

Activation Mechanism of Anionic Redox in the Cathode Electrodes of Li-Ion Batteries

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Nowadays, electric vehicles (EVs) are replacing the gasoline cars due to the boom of the technologies of energy storage, of which lithium-ion batteries (LIBs) predominantly play the role. The further commercial application of LIBs is hindered mainly by the low capacity of cathode electrodes. Conventional cathode materials, such as LiCoO₂, LiFePO₄, and LiMn₂O₄, have limited capacities (<200 mA h g⁻¹) because of that their redox processes rely solely on cations, as well as the restricted quantity of lithium ions. Upon the emergence of lithium-rich electrodes, which can be formulated as Li_{1+x}MO₂, the capacity was boosted to larger than 250 mA h g⁻¹ based on the cooperation of cationic and anionic redox that can afford multiple-electrons transfer, which leads the research to the era of high-capacity electrodes.¹⁻³ More and more lithium-rich electrodes were found to show superior performance due to the contribution of anionic redox.

Though anionic redox largely enhance the capacity, there are still some problems that have not yet been solved. The most underlying mechanism that how the anionic redox being triggered in these electrodes is still not fully understood. This may restrain the further invention of new high-capacity electrodes and modification of present cathodes.

Recently, we have accomplished a work that unravels a principle to guide the understanding of the triggering mechanism of anionic redox. The study shows that the substitution of Fe³⁺ in inactive cubic Li₂TiO₃ triggers oxygen redox activity. The theoretical investigation demonstrated that electron transfer mainly occurs at oxygen atoms surrounded by Fe rather than Ti ions. This was perfectly explained by a thermodynamic activation of the charge-transfer process facilitated by Fe ions, which was discerned by the relative values of Hubbard U and charge transfer energy Δ . The extension to sulfides expanded the universality of this theory in providing a further general understanding of the anionic redox process. This finding will enhance efficiency when utilizing an anionic redox process to acquire higher capacity by composition design, such as by the combination of specific metal ions.

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