

# Lowered Energy Efficiency in Anionic-Redox-based Li-rich Cathodes – What are its Origins?

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Li-rich cathodes, despite their promising specific energies that reach  $1000 \text{ Wh kg}_{\text{pos}}^{-1}$ , suffer from voltage fade, poor kinetics, and voltage hysteresis.<sup>[1]</sup> Among these drawbacks, the latter two are detrimental for energy efficiency but this largely remains neglected within the battery community. Such an energy inefficiency, besides causing energy wastage, imposes a direct cost on the consumers, expressed in  $\$ \text{ kWh}^{-1}_{\text{consumed}}$ .<sup>[2]</sup> In light of this, we herein pursue the fundamental origins of poor kinetics and voltage hysteresis in a variety of Li-rich cathodes, traversing practical (*3d*-metal-based) as well as model (*4d*- and *5d*-metal-based) systems and paying particular attention to the role of anionic redox chemistry ( $\text{O}^{2-} \leftrightarrow \text{O}^{n-}$ ,  $n < 2$ ) that is intrinsic to these materials.<sup>[3]</sup>

Starting with the commercially interesting Li-rich NMC that is derived from  $\text{Li}_2\text{MnO}_3$ , we will demonstrate bulk anionic redox activity using synchrotron-based hard-X-ray photoelectron spectroscopy (hard-XPS).<sup>[4]</sup> By exploiting the anionic–cationic redox mechanism revealed by hard-XPS, we will highlight a charge vs. discharge asymmetry in the anionic redox process, which leads to path dependence and hence voltage hysteresis. We will further demonstrate the fast kinetics of cationic redox in contrast to the sluggish anions. Anionic redox thus emerges to be correlated with hysteresis and poor kinetics, implying its crucial role in deteriorating the energy efficiency.

Interestingly, the model  $\text{Li}_2\text{RuO}_3$ -based system had already warned about these issues<sup>[5]</sup>, which we fully established via an in-depth characterization with *operando* X-ray absorption spectroscopy (XAS)<sup>[6]</sup> that allowed us to elegantly decouple the individual  $(dQ/dV)_{\text{cationic}}$  and  $(dQ/dV)_{\text{anionic}}$  contributions. Exploiting further this model cathode, we are presently investigating the nature of heat generation due to energy inefficiency and voltage hysteresis, since such thermal aspects can be decisive for practicability.

Lastly, to answer whether these issues can ultimately be overcome, we will present our fresh investigations of the model  $\text{Li}_2\text{IrO}_3$  system that enlists a simultaneous (iso-potential) anionic–cationic redox activity. Whether such a synergy can improve energy efficiency, and to what extent this can be pushed, is presently under investigation on a fundamental basis.

Overall, this poster, which will be a mix of freshly-published as well as in-progress investigations, will highlight the crucial role of anionic redox on energy inefficiency – an issue of fundamental as well as of practical interest for next-generation Li-rich cathodes.

## References:

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