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COMMUNICATION

A new O3-type layered oxide cathode with high energy / power density for rechargeable Na batteries

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A new O3 - $\text{Na}_{0.78}\text{Li}_{0.18}\text{Ni}_{0.25}\text{Mn}_{0.583}\text{O}_w$ is prepared as the cathode material for Na-ion batteries, delivering exceptionally high energy density and superior rate performance. The single-slope voltage profile and ex situ synchrotron X-ray diffraction data demonstrate that no phase transformation happens through a wide range of sodium concentrations (up to 0.8 Na removed). Ni^{2+} / Ni^{4+} is suggested to be the main redox center. Further optimization could be realized by tuning the combination and ratio of transition metals.

Na-ion batteries have recently gained increasing recognition as intriguing candidates for next-generation large scale energy storage systems, owing to significant cost advantages stemming from the high natural abundance and broad distribution of Na resources. Although in terms of absolute energy density, the currently available Na-ion battery materials are not competitive with their Li-ion systems which are one of the dominating energy technologies in this decade, there are studies suggesting that Na-ion systems should not be discarded.^{1, 2} In particular, Na-ion batteries operating at room temperature could be suitable for applications where specific volumetric and gravimetric energy density requirements are not as stringent as in EVs, namely in electrical grid storage of intermittent energy produced via renewable sources.³ This would also contribute to a significant reduction of the costs connected to the use of renewable sources, which could then penetrate the energy market more easily and make Na-ion technology complementary to Li-ion batteries for stationary storage.⁴⁻⁶

For the past several years, a variety of novel materials have been explored as electrodes for Na-ion batteries. Since Na ion has a relatively larger ionic radius than that of the Li ion, materials with an open framework are required for facile Na ion insertion / extraction. Following this strategy, many breakthroughs in cathode materials have been achieved, such as layered and polyanion compounds.^{7, 8} Among most of the Na cathode compounds reported to date, the P2 and O3 structured Na oxides (Na_xTMO_2 , TM = Transition Metal) have drawn significant attentions, since their relatively opened structures are able to accommodate large Na ions providing spacious diffusion path as well as the structural stability. The research on the structural properties of Na_xTMO_2 was started in 70's by Delmas et al.^{9, 10}

Recently, various P2- Na_xTMO_2 , and their binary or ternary derivatives, have been extensively investigated and some of them demonstrated superior electrochemical performances.¹¹⁻¹⁷ On the other hand, O3 structured materials have also shown great progress. For example, NaCrO_2 was investigated by Komaba et al., and showed 120 mAh/g of specific capacity near 2.9 V.^{18, 19} The O3- $\text{NaNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ electrodes delivered 105 mAh/g at 1C (240 mA/g) and 125 mAh/g at C/30 (8 mA/g) in the voltage range of 2.2 - 3.8 V and displayed 75% of the capacity after 50 cycles.^{19, 20} The Fe-substituted O3- $\text{Na}[\text{Ni}_{1/3}\text{Fe}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ exhibited the specific capacity of 100 mAh/g with average operating voltage at 2.75 V.²¹ The isostructural compound, $\text{Na}[\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}]\text{O}_2$, showed reversible intercalation of 0.5 Na-ions leading to the specific capacity of 120 mAh/g in the voltage range of 2.0 - 3.75 V.²² These relatively low capacity and limited cycling retention are presumably due to the fact that most of these materials undergo multiple phase transformations from O3 to O'3, P3, P'3 and then P''3 consecutively.²³ These transformations could be one of the major problems that limit the practical uses of Na-ion batteries since it deteriorates the cycle life and rate capabilities. Herein, to overcome this issue, a new O3 compound is prepared through Li-Na ion exchange, inspired by the idea in Li-ion batteries that Li-excess O3 compound has been demonstrated single slope voltage profile with significant improvement in capacity and cycling retention for Li layered electrodes.²⁴⁻²⁶

The $\text{Li}_{1.133}\text{Ni}_{0.3}\text{Mn}_{0.567}\text{O}_2$ was synthesized by heating a mixture of $\text{LiOH}\cdot\text{H}_2\text{O}$ and $\text{Ni}_{0.346}\text{Mn}_{0.654}(\text{OH})_2$. (for experimental details, see ESI) The obtained $\text{Li}_{1.133}\text{Ni}_{0.3}\text{Mn}_{0.567}\text{O}_2$ was firstly charged in the Li half cell to extract Li ions (the composition at this point is $\text{Li}_{0.073}\text{Ni}_{0.3}\text{Mn}_{0.567}\text{O}_w$) and then discharged in the Na half cell to prepare O3 - $\text{Na}_{0.719}\text{Li}_{0.073}\text{Ni}_{0.3}\text{Mn}_{0.567}\text{O}_w$. (Figure S1) To achieve higher capacity, the ratio among Li, Ni and Mn was further adjusted and the composition, $\text{Li}_{1.167}\text{Ni}_{0.25}\text{Mn}_{0.583}\text{O}_2$ was finally chosen, which improved the initial Na-insertion capacity from 220 mAh/g to 240 mAh/g. Figure 1a illustrates the electrochemical profiles for the initial "delithiation" (Li-extraction) and "sodiation" (Na-extraction) processes for $\text{Li}_{1.167}\text{Ni}_{0.25}\text{Mn}_{0.583}\text{O}_2$. The initial "delithiation" of Li-excess material showed a long plateau at 4.5V which involved oxygen loss (and/or oxidation). The stoichiometry for the ion-exchanged material is $\text{Na}_{0.78}\text{Li}_{0.18}\text{Ni}_{0.25}\text{Mn}_{0.583}\text{O}_w$, as determined by the electrochemical capacity and energy-dispersive X-ray

spectroscopy. We used subscript w ($0 < w < 2$) in the formula to describe the oxygen loss during initial charge. The as-prepared $\text{Na}_{0.78}\text{Li}_{0.18}\text{Ni}_{0.25}\text{Mn}_{0.583}\text{O}_w$ has particle size less than 500 nm, retaining same morphology with its parent material, $\text{Li}_{1.167}\text{Ni}_{0.25}\text{Mn}_{0.583}\text{O}_2$. (Figure S2) The cycling performance is tested between 1.5 and 4.2 V with current density at 125 mA/g. After 30 cycles, around 190 mAh/g capacity is well maintained as shown in Figure 1b. With 1.25 A/g current, the reversible capacity is still as high as 160 mAh/g, suggesting its high-power capability. (Figure S3) Figure 1c compares capacity and energy density for most of the recent cathodes in Na-ion batteries (highest reversible value is selected.) The $\text{Na}_{0.78}\text{Li}_{0.18}\text{Ni}_{0.25}\text{Mn}_{0.583}\text{O}_w$ exhibits not only the highest capacity but also the highest energy density: 675 Wh/kg energy density is delivered by this material during discharge, which is higher than recent results reported by Kataoka R. et. al. who used similar ion exchange method,²⁷ and even higher than LiFePO_4 (560 Wh/kg) and LiCoO_2 (560 Wh/kg) in Li-ion batteries.²⁸⁻³⁰ More interestingly, as displayed in the inset of Figure 1b, no voltage steps are seen in the electrochemical profiles upon cycling. It indicates that no phase transformations happen for this O3 material even after all the Na ions are extracted. Besides, the voltage depression problem which is usually observed in its parent material, $\text{Li}_{1.167}\text{Ni}_{0.25}\text{Mn}_{0.583}\text{O}_2$ in Li-ion batteries,³¹ is reduced to some degree in this ion-exchanged product in Na-ion batteries.

The synchrotron X-ray Diffraction (SXRD) was conducted at selected states of charge/discharge to detect the structural change. (Figure 2a) The refined lattice parameters were summarized at Table S1. As shown with the black line in Figure 2a, the as-synthesized material, $\text{Li}_{1.167}\text{Ni}_{0.25}\text{Mn}_{0.583}\text{O}_2$, is well crystallized and can be indexed as R-3m space group. The diffraction pattern illustrates typical Li-excess features, which have been discussed by our previous work.³¹ After initial delithiation (red line in Figure 2a), the c lattice is slightly increased (Table S1) due to less screening effect between neighbored oxygen layers when Li ions are mostly removed from the host.³² Upon initial sodiation (green line in Figure 2a), the whole spectrum is significantly shifted to lower angle, such as (003) and (110) peak. The shift is resulted from the overall lattice expansion, as the inserted Na ions have much larger ionic size than Li ions. Peak broadening is observed, which is probably ascribed to the stacking faults introduced during initial sodiation. The small reflection to the right of the (003) peak is probably the non-reacted residue Li compound phase. More work is undergoing to comprehensively investigate this process. It should be noted that although the diffraction peaks are moved systematically, all the peaks still belong to R-3m space group, in other words, O3 phase (Figure 2b), proving that there is no change in the host structure during ion-exchange process. To further monitor the electrode structural change upon cycling in Na batteries, two ex-situ samples were characterized. When the electrode is charged to 4.2 V (pink line in Figure 2a), the material is still maintained at O3 structure though the majority of Na ions are removed as suggested by charging capacity. Comparing with the material after initial sodiation, it is interesting to notice the (003) peak is moved to higher angle, indicating that c lattice is reduced at this state. Moreover, all the peaks positions are close

to those of the material after initial delithiation. Since Li moving to tetrahedral sites after first charge has been extensively observed in Li-ion batteries,³¹⁻³³ it is hypothesized that the tetrahedral Li would form similarly in our initial delithiation process as shown in Figure 2c. These tetrahedral Li ions play a critical role in stabilizing the O3 phase at subsequent cycles by locking the neighbored layer shifting. When the electrode is discharged to 1.5 V (blue line in Figure 2a), the spectrum is back to the similar positions with the material after initial sodiation, suggesting that the Na ions are re-inserted back reversibly. And most importantly, the O3 phase is still well maintained.

In order to investigate the charge compensation mechanism during Na-ions extraction and insertion, X-ray absorption spectroscopy (XAS) measurements were conducted with Ni and Mn K-edges at different states of charge. Normalized Ni and Mn K-edge X-ray absorption near edge structure (XANES) spectra are shown in Figure 3a and 3b, respectively. For the standards, Ni K-edge spectra of divalent Ni-ion (NiO) and Mn K-edge spectra of tetravalent Mn-ion (MnO_2) are included. It is evident that as-synthesized $\text{Li}_{1.167}\text{Ni}_{0.25}\text{Mn}_{0.583}\text{O}_2$ compound predominantly consists of Ni^{2+} and Mn^{4+} . Obvious changes are shown in the Ni XANES spectra upon the initial delithiation, sodiation, and followed charge and discharge process. The Ni K-edge absorption energy of initially delithiated electrode shifts to the higher energy region compared to that of as-synthesized state. The amount of absorption energy shift is ~ 3 eV, suggesting that oxidation state of Ni after initial delithiation is close to Ni^{4+} .³¹ After initial sodiation, the oxidation state of Ni ions returns back to divalent. The similar edge shift and recover are seen again between 4.2 V and 1.5 V ex-situ electrode samples suggesting that the $\text{Ni}^{2+}/\text{Ni}^{4+}$ redox reaction is completely reversible in Na-ion batteries. In contrast to the Ni XANES, Mn K-edge XANES shows that Mn ions mainly stay at tetravalent state and no dramatic changes are occurred in the valence upon the charge and discharge. The subtle variations in edge shape and position in XANES could be attributed to surface reaction of the particle, which has been reported in its Li analogue³⁴ and requires more advanced characterization to investigate. Based on the Ni and Mn XANES, it is proved that Ni is the only electrochemically active species and Mn supports the structural stability in the absence of Jahn-Teller active Mn^{3+} . More details on local structural change are revealed by the extended X-ray absorption fine structure (EXAFS) spectra. Ni EXAFS clearly shows that interatomic distances of Ni-O and Ni-TM are shortened after the initial delithiation and after the charge in Na-ion batteries, indicating that the oxidation of Ni ions. After initial sodiation, the interatomic distances are systematically larger than the as-synthesized state, resulted from lattice expansion when Na ions are inserted. However, Mn EXAFS does not show any significant changes in the Mn-O interatomic distance (small changes may be due to the local environment changes), although the second shell corresponding to Mn-TM distance is varied with different voltages. This is ascribed to the changes in the Ni oxidation states, which accordingly affect the distance among neighbored Mn-Ni.

To evaluate the practical application of $\text{Na}_{0.78}\text{Li}_{0.18}\text{Ni}_{0.25}\text{Mn}_{0.583}\text{O}_w$, the full cell was fabricated with $\text{Na}_{0.78}\text{Li}_{0.18}\text{Ni}_{0.25}\text{Mn}_{0.583}\text{O}_w$ as cathode and SnS_2 / rGO as anode. (Figure 4a) The anode is reported by our previous work.³⁵ In our

full cell configuration, both cathode material and anode material are casted on Al current collector, which will further reduce the cost and weight of Na ion battery. Upon charging, Na ions are extracted from the cathode and inserted into the anode. During discharge, Na ions are transferred reversely. By this process, the energy storage and released reversibly. Figure 4b represents voltage profiles of the full cell which shows a discharge capacity of ~210 mAh / g (capacity based on cathode weight). The overall capacity of Na full cell using our advanced cathode and anode can reach 175 mAh / g (considering the weight of cathode and anode materials). The operation discharge voltage is on average 2.5 V. As a result, the total energy density for this Na full cell is as high as 430 Wh / kg, which is to our best knowledge the highest energy so far reported for Na full cells. Furthermore, the capacity is well maintained for this Na full cell. As shown in Figure 4c, after 50 cycles, more than 165 mAh/g is delivered reversibly.

In fact, the ion-exchanged electrode performance could be further adjusted by mixing with other TM, such as Co. As shown in Figure S4a, if the parent Li compound is designed with Co in the stoichiometry as $\text{Li}_{1.167}\text{Ni}_{0.166}\text{Mn}_{0.5}\text{Co}_{0.166}\text{O}_2$, the discharged capacity is further increased to 245 mAh/g. In addition, the direct synthesis route has been tried preliminarily. The as-synthesized material, $\text{NaLi}_{0.067}\text{Co}_{0.267}\text{Ni}_{0.267}\text{Mn}_{0.4}\text{O}_2$, has demonstrated pure O3 phase. However, the direct synthesis by co-precipitation method will be hard to create tetrahedral Li, we can not exclude the possibilities from other method, more efforts are under development now.

Conclusions

In conclusion, a new O3 - $\text{Na}_{0.78}\text{Li}_{0.18}\text{Ni}_{0.25}\text{Mn}_{0.583}\text{O}_w$ is obtained by the electrochemical Na-Li ion exchange process of $\text{Li}_{1.167}\text{Ni}_{0.25}\text{Mn}_{0.583}\text{O}_2$. The new material shows exceptionally high discharge capacity of 240 mAh/g in the voltage range of 1.5-4.5 V, thus the total energy density at the materials level reaches 675 Wh/kg. It is the highest capacity as well as highest energy density so far among all the reported cathodes in Na-ion batteries. When cycled between 1.5-4.2 V, the discharge capacity is well maintained around 190 mAh/g after 30 cycles. The O3 phase is kept through ion-exchange and cycling process, as confirmed by SXRD. The stabilized O3 phase could be related to the tetrahedral Li formed upon initial lithiation, and breaks through the critical limitation for most of the O3 compounds. XAS results show that $\text{Ni}^{2+}/\text{Ni}^{4+}$ is the main active redox couple during cycling while Mn ions basically stay at tetravalent state. The Na full cell utilizing $\text{Na}_{0.78}\text{Li}_{0.18}\text{Ni}_{0.25}\text{Mn}_{0.583}\text{O}_w$ as cathode delivers 430 Wh / kg energy density, shedding light on the future of the Na-ion technologies. Future improvement could be realized through fine tuning the combination and ratio among TMs, and making the material by direct synthesis, which will be reported very soon.

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† Electronic Supplementary Information (ESI) available: Electrochemical profile for $\text{Li}_{1.133}\text{Ni}_{0.3}\text{Mn}_{0.567}\text{O}_2$ during initial delithiation and initial sodiation; SEM images for as-synthesized $\text{Li}_{1.167}\text{Ni}_{0.25}\text{Mn}_{0.583}\text{O}_2$ and $\text{Na}_{0.78}\text{Li}_{0.18}\text{Ni}_{0.25}\text{Mn}_{0.583}\text{O}_w$; Rate performance for $\text{Na}_{0.78}\text{Li}_{0.18}\text{Ni}_{0.25}\text{Mn}_{0.583}\text{O}_w$; The electrochemical profile for $\text{Li}_{1.167}\text{Ni}_{0.166}\text{Mn}_{0.5}\text{Co}_{0.166}\text{O}_2$ during initial delithiation and initial sodiation; XRD for as-synthesized $\text{NaLi}_{0.067}\text{Co}_{0.267}\text{Ni}_{0.267}\text{Mn}_{0.4}\text{O}_2$; Refined lattice parameter for $\text{Li}_{1.167}\text{Ni}_{0.25}\text{Mn}_{0.583}\text{O}_2$ and $\text{Na}_{0.78}\text{Li}_{0.18}\text{Ni}_{0.25}\text{Mn}_{0.583}\text{O}_w$ at different states. See DOI: 10.1039/b000000x/

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