Suppression of Monoclinic Phase Transitions of O3-Type Cathodes Based on Electronic Delocalization for Na-Ion Batteries

Hu-Rong Yao†,‡,§†† Wei-Jun Lv†,‡,§†† Ya-Xia Yin‡,§,∥ Huan Ye‡,‡‡ Xiong-Wei Wu‡,§‡‡ Yi Wang‡,§‡‡ Yue Gong‡,∥ Qinghao Li‡,∥ Xiqian Yu§,∥ Lin Gu§,∥ Zhigao Huang‡,§,∥∥ and Yu-Guo Guo‡,§,∥∥

† Fujian Provincial Key Laboratory of Quantum Manipulation and New Energy Materials College of Physics and Energy, Fujian Normal University, Fuzhou 350117, China
‡ CAS Key Laboratory of Molecular Nanostructure and Nanotechnology, CAS Research/Education Center for Excellence in Molecular Sciences, Beijing National Laboratory for Molecular Sciences (BNLMS), Institute of Chemistry, and § Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences (CAS), Beijing 100190, P. R. China
∥ Fujian Provincial Collaborative Innovation Center for Optoelectronic Semiconductors and Efficient Devices, Xiamen, 361005, China
‡‡ University of Chinese Academy of Sciences, Beijing 100049, China

Supporting Information

ABSTRACT: As high capacity cathodes, O3-type Na-based oxides always suffer from a series of monoclinic transitions upon sodiation/desodiation, mainly caused by Na+/vacancy ordering and Jahn–Teller (J–T) distortion, leading to rapid structural degradation and serious performance fading. Herein, a simple modulation strategy is proposed to address this issue based on refinement of electron localization in expectation to alleviate the charge ordering and change of electronic structure, which always lead to Na/vacancy ordering and J–T distortion, respectively. According to density functional theory calculations, Fe3+ with slightly larger radius is introduced into NaNi0.5Mn0.5O2 with the intention of enlarging transition metal layers and facilitating electronic delocalization. The obtained NaFe0.3Ni0.35Mn0.35O2 exhibits a reversible phase transition of O3hex–P3hex without any monoclinic transitions in striking contrast with the complicated phase transitions (O3hex–O′3mon–P3hex–P′3mon–P3hex) of NaNi0.3Mn0.7O2 thus excellently improving the capacity retention with a high rate kinetic. In addition, the strategy is also effective to enhance the air stability, proved by direct observation of atomic-scale ABF-STEM for the first time.

KEYWORDS: Na-ion batteries, cathode materials, monoclinic phase transitions, electronic delocalization, electrochemical properties

Lithium-ion batteries (LIBs) have got resounding success in the portable electronics and are expected to power electric vehicles owing to their high energy density. Nevertheless, the sharply increased demand for LIBs is in contradiction with the scarce abundance of Li. In this context, Na-ion batteries (NIBs) exhibit intrinsic advantages compared to their LIB counterparts owing to the high availability and low cost of Na resources, especially for the applications in large-scale energy storage devices. The huge utilization potentiality of NIBs motivates extensive researches on various Na-based cathodes, in which O3-type transition metal oxides (NaTmO2) are recognized as one of promising materials. NaTmO2, in which octahedrally coordinated active ions and transition metal ions are alternately accommodated in the cubic close-packed oxygen columns, has a similar structure to Li counterparts LiCoO2 and is expected to follow the successful use of LiCoO2 in LIBs. However, their practical application is limited by the low Na diffusion rate and poor cycling performance resulting from the much more complicated phase transitions upon sodiation/desodiation. During charging/discharging, the structure of NaTmO2 always undergoes multiple monoclinic phases mainly caused by the Na+/vacancy ordering and J–T effects of active transition metal ions. As reported, The NaNiO2 predicts four monoclinic transitions of O3hex–P3hex–P′3–O′3–O3 hex when charged from 1.5 to 4.0 V, exhibiting a poor capacity retention of 82% after 25 cycles. Doping various metal elements into transition metal layers has been proven effective at suppressing the complicated phase transition and thus improving the electrochemical properties. However, the mechanism of how dopant mediates the distortion remains unclear, and the strategic doping to suppress monoclinic transitions has rarely been studied.

In this work, considering Na+/vacancy ordering and J–T distortion of NaTmO2 mainly originates from the change of localized electronic structure upon sodiation/desodiation, an effective design strategy is suggested to suppress the
monoclinic transitions via refraining the electron localization around transition metal ions. On the basis of density functional theory (DFT) calculations, we successfully modulate the electronic structure via introducing heteroatom with a slightly larger radius in expectation to ensure a homogeneous incorporation and simultaneously enlarge transition metal layers thus to intensify the degree of electronic delocalization, well verified by the modulation on NaNi0.5Mn0.5O2 via Fe substitution. The obtained NaFe0.3Ni0.35Mn0.35O2 does not show any monoclinic phases throughout whole charging process. This is in sharp contrast to two monoclinic phases (O’3mon and P’3mon) for the original NaNi0.5Mn0.5O2 implied by the analysis of in situ X-ray diffraction (XRD). The difference results in an optimal electrochemical performances based on complete reversibility of double redox couples (Ni2+/Ni3+ and Fe3+/Fe4+) investigated by ex situ X-ray absorption near-edge structure (XANES) spectra. Furthermore, air stability of material is also excellently improved, directly verified by annular bright-field (ABF) STEM at atomic resolution for the first time.

First, we carry out DFT calculations to reveal the impacts of incorporated Fe3+ on crystal and electronic structure to verify feasibility of the strategy mentioned above. It is obvious that Fe doping leads to the expansion of transition metal layers as a result of slightly larger radius of high spin-polarization Fe3+ (64.5 pm) than the average value (61.0 pm) of high spin-polarization Ni2+ and Mn4+ (Figure S1), which is also consistent with the powder XRD refinement results discussed below. Furthermore, the degree of electronic localization around transition metal ions in NaNi1-xMnxO2 and NaFe0.3Ni0.35Mn0.35O2 are compared by the electronic localization functions (ELF) calculations. As shown in Figure 1, the two-dimensional ELF slice along (106) surface comprises between 0 and 0.75, in which the bigger ELF value indicates the stronger localization of electron. To enable a visual comparison, the contour lines for ELF = 0.15 are also displayed. It is obvious that the degree of electron localization around transition metal ions is significantly refrained upon Fe substitution because of the expansion of TmO2 layers. Considering the main effect of Ni3+ with J−T distortion to monoclinic transitions, the ELFs around Ni (insets) are shown in more detailed comparison from 0.06 to 0.08, clearly indicating the stronger electron delocalization of NaFe0.3Ni0.35Mn0.35O2. The results of DFT calculations imply modulation on the microstructure of NaNi0.5Mn0.5O2, expansion of TmO2 layer spacing, and refraining of electron localization, is accessible via Fe3+ substitution with a slightly larger radius.

Based on the calculated results discussed above, we prepare the NaFeNi0.5−xMnx0.5−x/2O2 (x = 0, 0.3) samples by high-temperature solid-state method. The morphology of NaFe0.3Ni0.35Mn0.35O2 with particle size of approximately 2 to 5 μm (Figure S2) is observed by scanning electron microscopy (SEM). As shown in energy dispersive spectroscopy (EDS) elementary mappings (Figure S3), Na, Fe, Ni, Mn, and O are uniformly distributed in the particle of prepared NaFe0.3Ni0.35Mn0.35O2. The collected powder XRD patterns shown in Figure 2 reveal that Fe doping maintains original R3̅m hexagonal lattice with α-NaFeO2 stacking structure, except for a trace amount of NiO impurity. The corresponding Rietveld refined crystallographic data (Tables S1 and S2) show that the Fe, Ni, and Mn ions occupy 3b Wyckoff sites, identical to the expected design of a uniform substitution of Fe3+ in transition metal layers. The distance of TmO2 layers of NaFe0.3Ni0.35Mn0.35O2 (2.04 Å) distinctly increase in comparison to 1.87 Å of original NaNi0.5Mn0.5O2, well consistent with the results of DFT calculations.

Following the successful structure design of NaFe0.3Ni0.35Mn0.35O2, the Na storage performances are examined by galvanostatic charge/discharge test and cyclic voltammogram (CV) in Na half-cells over 2.0–4.0 V voltage range. The charge/discharge profiles (Figure 3a) of Fe free NaNi0.5Mn0.5O2 exhibits several voltage plateaus, corresponding to a series of complicated phase transitions of O3hex−O′3mon−
P3\textsubscript{hex}−P3\textsuperscript{′}\textsubscript{mon}−P3\textsubscript{′}\textsubscript{hex} (Figure S4) originating from the gliding of TmO\textsubscript{2} layers and structure distortion.33 By comparison, NaFe\textsubscript{0.3}Ni\textsubscript{0.35}Mn\textsubscript{0.35}O\textsubscript{2} displays a much smoother charge/discharge curve, a plateau around 2.8−2.9 V and a completely sloping profile above 3.0 V, corresponding to the phase transition of O3\textsubscript{hex}−P3\textsubscript{hex} and a large solid-solution region discussed in the later section. In addition, Fe substitution leads to a higher capacity of 130.3 mAh g\textsuperscript{−1} (116.7 mAh g\textsuperscript{−1} of NaNi\textsubscript{0.5}Mn\textsubscript{0.5}O\textsubscript{2}) and a higher average voltage of 3.11 V (2.98 V of NaNi\textsubscript{0.5}Mn\textsubscript{0.5}O\textsubscript{2}). The CV curves of pristine materials tested at 0.05 mV s\textsuperscript{−1} are compared as displayed in Figure 3b. In comparison with the four distinguishable oxidation/reduction peaks of NaNi\textsubscript{0.5}Mn\textsubscript{0.5}O\textsubscript{2}, the major CV feature of NaFe\textsubscript{0.3}Ni\textsubscript{0.35}Mn\textsubscript{0.35}O\textsubscript{2} is only one peak in correspondence with the charge/discharge measurement results. The oxidation/reduction peaks marked by “1” are chosen to compare polarizability. The polarization of NaFe\textsubscript{0.3}Ni\textsubscript{0.35}Mn\textsubscript{0.35}O\textsubscript{2} (204 mV) is much smaller than that of NaNi\textsubscript{0.5}Mn\textsubscript{0.5}O\textsubscript{2} (296 mV), in good agreement with the improved rate performance. Benefiting from the suppression of monophase transitions and the large solid-solution region, NaFe\textsubscript{0.3}Ni\textsubscript{0.35}Mn\textsubscript{0.35}O\textsubscript{2} exhibits excellent rate performance (Figure 3c). NaFe\textsubscript{0.3}Ni\textsubscript{0.35}Mn\textsubscript{0.35}O\textsubscript{2} still preserves a specific capacity of 82.3 mAh g\textsuperscript{−1} (more than 63% of capacity at 0.1C) even with the 5C rate shown in Figure 3d. Also, the effect of the strategy on improvement of cyclability is proved by the cyclic test at 1C. As shown in Figure S5, the crystal structure of NaNi\textsubscript{0.5}Mn\textsubscript{0.5}O\textsubscript{2} cannot completely recover back to initial O3-phase after cycling 10 times, which leads to a rapid fade of capacity. Comparatively, NaFe\textsubscript{0.3}Ni\textsubscript{0.35}Mn\textsubscript{0.35}O\textsubscript{2} (Figure 3e) demonstrates its optimized cyclability by a doubled capacity retention increase after 100 cycles (80% of NaFe\textsubscript{0.3}Ni\textsubscript{0.35}Mn\textsubscript{0.35}O\textsubscript{2} and 41% of NaNi\textsubscript{0.5}Mn\textsubscript{0.5}O\textsubscript{2}). These results show that Fe substitution into the transition-metal layers of NaNi\textsubscript{0.5}Mn\textsubscript{0.5}O\textsubscript{2} represents an improved Na storage behavior in terms of capacity, average voltage, energy density, rate, and cycling performance.

To grasp the detailed mechanism under optimized electrochemical performances and testify the effect of modulation strategy, we carry out the structural evolution of NaFe\textsubscript{0.3}Ni\textsubscript{0.35}Mn\textsubscript{0.35}O\textsubscript{2} compounds during sodiation/desodiation over a 2.0−4.0 V voltage range by in situ XRD measurement along with the first charge/discharge cycle (Figure 4a). The asterisks and pounds represent the diffraction peaks of NiO (impurity) and Al (current collector and X-ray window), respectively. Upon initial charge, the sample structure experiences a monophase reaction indicated by all peaks being indexed to the hexagonal O3 phase. Upon further Na extraction, the new diffraction peaks indexed to hexagonal P3 phase are found with the coexistence of the O3 phase through the suppression of monoclinic phase transitions and the large solid-solution region. These results show that Fe substitution into the transition-metal layers of NaNi\textsubscript{0.5}Mn\textsubscript{0.5}O\textsubscript{2} represents an improved Na storage behavior in terms of capacity, average voltage, energy density, rate, and cycling performance.
the O$_3$hex$\rightarrow$P$_3$hex phase transition, responsible for the long voltage plateau of around 2.8 V. With the completion of the transition from O$_3$ to P$_3$, the (003) and (006) of P$_3$ diffraction peaks continuously shift toward a lower angle without any new phases until the end of charged to 4.0 V, implying a large solid-solution region consistent with the sloping profiles above 3.0 V, with a gradually expanded interlayer distance due to the decreased electrostatic shielding upon desodiation. Upon the reverse discharge, an opposite evolution is exhibited and a set of well-defined O$_3$ phase peaks are recovered to the original position when discharged to 2.0 V, indicating the high reversibility of Na-insertion mechanism. It is obvious that no any monoclinic O$'$$_3$ or P$'$$_3$ phase can be detected for the entire electrochemical structure evolution of NaFe$_{0.3}$Ni$_{0.35}$Mn$_{0.35}$O$_2$, with significant difference from NaNi$_{0.5}$Mn$_{0.5}$O$_2$.34 The excellent structure stability is also confirmed by the ex situ XANES spectra of Ni, Fe, and Mn K-edges at different electrochemical states. Upon charging to 4.0 V, the Ni and Fe K-edge spectrum (Figure 4b, c) clearly shift toward a higher-energy region, showing that Na extraction is charge-compensated by the oxidation of Ni and Fe ions, demonstrated by a shift similar to previously reported results.35,36 In contrast, the Mn K-edge spectrum exhibits only a change in shape attributed to the adjustment in the local coordinational structure instead of the oxidation of Mn$^{4+}$(Figure S6).31 Upon discharge to 2.0 V, K-edge absorptions of transition metal ions shift back and overlap with that of the original sample, implying complete reversibility of the redox reaction and structure evolution accompanied by Na insertion/deinsertion.

Along with the improved cycling performance originating from the high reversibility of the structure evolution, the enhancement of the rate property is investigated by quantifying the apparent Na$^+$ diffusion coefficient $D$ using CV analysis based on the Randles–Sevcik equation.37 The peaks marked "1" shown in Figure 5a, b are chosen for calculations. The smaller shift of peak potential (0.54 V) with an increase in scan rates from 0.05 to 1 mV s$^{-1}$ of NaFe$_{0.3}$Ni$_{0.35}$Mn$_{0.35}$O$_2$ compared to 0.68 V of NaNi$_{0.5}$Mn$_{0.5}$O$_2$ suggests the weaker polarization and faster kinetics. The linear relationship between peak current $I_p$ and the square root of scan rate $\nu^{1/2}$ implies predominant diffusion-determining process during electrode reaction. The value of $D$ for NaFe$_{0.3}$Ni$_{0.35}$Mn$_{0.35}$O$_2$ calculated from the slope of linear relationship is 2.81 $\times$ 10$^{-11}$ cm$^2$ s$^{-1}$, a magnitude higher than 1.98 $\times$ 10$^{-12}$ cm$^2$ s$^{-1}$ of NaNi$_{0.5}$Mn$_{0.5}$O$_2$ (Figure 5c, d).

It is worth noting that the enhanced electron delocalization is also especially effective in enhancing air stability. The aging experiment of exposing materials to air are carried out, followed by recording the structure evolution by XRD and ABF-STEM. For NaNi$_{0.5}$Mn$_{0.5}$O$_2$, an obvious structure transition is evidenced just for 2 h of air exposure.
6a), whereas no clear structure change is observed after exposed NaFe0.3Ni0.35Mn0.35O2 to air for 1 day (Figure 6b).

Identified directly at atomic-scale by ABF-STEM, aged NaNi0.5Mn0.5O2 exhibits the P3 phase verified by the prismatic coordinated Na sites and head-to-head stacking model of O columns (Figure 6c). In contrast, aged NaFe0.3Ni0.35Mn0.35O2 (Figure 6d), characterized by octahedral Na sites and ABCABC stacking O columns, remains pristine O3 phase.

In summary, an effective structure modulation strategy based on the enhancement of electron delocalization is presented to suppress monoclinic phase transitions and improve electrochemical performances and air stability. On the basis of DFT calculations and the relationship between crystal and electronic structure, Fe3+ with a slightly large radius is introduced into the transition metal layers of NaNi0.5Mn0.5O2 to realize the strategy. The complete suppression of monoclinic phase transitions and high reversibility of structural evolution upon sodiation/desodiation is demonstrated by in situ XRD and ex situ XANES tests. In addition, the obtained NaFe0.3Ni0.35Mn0.35O2 shows twice the capacity retention and

Figure 5. CV profiles of (a) NaNi0.5Mn0.5O2 and (b) NaFe0.3Ni0.35Mn0.35O2 cathode under various scanning rates. Linear fitting of peak currents $I_p$ by $a+bν^{1/2}$ function for (c) NaNi0.5Mn0.5O2 and (d) NaFe0.3Ni0.35Mn0.35O2.

Figure 6. Comparison of XRD patterns of prepared and air-exposed (a) NaNi0.5Mn0.5O2 and (b) NaFe0.3Ni0.35Mn0.35O2. ABF-STEM images of (c) NaNi0.5Mn0.5O2 and (d) NaFe0.3Ni0.35Mn0.35O2 after exposed to air for 1 day.
10 times longer stable air-exposing time than the original NaNiO₂MnO₂ recorded under various electrochemical states, and refined crystallographic parameters (PDF)

**REFERENCES**


