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BATTERY CATHODES

Oxygen release or oxygen redox

Wanli Yang

Voltage fade, a major barrier to the commercialization of a series of high energy-density battery electrodes for more than a decade, is now re-examined with advanced characterisation techniques. The origin of voltage fade is correlated to oxygen activities.

Developing high energy-density, stable and low-cost energy storage systems is a critical but formidable challenge in today's sustainable energy applications, especially electric vehicles (EVs). Among various energy storage technologies, Lithium-ion batteries (LIBs) remain the most promising candidate to power EVs, provided their energy density could be improved to meet commercial requirements to ease the range anxiety. Lithium-rich (LR) *3d* transition-metal (TM) oxides have long been proposed to replace the conventional cathodes because of their significant higher capacity (> 250 mAh/g) than conventional ones (< 200 mAh/g). However, these advanced cathodes would undergo a continuous decrease of the average voltage upon electrochemical cycling, dubbed as "voltage fade", which seriously reduces the energy efficiency and complicates the battery management system. Therefore, fundamental mechanisms of voltage fade and practical approaches for alleviating it, including both lattice doping and surface/interface modifications, have been intensively studied since the discovery of the LR materials[1,2]. However, questions remain on the origin of voltage fade, and truly effective solutions are yet to emerge to eliminate the voltage fade while maintaining the high capacity.

Now, two studies in *Nature Energy* re-tackle the voltage fade problem in LR electrodes, offering new insights for understanding its origin and suggesting new ways to address the effect. In one study[3], Jun Lu and colleagues examine a $Li_{1.2}Ni_{0.15}Co_{0.1}Mn_{0.55}O_2$ cathode and attribute the voltage fade to the change of TM redox activities upon extended electrochemical cycles based on spectroscopic analyses. Although TM redox mechanisms in Li- and Mn-rich electrodes have been previously studied, detailed elemental analysis were mostly limited to early cycles[4]. By performing analyses upon extended cycling up to 83 cycles, Lu and colleagues reveal that all TMs evolve towards low-valence states. In particular, the researchers report that the evolution of the Co redox couple from $Co^{3+/4+}$ to $Co^{2+/3}$ and the emerging Mn redox couple of $Mn^{3+/4+}$ directly contribute to the drop of discharge voltage. In a second study[5], Andrej Singer and co-works find a large amount of structural dislocations in LR electrodes: the dislocation density (1×10^{10} cm^{-2}) is an order of magnitude higher than that in electrode materials with same type of structure but without the excessive Li. They explain that the dislocation induces a significant oxygen-layer stacking change in the lattice structure of the LR electrodes, and such structural re-arrangement leads to significant drop of the discharge voltage.

Interestingly, although the two studies discuss the voltage fade from different angles, both works emphasize the links between their findings and oxygen activities. In the work of Lu and co-workers, release of oxygen gas, associated with structural changes upon cycling such as appearance of large pores, is believed to drive the TM redox couples towards lower valences, leading to the voltage fade. On the other hand, Singer and co-workers consider the high-density dislocations not only being structurally responsible to the voltage fade, but also a characteristic behavior of lattice oxygen redox activities. They argue that the dislocation network could enhance the mobility of oxidized oxygen species in the bulk electrode. It is worth mentioning that in earlier works, voltage fade was mostly attributed to various structural changes that were also associated with oxygen activities in LR electrodes. E.g., the layer-to-spinel transition is accompanied by oxygen release. Cation migration, especially to the tetrahedral sites, also leads to voltage face[6], which is recently associated with lattice oxygen redox activities[7]. All these findings are summarized in Fig. 1 with the proposed causality and mutual interactions indicated by single and double arrows, respectively. Overall, the debate remains between oxygen release and lattice oxygen redox activities on understanding voltage fade.

Intuitively, oxygen release could be viewed as an irreversible part of oxygen redox activities. However, with the elusive fundamental mechanism of oxygen redox reactions, the exact relationship between oxygen gas release and lattice oxygen redox is unknown and could be more complex than an intuitive thought. Another important question is whether or not a unified explanation for the origin of voltage fade can be found; for example, most voltage-fade related observations are attributed to only oxygen release, others are associated with lattice oxygen redox (Fig. 1). Which one is the intrinsic cause of voltage fade, the oxygen release only, the lattice oxygen redox, or any type of oxidized oxygen? The same question remains for the origin of the sluggish kinetics in oxygen redox systems[8]. To clarify these questions requires a reliable distinction of the oxygen redox activities, calling for direct detections and quantifications of the oxygen chemical states in batteries. Note that Lu and coworkers indirectly calculate the amount of lattice oxygen redox contribution by deducting the TM contribution from the total capacity. Unfortunately, a direct detection of oxygen redox reactions is technically very challenging, because conventional oxygen spectroscopies are not reliable due to the influences from strong surface signals and/or dominating TM contributions to oxygen spectra through hybridizations[9]. Therefore, direct and reliable characterizations with improved chemical and elemental sensitivities, such as full mapping of oxygen-edge inelastic scattering[9], become essential for clarifying the fundamental link between oxygen activities and practical hurdles like voltage fade.

Finally, both works suggest guidelines for testing and solving the voltage fade problem. In addition to the central claim of chemical mechanism of voltage fade, Lu and colleagues show a close relationship between the material's thermal stability and the voltage fade behavior, proposing that a speedy heating test of thermal stability could assess the voltage fade. Singer and colleagues present an intriguing recovery of voltage through an annealing of the cycled electrode materials. They argue that annealing restores the structure that was changed by dislocations, thus bringing back the decreased voltage. Although complicated mechanism could be involved in such a re-annealing and re-manufacturing process, and an ultimate solution to eliminate voltage fade is yet to be developed, these works provide important insights towards the final goal.

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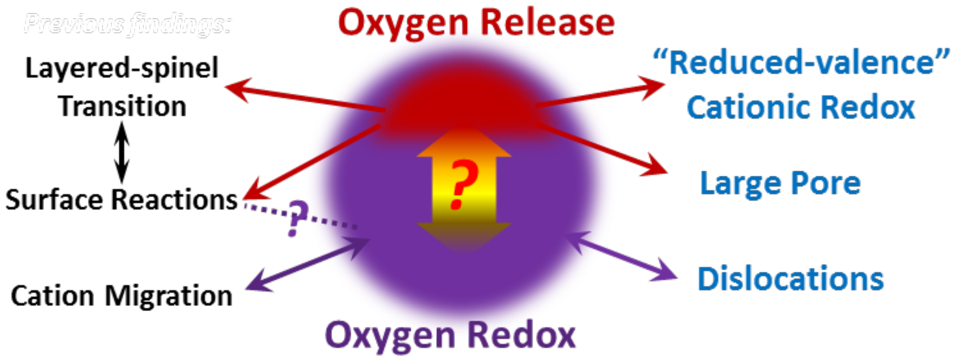

Fig. 1 Voltage Fade factors and their associations with redox-active oxygen. Oxygen redox and oxygen release are represented by purple and red spheres respectively. Oxygen release could be naively viewed as an irreversible part of oxygen redox activities, it is represented by a smaller sphere. It is important to note though that the relationship between oxygen redox and oxygen release is yet to be clarified. The red arrows refer to literature findings that were attributed to oxygen release. Note surface

reactions are often discussed based on radical oxygen migrated to the surface, and is related to the layered-spinel structural transition[1,2], and thus they are linked with a double-headed arrow. The purple double-headed arrows refer to those findings that could be mutually associated with oxygen redox activities. Although oxidized oxygen is chemically active in general, it is yet to be clarified whether surface relations and the lattice oxygen redox activities in the bulk are also associated (dotted line)[10].