *voltage fade*). As commercialization of the latter (e.g. Li_2RuO_3 or Li_2IrO_3) is not feasible due to the scarcity and high price of the respective 4d and 5d transition metals, improving the reversibility of the anionic redox chemistry, coupled with cationic redox, of 3d transition metal-containing Li-rich oxides is of great interest.

A potential strategy to inhibit voltage fade is to stabilize the layered structure by partial substitution of redox-active transition metal cations by redox inactive, isovalent cations, showing a stronger metal-oxygen bonding. The second part of this lecture will focus on the implementation of Ti^{4+} substitution in Li_2MnO_3 to understand its influence on the anionic redox and the electrochemical performance when applied as a cathode material for Li-ion batteries.

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