Short communication

Exploring Li substituted O3-structured layered oxides NaLi$_x$Ni$_{1/3-x}$Mn$_{1/3+x}$Co$_{1/3-x}$O$_2$ (x = 0.07, 0.13, and 0.2) as promising cathode materials for rechargeable Na batteries

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ABSTRACT

A series of new O3 cathode materials, NaLi$_x$Ni$_{1/3-x}$Mn$_{1/3+x}$Co$_{1/3-x}$O$_2$ (x = 0.07, 0.13, and 0.2), are explored by substituting Li in the layered structure. Single phase is achieved at low Li content (x = 0.07) while the increase in the amount of Li leads to impurity phase. The optimized composition, NaLi$_{0.07}$Ni$_{0.26}$Mn$_{0.4}$Co$_{0.26}$O$_2$, demonstrates good capacity retention and excellent rate performance. Ex-situ synchrotron XRD suggests that the O3 phase is maintained upon cycling, thus results in the excellent performance. X-ray absorption spectroscopy data shows that Ni^{2+}/Ni^{4+} is the main redox couple while Co^{3+}/Co^{4+} partially contributes to balancing the charge.

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1. Introduction

Rechargeable Na batteries have recently drawn increasing attention as promising candidates for large scale energy storage systems, due to the broad distribution and high natural abundance of sodium raw materials. Among most of the Na cathodes reported to date, O3 structured Na oxides (Na$_x$MO$_2$, M = transition metal) have attracted considerable interest, because their structures are able to accommodate large Na ions and provide spacious diffusion path [1–9]. Although significant improvement has been achieved, the O3 structure materials still suffer from multiple phase transformations from O3 to O′3, P3, P′3 and then P′′3 consecutively, that severely deteriorates the structural integrity and performance reversibility [10]. To overcome these issues, novel cathode materials are needed. Considering for P2-structured cathodes which are another family of layered material as electrode candidates for Na-ion batteries, several Li-substituted materials have been reported with the suppressed phase transformation [5,11,12]. Furthermore, our group has shown that the excess Li ions also play a significant role in improving the capacity of traditional layered oxides as cathode for Li-ion batteries [13]. Herein, in this work we substitute Li in the O3-structured Na oxides to explore its effect on the battery performance. The materials with good capacity retention/rate performances are obtained. The crystal and electronic structural changes upon cycling are characterized.

2. Experimental

A co-precipitation method was used for the synthesis of transition metal hydroxides as precursor for the O3 type Li substituted Na layered oxides [14]. The obtained TM hydroxides were then mixed with Na$_2$CO$_3$ (Fisher, 5% excess) and Li$_2$CO$_3$ (Fisher) by the stoichiometric ratio and calcinated at 1000 °C for 24 h in air. Electrochemical measurement, XAS and XRD characterization are described with details in our previous work [15].

3. Results and discussions

A series of Li substituted Na layered oxides were synthesized. The XRD patterns in Fig. 1a compare the crystal structures of different compositions. All the major peaks adopted to the parent hexagonal structure with R$\bar{3}$m space group [15]. For the compounds with high Li content, NaLi$_{0.2}$ (in black) and NaLi$_{0.13}$ (in red), extra peaks are observed around 18°, suggesting some impure phases presumably due to large amount of excess Li, which may be associate with LiTMO$_x$. We decreased the Li amount during synthesis, then achieved phase pure NaLi$_{0.07}$Ni$_{0.26}$Mn$_{0.4}$Co$_{0.26}$O$_2$. In the O3 structure (Fig. 1b), all the cations sit in octahedral sites, coordinated by 6 nearest oxygen ions. The Na layers and TM layers are alternatively located between two neighboring oxygen layers. Considering the size similarity between Li ion and TM ions, we propose that these substituted Li ions are located in TM layers [15]. The SEM image in Fig. 1c illustrates that the as-synthesized

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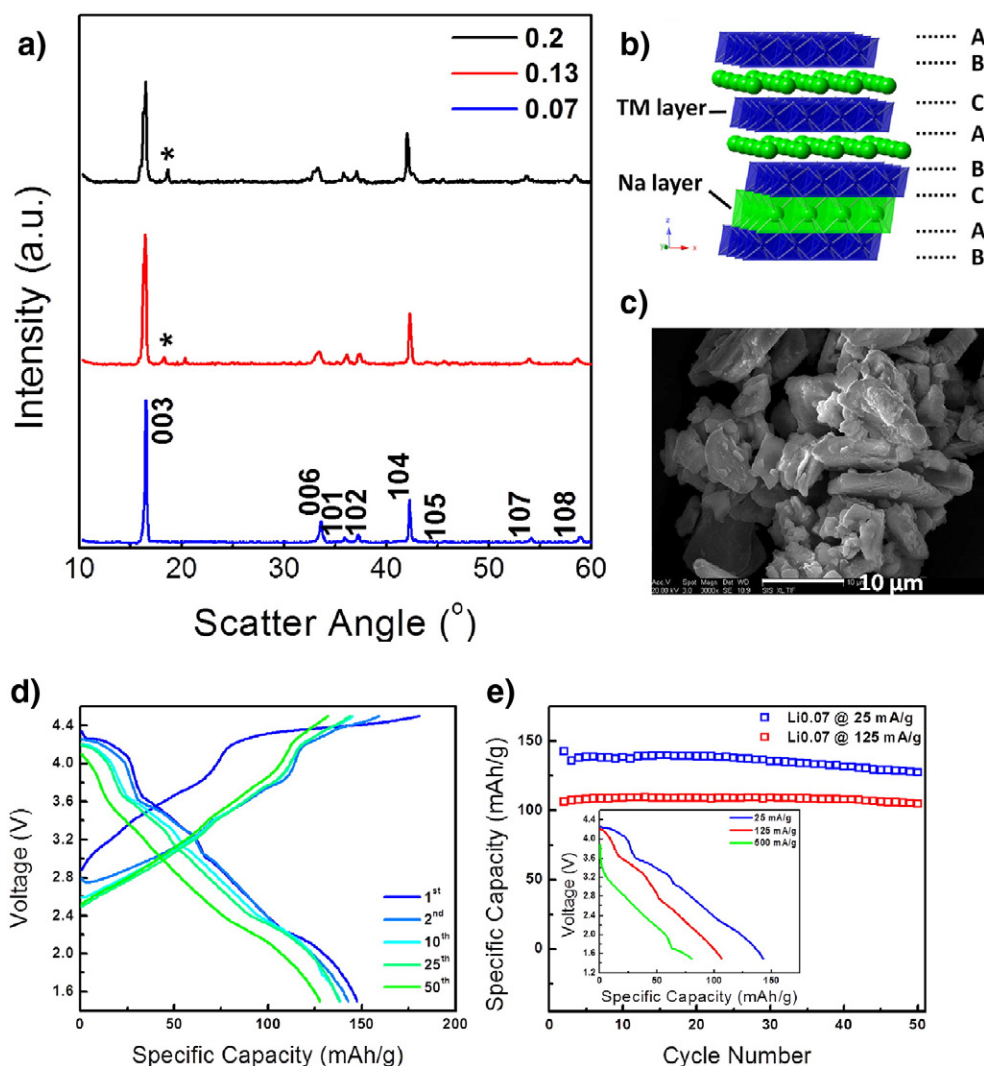*E-mail address:* shmeng@ucsd.edu (Y.S. Meng).

Fig. 1. (a) Powder XRD for $NaLi_xNi_{1/3 - x}Mn_{1/3 + x}Co_{1/3 - x}O_2$ (x = 0.07, 0.13, and 0.2). (* is the peak from impurity phase). (b) Schematic of the typical O3 structure. (c) SEM of the $NaLi_{0.07}Ni_{0.26}Mn_{0.4}Co_{0.26}O_2$. (d) Electrochemical profiles of $NaLi_{0.07}Ni_{0.26}Mn_{0.4}Co_{0.26}O_2$ in half cell. (e) Cycling performance for $NaLi_{0.07}Ni_{0.26}Mn_{0.4}Co_{0.26}O_2$ at different current densities. Inset is the electrochemical profiles of $NaLi_{0.07}Ni_{0.26}Mn_{0.4}Co_{0.26}O_2$ at 25 mA g^{-1}, 125 mA g^{-1}, and 500 mA g^{-1} current density.

$NaLi_{0.07}Ni_{0.26}Mn_{0.4}Co_{0.26}O_2$ agglomerates into plate-like secondary particles.

The pure phase $NaLi_{0.07}Ni_{0.26}Mn_{0.4}Co_{0.26}O_2$ was selected to explore the electrochemical performances. The first cycle of this material was performed between 1.5 V and 4.5 V at 25 mA g^{-1} current density. The material delivers a capacity of 181 mAh g^{-1} in the first charging, followed by 147 mAh g^{-1} in the first discharging. The irreversible capacity in the first cycle is believed to be related to the oxygen evolution, as suggested by the electrochemical profile. (Fig. 1d) The long, irreversible plateau at 4.2 V (vs Na anode) in the first charging process has been observed in most Li-excess cathodes (4.5 V in Li-excess cathode vs Li anode) for LIBs, which were mainly attributed to the oxygen loss from the lattice [14,16]. After 50 cycles, the capacity is well maintained at 128 mAh g^{-1}. When the battery is tested at 125 mA g^{-1}, the material could still deliver around 110 mAh g^{-1} and the capacity retention is above 98% after 50 cycles (Fig. 1e). In addition to the good performance retention, superior rate capabilities are obtained as well: as shown in Fig. 1e inset, even with 500 mA g^{-1} current, the reversible capacity is still as high as 80 mAh g^{-1}, suggesting its high-power capability. More interestingly, we don't see any pronounced voltage steps in its electrochemical profiles (Fig. 1d) as observed in majority of O3-structred cathodes. It indicates that the phase transformations are partially suppressed for this O3 material even up to 4.5 V. Its cycling
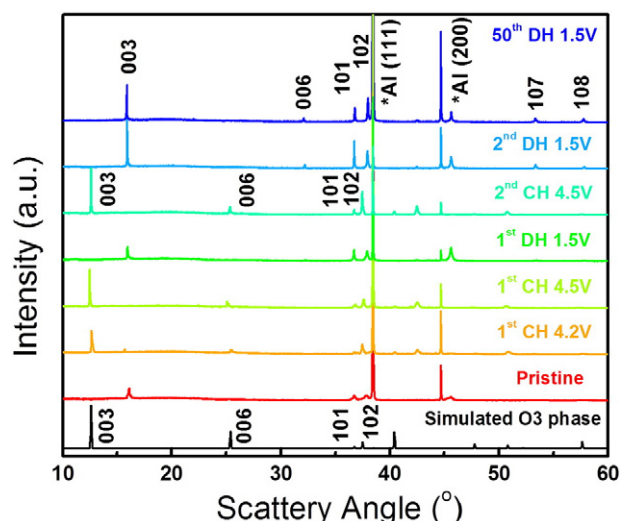

Fig. 2. Ex-situ SXRD for $NaLi_{0.07}Ni_{0.26}Mn_{0.4}Co_{0.26}O_2$ at different states.

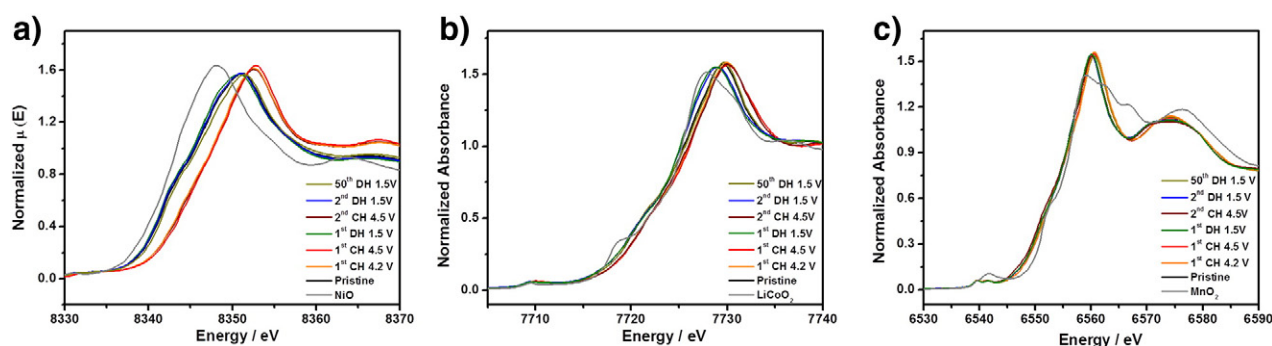**Fig. 3.** Ex-situ XAS analysis for NaLi$_{0.07}$Ni$_{0.26}$Mn$_{0.4}$Co$_{0.26}$O$_2$ at different states. XANES spectra for (a) Ni, (b) Co and (c) Mn K-edge respectively.

stability within a wide voltage window surpasses most of other Na layered O3 oxides due to the existence of substituted Li in the lattice stabilizing the structure through cycling.

The synchrotron X-ray diffraction (SXRD) was collected at selected states along voltage profiles to characterize the structural change. As shown with the red line in Fig. 2, the as-synthesized material, NaLi$_{0.07}$Ni$_{0.26}$Mn$_{0.4}$Co$_{0.26}$O$_2$, has good crystallinity. Before 4.2 V, no flat voltage plateau is observed indicating that there is no first-order phase transformation. When the electrode is charged to 4.2 V (orange line in Fig. 2), both hydrated and non-hydrated O3 phases are observed. The hydrated O3 phase happened during XRD measurement, and facilitated by c lattice expansion due to less screening effect between neighbored oxygen layers when most Na ions are extracted [14]. At the end of the first charge (4.5 V), the hydrated O3 phase dominates the structure. Upon the first discharge (green line in Fig. 2), the whole spectrum is systematically shifted back to higher angle than the fully charged state, such as (003); and we only observed the O3 Li-substituted Na phase. When the electrode is charged to 4.5 V in the second cycle, the hydrated O3 phase appears again. After discharging to 1.5 V, the O3 Li-substituted Na phase is observed at the end of second cycle and even after 50 cycles. All the peak positions are close to those of the pristine material. Such good phase stability is the main reason for our excellent capacity retention and rate performance. In addition, although small plateaus are seen in the electrochemical profiles, no phase changes are detected by SXRD during cycling. Thus those small steplike features could be resulted from transitions between different Na-ion in-plane orderings, which have been broadly noticed in most Na layered materials. As known to all that some Li atoms moving to tetrahedral sites after first charging have been observed in layered cathode materials for Li-ion batteries, it is hypothesized that the tetrahedral Li would form likewise in our first charge [13]. These tetrahedral Li ions have essential effect in stabilizing the O3 phase at subsequent cycles by pinning down the neighbored layers.

To understand the charge compensation mechanism upon cycling, X-ray absorption spectroscopy (XAS) measurements were conducted at selected states of charge. Normalized Ni, Co and Mn K-edge X-ray absorption near edge structure (XANES) spectra are plotted in Fig. 3a, b and c, respectively. It is clear that the pristine NaLi$_{0.07}$Ni$_{0.26}$Mn$_{0.4}$Co$_{0.26}$O$_2$ compound predominantly consists of mixed Ni^{2+} and Ni^{3+} (small amount of Ni^{3+} exists due to the Na loss during high temperature calcination), Co^{3+} and Mn^{4+}. There are systematic changes in the Ni XANES spectra with different voltages along the electrochemical profile. In the first charge, the Ni K-edge absorption energy shifts to the higher energy than that at the as-synthesized state, suggesting that oxidation state of Ni after first desodiation is close to Ni^{4+} [11,13,17]. After first full cycle, the oxidation state of Ni ions returns back to divalent. The similar edge shift and recover are observed in the second cycle consistently, demonstrating that the Ni^{2+}/Ni^{4+} redox reaction is reversible. The Co K-edge moves to higher energy towards the end of charge and returns back after discharge, while Mn K-edge XANES proves that Mn ions are maintained at tetravalent state

upon cycling. Based on these, we could conclude that Ni and Co are the electrochemically active species and Mn assists the structural stability owing to the absence of Jahn-Teller distortion from Mn^{3+}. Another point which should be noted is that in the first cycle, the edge positions for Ni, Co and Mn have no evident change above 4.2 V. This is consistent with our hypothesis that the irreversible capacity could result from the oxygen loss from the lattice. Similar phenomenon has been reported for Li-excess cathodes in Li-ion batteries as well [14,16]. Further investigation on oxygen evolution in Na cathodes is still undergoing.

Based on the above discussions, the substituted Li in the structure helps to prevent phase transformation, thus minimizing the structure degradation. Although the underlying role of Li in stabilizing the P2 structure has been revealed [11], the exact mechanism in O3 cathodes is still unclear, given that the phase transformation routes and cation sites are intrinsically different between P2 and O3 and structures. For future work, a suite of advanced characterization tools should be applied to understand Li contribution, including identifying the site variation of Li, monitoring the content of Li, and detecting the Li local environment and distribution upon charge/discharge. At the same time, more effort should be spent to develop Co free Li-substituted O3 cathodes for rechargeable Na batteries, in order to further reduce the cost of raw materials.

4. Conclusion

A new Li substituted Na layered oxide with pure O3 phase, NaLi$_{0.07}$Ni$_{0.26}$Mn$_{0.4}$Co$_{0.26}$O$_2$, is successfully achieved, demonstrating a considerably high reversible capacity of 147 mAh g^{-1} and excellent rate performance. The phase is stabilized throughout the cycling, which could be the main reason for its good electrochemical properties. Ni^{2+}/Ni^{4+} is the main active redox couple during cycling, and Co^{3+}/Co^{4+} partially contributes to the charge compensation. The findings would contribute to the future improvement and design of practical cathode materials for Na-ion batteries.

Conflict of interest

The authors declare no conflict of interest.

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