

OXYGEN REDOX ACTIVITY IN P2-TYPE LAYERED OXIDES AS HIGH-ENERGY CATHODE FOR Na-ION BATTERY: NEW INSIGHTS FROM FIRST-PRINCIPLES

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Na-ion batteries (NIBs) are rapidly emerging as convenient alternative to state-of-the-art Li-ion battery for large-scale applications, thanks to wide availability and consequent low cost of raw materials [1]. Layered transition metal oxides (Na_xTMO_2) have been proposed as promising active components at the cathode side of NIB cells, where design and optimization seem to rely on enhanced energy density and stability. Higher operating voltage in P2-type polymorphs of Na_xTMO_2 can be achieved by enabling anionic reactions, but the irreversibility of $\text{O}^{2-}/\text{O}_2^{\cdot-}/\text{O}_2$ evolution leads to large capacity loss at first charge cycle [2, 3]. Here we propose a first-principles investigation of P2-type $\text{Na}_x\text{Ni}_{0.25}\text{Mn}_{0.68}\text{O}_2$ as a case study. Computational strategies are employed to dissect the structural and electronic features of the redox-active elements in this material at different sodiation stages [4]. In particular, we address the oxygen redox processes by investigating the formation of oxygen vacancies and dioxygen-metal complexes at low Na loads (high voltage range). Our PBE+U-(D3BJ) calculations show that low-energy superoxide moieties can be formed at $x \text{ Na} = 0.25$ in the Mn-deficient site, while the $x \text{ Na} = 0.125$ content enables the release of molecular O_2 via preferential breaking of Ni-O bonds. Mechanistic insights show that dioxygen formation is driven by the M-O covalency and unveil that O_2 loss can be effectively suppressed by Fe doping [5]. Our findings pave the route for the rational design of high-energy Na_xTMO_2 cathodes that feature enhanced reversible capacity and thus boost the development of efficient NIB devices.

References

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