Controlled Oxygen Redox for Excellent Power Capability in Layered Sodium-Based Compounds

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Recently, anionic oxygen redox ($O^{2-/1-}$) become a main research subject for realizing high power capability [1]. Unfortunately, although the delivered capacity obtained from the transition-metal redox and oxygen redox is one of highest among sodium cathodes, the system suffers from not only serious capacity fading but also poor rate capability because of the sluggish kinetics of the oxygen redox [2]. To come up with this drawback, cobalt substitution in layered sodium-based compounds is conducted to achieve a high-rate of oxygen redox. The rationally designed $Na_{0.6}[Mg_{0.2}Mn_{0.6}Co_{0.2}]O_2$ exhibits outstanding electrode performance, delivering a discharge capacity of 214 mAh g^{-1} (26 mA g^{-1}) with capacity retention of 87% after 100 cycles. High rate performance is also achieved at 7C (1.82 A g^{-1}) with a capacity of 107 mAh g^{-1}. Surprisingly, the $Na_{0.6}[Mg_{0.2}Mn_{0.6}Co_{0.2}]O_2$ compound is able to deliver capacity for 1000 cycles at 5C (at 1.3 A g^{-1}), retaining 72% of its initial capacity of 108 mAh g^{-1}. X-ray absorption spectroscopy analysis of the O K-edge indicates the oxygen-redox species ($O^{2-/1-}$) is active during cycling. First-principles calculations show that the addition of Co reduces the bandgap energy from ≈2.65 to ≈0.61 eV and that overlapping of the Co 3d and O 2p orbitals facilitates facile electron transfer [3], enabling the long-term reversibility of the oxygen redox, even at high rates. To the best of the authors' knowledge, this is the first report on high-rate oxygen redox in sodium-based cathode materials, and it is believed that the findings will open a new pathway for the use of oxygen-redox-based materials for sodium-ion batteries.

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