Off-Stoichiometry-Induced Surface Protective Layer for High Performance Layered Lithium Cobalt Oxide

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Despite the long history in commercial lithium-ion batteries, layered lithium cobalt oxide (LiCoO\textsubscript{2}) suffers from structural degradations that shorten the cycle life when operating at high voltages (i.e., 4.5 V vs Li/Li\textsuperscript{+}) in organic electrolytes or even at moderate voltages in aqueous electrolytes. This limited performance originates from the O\textsubscript{3}-to-O\textsubscript{1} phase transition involving cobalt ion dissolution or surface oxidation followed by Li\textsubscript{2}O leaching, respectively. Here, we report a one-pot synthesis that yields LiCoO\textsubscript{2} bearing a spinel-Co\textsubscript{3}O\textsubscript{4} surface structure with a thickness of 2 nm \textit{via} lithium-deficient stoichiometry (Li:Co=0.98:1). The lithium-deficiency induces the spinel structure, a thermodynamically preferred phase at the given stoichiometry, by temperature-specific phase separation. The cobalt ion in the spinel layer is at the oxidation state of 2+ or 3+ and thus mitigates its dissolution and oxygen gas evolution even at fully charged state where the oxidation state of cobalt in the bulk reaches 4+, improving cyclability in both organic and aqueous electrolytes markedly.

References: