Increasing the Energy Density of Battery Materials with Anionic Redox: Dream or Reality?

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Our increasing dependence on lithium-ion batteries for energy storage calls for continual improvement in the performance of their positive electrodes, which have so far relied solely on cationic redox of transition-metal ions for driving the electrochemical reactions. Anionic redox has reshaped the conventional way of exploring advanced cathode materials for Li-ion batteries. This phenomenon is typically observed in the so-called Li-rich transition metal oxides (Li-rich TMOs) among which $Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.54}O_2$ (Li-rich NMC) is the archetype. [1-3] The anionic redox reaction provides an additional electron reservoir beyond the cationic redox reaction, which is typically seen in conventional $LiMO_2$ oxides, allowing for theoretical capacities that can reach up to 300 mAh/g. [3] This increase of capacity has the potential to greatly enhance the energy density of batteries. However, while the anionic redox reaction offers these promising benefits, it also introduces several practical challenges, such as voltage fade, O_2 release, and voltage hysteresis. [4] These issues significantly impact the cycling stability and overall lifespan of the batteries, posing considerable barriers to the commercialization of Li-rich TMO cathodes. To address these challenges, we have developed a comprehensive theoretical framework based on chemical bonding concepts. [5] Combined with electronic structure DFT calculations and molecular dynamics simulations, this approach allowed us to rationalize the underlying mechanism of the anionic redox process and to identify the number of holes generated on oxygen sites during charge as the key parameter for the reversibility of the reaction. [5,6] By understanding and controlling the number of these holes, [7] we can better predict and manipulate the behavior of anionic redox, offering pathways to enhance the stability and performance of Li-rich cathode materials in practical applications.

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