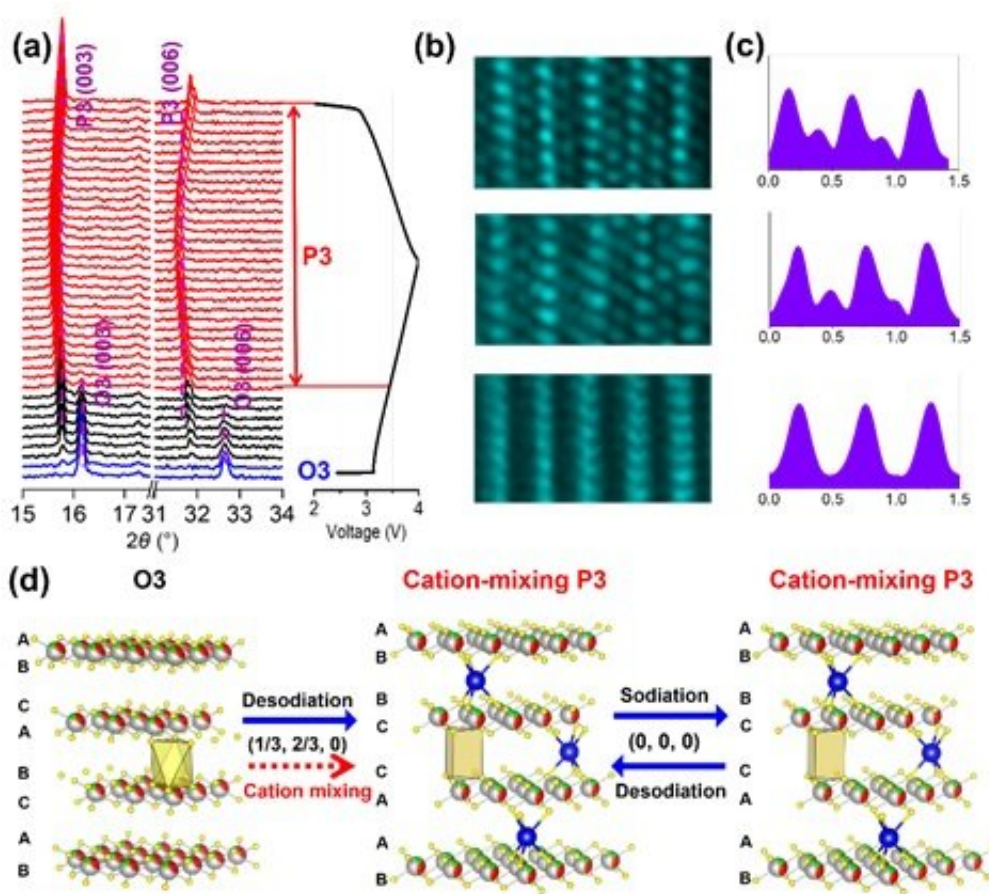


Cation mixing induces highly efficient sodium storage for layered cathodes

April 4 2018



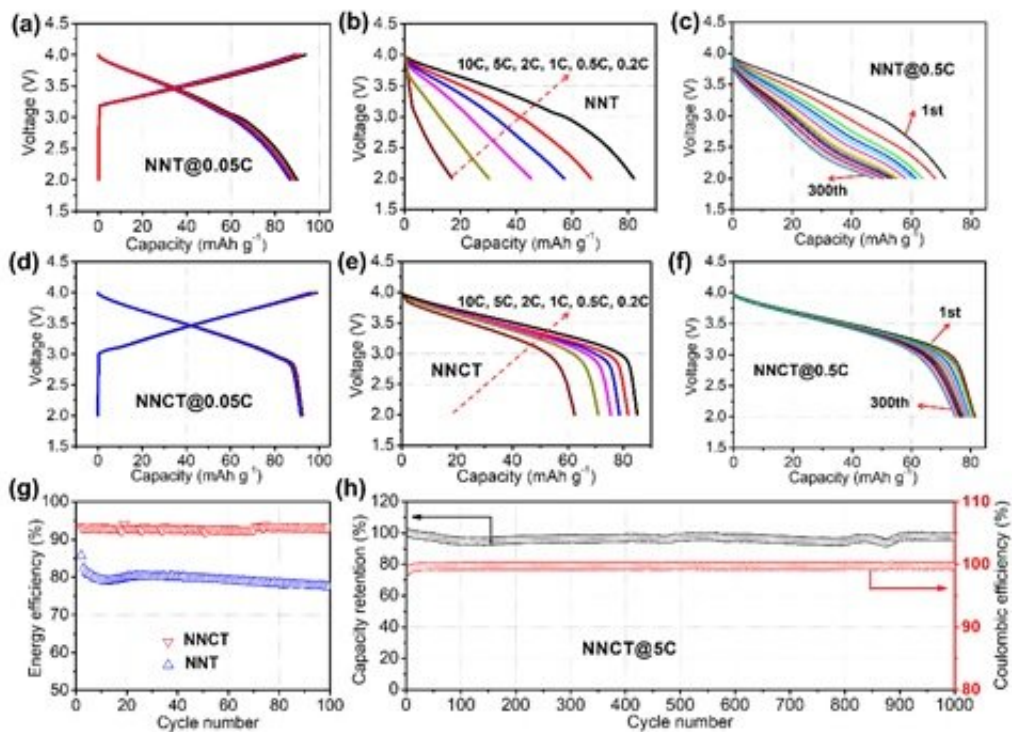
Structural evolution of NNCT electrode during the first cycle. In-situ XRD patterns collected for NNCT electrode cycled in the voltage range of 2.0-4.0 V (a); STEM images of the pristine (bottom), fully charged (middle), and fully discharged (top) NNCT electrodes (b) and the corresponding line profiles (c); Schematic illustration of the structural evolution of NNCT electrode during charge/discharge (d). Credit: Science China Press

Sodium is one of the most abundant elements, widely distributed on the Earth and in the ocean. Thus, sodium-ion batteries attract much attention for application in large-scale energy storage. The most popular cathodes for SIBs, i.e., the layered sodium-containing oxides, usually exhibit reversible host rearrangement between P-type and O-type stacking upon charge/discharge. Such a host rearrangement is unfavorable due to several factors: (1) The O-type phase is undesirable relative to the P-type, as the latter possesses a more open framework for Na-ion transport; (2) The rearrangements of host structure indicate sluggish reaction dynamics, which contributes to the voltage hysteresis and poor rate capability of the electrode; (3) The large variation in lattice parameters between P-type and O-type leads to elastic strain, causing the loss of active material and the resulting capacity fade.

On the basis of the above reasons, Haoshen Zhou and Shaohua Guo's Group from Nanjing University synthesized the O3-type $\text{Na}_{0.8}\text{Ni}_{0.3}\text{Co}_{0.1}\text{Ti}_{0.6}\text{O}_2$ (NNCT), and found that the NNCT electrode exhibited the cation-mixing characteristic by introducing transition-metal ions into Na layers during initial charge, thus suppressing host rearrangement upon charge/discharge by the induced "pinning effect." Moreover, the O-type phase is undesirable relative to the P-type, as the latter possesses a more open framework for Na-ion transport. Consequently, the NNCT with stable P3-stacking after initial charge process exhibits superior rate capability, high energy efficiency and excellent cycling performance. This group characterized the structural evolution during electrochemical sodium insertion/extraction by in-situ XRD and ex-situ STEM experiments. Fig. 1 shows the structural evolution of the NNCT electrode during the first cycle. NNCT transforms to P3-type in the initial charge process as do most others, but unexpectedly maintains the P3-stacking in the subsequent cycles. STEM results indicate the presence of transition-metal ions in sodium layers at the charged NNCT electrode, exhibiting the cation-mixing phenomenon.

The electrochemical performances of NNT and NNCT cathodes were comparatively studied in Fig. 2. The almost overlap curves suggest the high reversibility of NNCT with a reversible capacity of $92 \text{ mAh} \cdot \text{g}^{-1}$ at 0.05C rate. The discharge curves show a high capacity retention (92 percent) and negligible voltage degradation (0.03V) over 300 cycles are observed. The round-trip energy efficiency is stabilized at 93 percent for the NNCT electrode, and the Coulombic efficiency of NNCT cathode is around 99.7 percent. More importantly, NNCT cathode performs excellent long-term cycling performance, i.e., 98 percent capacity retention after 1000 cycles.

This work proposes that the "pinning effect" induced by introducing cation-mixing could effectively suppress the phase transition and relative host arrangement, thus greatly enhancing the structural stability. The findings underline the critical role of stable [sodium](#) storage framework, and also open a new path for design of high-efficiency energy storage materials.



(a) The typical voltage profiles of NNT at a 0.05C rate. (b) The rate capability of NNT. (c) The discharge curves of NNT at the first and every 25 cycles with a 0.5C rate, up to 300 cycles. (d) The typical voltage profiles of NNCT region at a 0.05C rate. (e) The rate capability of NNCT. (f) The discharge curves of NNCT at the 1st and every 25 cycles with a 0.5C rate, up to 300 cycles. (g) The round-trip energy efficiency curves of NNCT and NNT electrodes at a 0.5C rate for 100 cycles. (h) The long cycle performance and Coulombic efficiency of NNCT for 1,000 cycles at the 5C rates. Credit: Science China Press

More information: Shaohua Guo et al, Cation-mixing stabilized layered oxide cathodes for sodium-ion batteries, *Science Bulletin* (2018). DOI: [10.1016/j.scib.2018.02.012](https://doi.org/10.1016/j.scib.2018.02.012)

Provided by Science China Press

Citation: Cation mixing induces highly efficient sodium storage for layered cathodes (2018, April 4) retrieved 26 April 2024 from <https://phys.org/news/2018-04-cation-highly-efficient-sodium-storage.html>

This document is subject to copyright. Apart from any fair dealing for the purpose of private study or research, no part may be reproduced without the written permission. The content is provided for information purposes only.