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 ($LiCoO_2$) suffers from structural degradations that shorten the cycle life when operating at high voltages (i.e., 4.5 V *vs* Li/Li^+) in organic electrolytes or even at moderate voltages in aqueous electrolytes. This limited performance originates from the O3-to-O1 phase transition involving cobalt ion dissolution or surface oxidation followed by Li_2O leaching, respectively. Here, we report a one-pot synthesis that yields $LiCoO_2$ bearing a spinel-Co_3O_4 surface structure with a thickness of 2 nm *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:

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