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Designing Air-Stable O3-Type Cathode Materials by Combined Structure Modulation for Na-Ion Batteries

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Supporting Information

ABSTRACT: As promising high-capacity cathode materials for Na-ion batteries, O3-type Na-based metal oxides always suffer from their poor air stability originating from the spontaneous extraction of Na and oxidation of transition metals when exposed to air. Herein, a combined structure modulation is proposed to concurrently tackle the two handicaps via reducing Na layers spacing and simultaneously increasing valance state of transition metals. Guided by density functional theory calculations, we demonstrate that such a modulation can be subtly realized through co-substitution of one kind of heteroatom with comparable electronegativity and another one with substantially different Fermi level, by adjusting the structure of NaNi_{0.5}Mn_{0.5}O_2 via Cu/Ti co-doping. The as-obtained NaNi_{0.5}Cu_{0.05}Mn_{0.1}Ti_{0.1}O_2 exhibits an increase of 20 times in stable air-exposure period and 9 times in capacity retention after 500 cycles, and even retains its original structure and capacity after being soaked in water. Such a simple and effective structure modulation reveals a new avenue for developing high-performance O3-type cathodes and pushes the large-scale industrialization of Na-ion batteries a decisive step forward.

Large-scale energy storage systems have attracted increasing interest recently, since they are regarded as one of the greatest challenges for the development of smart electrical grid. The large demand and cost considerations may require the application of Na-ion batteries (NIBs) rather than Li-ion batteries, due to the abundance and wide distribution of Na. Recently, great efforts have been devoted to improve the overall performance of NIBs, in which the advancements of cathode materials play a crucial role.

Among various cathode candidates, O3-type Na-based layered transition metal oxides NaTMO_2 (where TM=transition metal, e.g., Co, Ni, Mn, Fe, etc.) are considered as one of the most appealing candidates due to their good electrochemical activity and simple synthesis process. However, when exposed to air, the capacity of O3-type cathodes are rapidly reduced originating from the spontaneous extraction of Na, oxidation of transition metals, and the concurrent transition to Na-deficient phases. The poor air stability greatly raises the cost for material storage, transportation, and battery manufacture, and thus limits the practical applications of O3-type oxides. At present, the rational strategies for improving the air stability of O3-NaTMO_2 have not been well developed. Therefore, the systematic research is urgently needed regarding to the mechanism governing improved air stability, in order to guide the design and development of O3-type cathode materials with both good air stability and excellent electrochemical properties.

Herein, a combined structure modulation is proposed to effectively improve the air stability of O3-type metal oxides via reducing the interlayer distance of Na layers and simultaneously increasing valance state of transition metals. Guided by density functional theory (DFT) calculations, we demonstrate that such a modulation can be subtly realized through co-substitution of one kind of heteroatom with comparable electronegativity and another one with substantially different Fermi level, by adjusting the structure of NaNi_{0.5}Mn_{0.5}O_2 (NaNM) via Cu/Ti co-substitution. Due to effective suppression of spontaneous Na extraction and improvement of oxidizability, the as-obtained NaNi_{0.45}Cu_{0.05}Mn_{0.05}Ti_{0.05}O_2 (NaNCMT) exhibits an increase of 20 times in stable air-exposure period, and even retains its original structure and capacity after being soaked in water. In addition, the electrochemical properties are significantly improved upon the combined modulation as the suppression of charge ordering and complicated phase transitions during cycling.

First DFT calculations were performed to examine feasibility of the combined structure modulation. Due to the substantial difference in Fermi level between Ti^4+ and Ni^2+/Mn^4+, substituting a small number of Mn^4+ with Ti^4+ is effective for preventing charge ordering and decreasing the electronic localization. The electronic delocalization results in expansion of TM layers and contraction of Na layer spacing, associated with decrease in interaction between TM and O, and enhancement of the binding energy between Na and O. DFT calculations predict that contraction of Na layer spacing in NaNM is accessible via Ti substitution (Figure 1a), which is in
excellent agreement with the results of X-ray diffraction (XRD) refinement of NaNM and NaNi_{0.5}Mn_{0.5}Ti_{0.5}O_{2} (NaNCMT) (Figure S1, Table S1, S2). Furthermore, Ti substitution effectively increases the valence state of Ni because the electronic delocalization decreases the number of electrons around Ni (Figure 1b). In addition, a mixing transition metal method\textsuperscript{49} was applied to further increase the valence state of Ni. The deformation of TMO\textsubscript{6} octahedrons and rearrangement of electrons were achieved with heterogeneous transition metal doping. Considering the electronegativity and electrochemical activity, Cu were introduced into this system,\textsuperscript{11} and the increase in valance state of Ni was also indicated (Figure 1b). The increase in Ni valance state upon Cu/Ti co-substitution was also experimentally confirmed by X-ray photoelectron spectroscopy (XPS) (Figure S2). The results of DFT calculations demonstrate that the structure modulation for NaNM, contracting Na layer spacing and increasing the valence state of Ni, is accessible via Cu/Ti co-substitution in theory.

Figure 1. DFT calculations. (a) Comparison of calculated configuration of NaNM and NaNCMT. (b) Electronic density of states projected on Ni ion of NaNM, NaNCM, and NaNCMT.

Based on the above calculative results, we prepared NaNi_{0.45}Cu_{0.05}Mn_{0.45}Ti_{0.1}O_{2} (NaNCMT) and NaNM, which are composed of large particles with several micrometers in dimension (Figure 2a and S3a). The energy dispersive spectroscopy (EDS) mappings (Figure 2b and S3b) clearly show that various elements uniformly distribute in particles. It can be seen that Cu/Ti co-substitution maintains the O\textsubscript{3} structure with R\textsuperscript{3}m space group (Figure 2c, 2d, S4, Table S2, S3), except for a small amount of NiO impurity.

Figure 2. (a) SEM image of NaNCMT. (b) EDS maps of NaNCMT. Rietveld refinement patterns of XRD data for (c) NaNM and (d) NaNCMT.

To test the air stability, aging experiments (exposing materials to air for 2 days or soaking in water for 10 min followed by drying at 100 °C overnight) were carried out, and then the structure of pristine and aged materials were compared by XRD measurements. As shown in Figure 3a, NaNM undergoes apparent structure change after aging experiments. The structure change is already observed just after 2 hours of air exposure as the formation of O\textsubscript{3} and P\textsubscript{3} type Na_{x-y}Ni_{y}Mn_{x}O_{2} (Figure S5).\textsuperscript{12} The proportion of Na-deficient P\textsubscript{3} phase gradually increases with the prolongation of air-exposure time, and the majority of water-soaked material transform into P\textsubscript{3} phase (Figure S6), indicating serious destruction of structure in water-soaked material triggered by excessive extraction of Na and insertion of H\textsubscript{2}O molecules.\textsuperscript{23} In contrast, a small amount of Cu/Ti co-substitution is sufficient to inhibit the spontaneous phase transition. The XRD patterns of NaCMT, whether exposed to air or soaked in water, are nearly identical to that of as-synthesized sample (Figure 3b). In addition, the water-soaked NaNCMT material shows no obvious morphological change compared with the pristine ones (Figure S7), indicating the good morphological stability. The improvement of air stability is also exhibited in the electrochemical data. Pristine NaNM shows an initial charge capacity of 106.4 mA h g\textsuperscript{-1}, however, the aged NaNM delivers a poor charge capacity of approximately 50 mA h g\textsuperscript{-1} (Figure 3c). It is worth noting that both the discharge capacity of the first cycle and the charge capacity of subsequent cycles approach 100 mA h g\textsuperscript{-1} (Figure S8), consistent with the conclusion of extraction of Na and formation of Na\textsubscript{0.5}Ni\textsubscript{0.5}Mn_{0.5}O\textsubscript{2} phases. In contrast, NaNCMT shows high capacity retention after aging experiments (Figure 3d). In addition, owing to the apparent difference in degree of reaction with water between NaNM and NaNCMT, the reaction heats of these two samples and water are also significantly different from each other. Supporting Video shows that with the addition of 5 g NaNM to 10 mL water, the temperature of water rises from 24.4 °C to 30.8 °C, while added with NaNCMT only increases to 24.6 °C from 24.5 °C.

Figure 3. XRD patterns of as-synthesized and aged (a) NaNM and (b) NaNCMT. The first charge/discharge curves of as-synthesized and aged (c) NaNM and (d) NaNCMT.

To further obtain information on the aging process of materials, ex-situ XANES data at the Ni and Mn K-edge were recorded to detect oxidation state changes. The position of Ni K-edge absorption peak of aged NaNM (Figure 4a) obviously shifts to the higher energy region. The shift closely resembles that of the charge process\textsuperscript{48} corresponding to Ni oxidation. The Mn K-edge spectrum of aged NaNM (Figure 4b) show only a change in shape, implying that the Mn remains at Mn\textsuperscript{3+}. The shape change originates from the adjustment in the local coordinational environment of Mn.\textsuperscript{44} In contrast, no shifts of Ni (Figure 4c) or Mn K-edge absorption peak (Figure 4d) are observed in aged NaNCMT, indicating significant improvement of inoxidizability consistent with the predictive results of DFT calculations.
Figure 4. XANES spectra at (a) Ni K-edge and (b) Mn K-edge of NaNM; (c) Ni K-edge and (d) Mn K-edge of NaNCMT.

Furthermore, structures of water-soaked materials were directly identified at atomic-scale by annular bright field (ABF) and high-angle annular dark field (HAADF) STEM. The ABF image of water-soaked NaNM (Figure 5a) shows significant contrast attributed to prismatic coordination siting Na columns. In particular, the O columns stack in a head-to-head stacking (ABBCCA) mode of P3 phase. In contrast, water-soaked NaNCMT remained original O3 phase (Figure 5b), verified by the octahedral sites of Na and ABCABC stacking model of O columns. Moreover, in HAADF images, the adjacent layer distance, \( d_c \), of aged NaNM (Figure 5c) is larger than that of NaNCMT (Figure 5d), although the lattice parameter of the c-axis of as-synthesized NaNM is smaller than NaNCMT. The increase in \( d_c \) of water-soaked NaNM is attributable to increased repulsion between adjacent O layers due to the decreased shielding effect of Na ions,\(^5\) which agrees well with the in-situ XRD result.

Figure 5. ABF-STEM images of water-soaked (a) NaNM and (b) NaNCMT. HAADF-STEM images of water-soaked (c) NaNM and (d) NaNCMT.

Based on the modulation strategy discussed above, we further designed Cu/Sn co-substituted NaNCMS, which also exhibits excellent air stability (Figure S9). As discussed above, the remarkable improvement in air stability is characterized from macro- to micro-scale for Cu/Ti co-doping into NaNM, inducing crystal and electronic structure modulation.

Complementing the excellent air stability, the electrochemical properties are also improved upon Cu/Ti substitu-

Figure 6. (a) Comparison of the first charge/discharge curves tested at 0.1C. (b) Comparison of cycling stability and Coulombic efficiency tested at 1C. (c) Rate performance of samples. (d) Discharge curves of NaNCMT cycled at constant charge at 0.5C/discharge rates from 0.1C to 10C. (e) In-situ XRD patterns collected during the first charge/discharge process of NaNCMT.

The excellent electrochemical performance discussed above is related to the Na deintercalation/intercalation mechanism, which was investigated by in-situ XRD pattern evolution (Figure 6e). With initial Na extraction, the (003) peaks of the O3 phase shift to a lower angle and a new P3 phase start to form through a two-phase reaction, corresponding to the low-voltage plateau region. Upon subsequent charge, the P3 phase peaks shift continuously until charged to 4.0 V with no the appearance of any new peaks, indicating a solid-solution reaction in this large region con-
sistent with the sloping charge/dischARGE curves. Upon discharge, the P3 phase transforms back to a single O3 phase, which is an exact opposite evolution of the charge process, indicating the phase transition processes are highly reversible. For the entire charge/discharge cycle of NaNCMT, no spontaneous Na extraction and enhanced inoxidizability. For the entire charge/discharge cycle of NaNCMT, no

In summary, a combined structure modulation is suggested and shown to effectively improve the stability of air exposure period for NaNM, and even retains its original structure and capacity after being soaked in water. Furthermore, charge ordering and complex phase transitions were both effectively suppressed during cycling, and thus after 500 cycles NaNCMT showed high capacity retention of nine times that of NaNM. The combined structure modulation is simple, yet effective, and paves a way for the development of high-performance O3-type cathodes and will be proved to be a milestone for the massive application of NIBs.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge via the Internet at http://pubs.acs.org. More details for experimental and characterizations;

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Notes
The authors declare no competing financial interest.

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