Surface Doping Enhanced Electrochemical Performances of Li-rich Layered Materials
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Li-rich layer-structured oxides are regarded as the most promising cathode material for their high energy density, but still suffer from severe problems such as capacity fading, poor rate performance and continuous potential decay. Herein, the most popular Li-rich Mn-based cathode material Li$_{1.2}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$O$_2$ (or Li$_2$MnO$_3$·LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$, LMR) is surface doped with element X to address these issues. Atomic-scale recognition by aberration-corrected scanning transmission electron microscopy (STEM) shows that the X atom enters the Li layer by a depth of 4 to 5 atomic layers (~1 nm). Raman spectroscopic analysis demonstrates the structural integrity of the material and the absence of the usual layer-to-spinel structural transition in most of the Li-rich oxide cathode material after repeated cycling between 2.5 and 4.8 V vs. Li$^+$/Li. Electrochemical evaluation indicates that the capacity remains 284 mAh g$^{-1}$ (a retention of 94.5%) and the discharge potential drops only 190 mV in 100 cycles. These improvements are attributed to the pillaring effect of the heavy X atom within the lithium layer and the oxygen-capturing function of the X-based oxide on the surface, as well as the strong X-O bonds that mitigate the migration of the transition metals. Our surface modification strategy provides a vital approach to inhibit the undesired side reactions and structural deterioration of Li-rich cathode materials.

Figure 1. Comparison of the selected normalized discharge potential profiles of LMR-X and LMR in the initial and after 100 cycles (inset for the dependence of their average potentials on the cycling number) (a), the cycling performance of LMR and LMR-X (b); The STEM HADDF (c and d) and the corresponding ABF (e) images of a LMR-X particle.

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