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Coulombic self-ordering upon charging a large-capacity layered cathode material for rechargeable batteries

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Abstract

Lithium- and sodium-rich layered transition-metal oxides have recently been attracting significant interest because of their large capacity achieved by additional oxygen-redox reactions. However, layered transition-metal oxides exhibit structural degradation such as cation migration, layer exfoliation or cracks upon deep charge, which is a major obstacle to achieve higher energy-density batteries. Here we demonstrate a self-repairing phenomenon of stacking faults upon desodiation from an oxygen-redox layered oxide Na_2RuO_3, realizing much better reversibility of the electrode reaction. The phase transformations upon charging A_2MO_3 (A: alkali metal) can be dominated by three-dimensional Coulombic attractive interactions driven by the existence of ordered alkali-metal vacancies, leading to counterintuitive self-repairing of stacking faults and progressive ordering upon charging. The cooperatively ordered vacancy in lithium-/sodium-rich layered transition-metal oxides is shown to play an essential role, not only in generating the electro-active nonbonding 2*p* orbital of neighbouring oxygen but also in stabilizing the phase transformation for highly reversible oxygen-redox reactions.