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Communication

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High stable post-spinel NaMn_2O_4 cathode of sodium ion battery

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CaFe₂O₄-type NaMn₂O₄ based on resourceful manganese and sodium have been synthesized under high pressure 4.5 GPa as cathode of sodium ion battery. It exhibits a one-step voltage profile, limited polarization and good capacity retention both at room and high temperatures. The capacity retention is 94% after 200 cycles at room temperature. The stable battery performance is due to the high barrier of structure rearrangement and suppressed Jahn-Teller distortions in this post spinel structure.

Sodium ion batteries (SIBs) have retriggered an increasing industrial and academic interest in its potential utilizations as energy storage devices instead of lithium ion batteries (LIBs) as the emerging concerns of potential limit of lithium supplies available in terrestrial reserves, and also the element abundance of sodium.^{1,2} Battery performance is mainly determined by the electrochemical properties of the electrode materials. Therefore, the major challenge in SIBs lies in investigating electrode materials as reversible sodium-ion host which can meet commercial standard. The fundamental principles of SIBs is identical to that of LIBs, except the sodium ions shuttle back and forth between the cathode and anode. Thus, many of the electrode materials for LIBs have been mimicked in designing various SIBs electrode materials.³⁻¹²

Manganese-based materials have witnessed great progress as electrode materials because the abundant manganese resources and low cost advantages. Among them, sodium manganese oxides cathode materials Na_xMnO_2 with different sodium contents x showed fascinating battery performance and have been highlighted widely. There are two main structures of sodium manganese oxides according to the sodium contents in Na_xMnO_2 . When the $x < 0.5$, it usually exhibit a tunnel-type oxides, such as $\text{Na}_{0.44}\text{MnO}_2$ ($\text{Na}_4\text{Mn}_9\text{O}_{18}$). Many groups include us have reported that the $\text{Na}_{0.44}\text{MnO}_2$ nanowires materials exhibited a discharge capacity of 128 mAh/g at 0.1 C, good rate capability and excellent cycle life.^{13,14} With the sodium contents increased to $x > 0.5$, it usually shows a layered P2 structure which achieve a higher capacity of more than 160 mAh/g (the theoretical capacity is 170 mAh/g).^{15, 16} However, for most layered and tunnel type manganese oxides, it is inability to accommodate Jahn-Teller distortion following the reduction of Mn^{4+} to Mn^{3+} within the rigid, close-packed oxide ion structure, which have been

considered as the main cause of the structural instability during repetitive insertion/extraction of sodium ions.¹⁷ As a consequence, there are many voltage steps in the charge/discharge profiles and unsatisfactory cycle life. This disadvantage largely prohibited the large-scale applications of this kind of materials. The P2-type $\text{Na}_x[\text{Fe}_{1/2}\text{Mn}_{1/2}]\text{O}_2$ showed a discharge capacity of 190 mAh/g with the electrochemically active $\text{Fe}^{3+}/\text{Fe}^{4+}$ redox.⁶ Other group also reported that this structure may be stabilized by substituting Mn by expensive and toxic Co, but at the sacrifice of capacities.¹⁸ In very recent report, $\text{Na}_{0.67}\text{Mn}_{0.95}\text{Mg}_{0.05}\text{O}_2$ with Mg-substitution have been synthesized and showed a smoothed charge/discharge profile, reduced polarization and improved capacity retention performance to some extent.¹⁹

Both in industry and academia, spinel LiMn_2O_4 have achieved great success as cathode for LIBs due to its comprehensive advantages in terms of performance and cost. However, to our best knowledge, there are still no report of spinel or spinel-related structure compounds used in SIBs. S. Komaba et al. reported the electrochemical behavior of spinel-type LiMn_2O_4 samples in sodium battery, Li ions were extracted in the first charge process and sodium ions were inserted back to the cathode during the discharge process. However, the spinel phase transfer into a layered structure after several cycles.²⁰ The first principles calculations revealed that the Na can enhance the structural stability in the layered O3 structure at $\text{A}_{0.5}\text{MO}_2$ composition. While the Li compounds with a $\text{A}_{0.5}\text{MO}_2$ composition strongly favor the spinel structure, no such driving force exists for the layered Na compounds.¹⁷ From the research of high-pressure technology, many spinel compounds or compositions transformed into denser structure of post spinel phases at high pressure. These materials usually shows a high tap density and unexpected electrochemical performance when used as electrode materials.^{21,22} Recent report indicated the high sodium mobility and structure stability in post-spinel phase.²³ In this structure, there are mainly CaFe_2O_4 , CaTi_2O_4 and CaMn_2O_4 three types. However, to our best knowledge, there are still no reports on spinel or spinel-related structure compounds used in SIBs. In this study, the CaFe_2O_4 -type NaMn_2O_4 is prepared under high pressure, and the electrochemical performance of this material as cathode of SIBs has been studied for the first time. Different from other manganese-based cathode in SIBs, this material showed a

smooth charge/discharge profile and ultrahigh stable cycle performance both in room temperature and 55 °C. It shows almost no capacity and voltage degradation even after 200 charge/discharge cycles at room temperature.

Black powder sample NaMn_2O_4 was synthesized under high pressure using Na_2O_2 and Mn_2O_3 as starting materials.²⁴ The raw materials were mixed together and pressed into a pellet. The pellet was sealed in an Au-capsule and heated at 1223 K under a pressure of 4.5 GPa for 1 h. The morphology of the as-prepared NaMn_2O_4 was characterized by scanning electron microscopy (SEM) and transmission electron microscope (TEM) as shown in Fig. 1a and 1b. It showed as a uniform rod-like structure with a diameter about 100 nm and length of 3-5 μm . The microrods aggregate together to form larger micro particles as shown in Fig. 1a. The rod-shaped primary particles can be further confirmed by TEM. The high-resolution image demonstrated the well crystalline of the material. XRD patterns further evidenced the structure and phase purity of the synthesized materials (Fig. 1c). All of the diffraction peaks could be indexed as a orthorhombic CaFe_2O_4 -type structure with a space group of $Pnam$. The present result indicated that the as-prepared material was NaMn_2O_4 and can be well consisted with reported compound with ICSD 172604.²⁵ The structure of NaMn_2O_4 is shown in Fig. 1d. The edge-shared two MnO_6 octahedral units pile up with sharing edges to form a chain, and adjacent MnO_6 chains connected together with sharing vertices. The three-dimensional framework structure with a single tunnel was formed by four vertices-shared chains. All of the sodium ions locate in this tunnel and a mean Na-O length of 2.436 Å, which authorized great potentials of reversible extraction/insertion during charge/discharge processes.²⁵

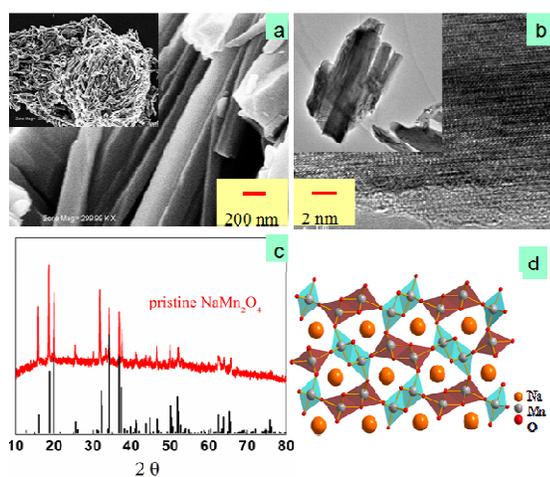


Fig. 1 Characterizations of CaFe_2O_4 -type NaMn_2O_4 , SEM images (a), TEM images (b), XRD patterns (c) and crystal structure, the two kinds of octahedral: MnO_6 (d).

Sodium ions extraction/insertion properties of the CaFe_2O_4 -type NaMn_2O_4 was investigated by fabricated into coin cells and the details was shown in SI. The initial discharge capacity is 83 mAh/g when charge/discharge in the voltage range of 1.5-4.8 V at a current density of 5 mA/g as shown in Fig. 2a. It shows smooth charge/discharge profiles which is rare for other manganese-based cathode of SIBs. The coulombic efficiency is

63% in the first cycle. Carefully comparing the charge/discharge profiles, the extracted sodium ions above 4.0 V cannot be well inserted back to the electrode materials. Thus, we performed the charge/discharge test in the voltage range of 2.0-4.0 V. The discharge capacity is 65 mAh/g at a current density of 5 mA/g (red line in Fig. 2a). The initial coulombic efficiency (CE) improved to nearly 100%. This capacity is less than the theoretical value of 136.18 mAh/g. It maybe attributed to the large particle size of CaFe_2O_4 -type NaMn_2O_4 cathode (3-5 μm). As we know, the size of electrode material profoundly affect its electrochemical performance. Fortunately, it shows ultrahigh cycle stability, and neither capacity fading nor voltage degradations can be found during the 100 charge/discharge cycles as shown in Fig. 2b. Further prolonged cycle performance was conducted in the same voltage range but a larger current density of 20 mA/g. As shown in Fig. 2c, there are almost no obvious performance degradations up to 200 cycles. Two prominent features can be concluded compared with other reported manganese-based cathode of SIBs: one-voltage step in the charge/discharge profiles and ultrahigh cycle stability. These two features are complementary to each other. The one-step profile demonstrated the main structure undergoes no obvious changes during the extraction/insertion of sodium ions. Although the Jahn-Teller active Mn^{3+} ions present in this compound, no distortions can be found in the electrochemical window. These phenomena can be explained by the higher barrier that must be overcome to rearrange MnO_6 octahedrons in this kind of material synthesized under high-pressure.²³ The stable structure contributed to the ultrahigh stable cycle performance. This result also verify the calculation result that the CaFe_2O_4 -type NaMn_2O_4 is the most stable phase than materials with other different structures with same AB_2O_4 constitute.²³

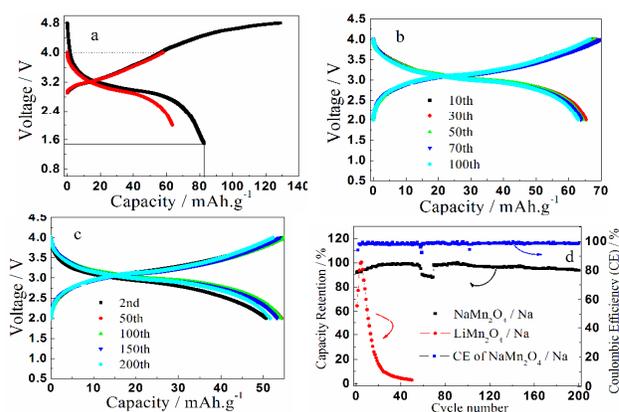


Fig. 2. Charge-discharge profiles and cycle performance of NaMn_2O_4 at different conditions. The first cycle profile with different cutoff voltage (a), with a current density of 5 mA/g in the voltage of 2.0-4.0 V (b), with a current density of 20 mA/g in the voltage of 2.0-4.0 V (c), comparison of capacity retention of NaMn_2O_4 and LiMn_2O_4 in sodium ion batteries and coulombic efficiency of NaMn_2O_4 (d).

In contrast, the popular spinel LiMn_2O_4 was also investigated as cathode of SIBs. The LiMn_2O_4 fabricated battery was subjected to the extraction of Li^+ first, and then taking the Na^+ insertion/extraction process. Three-electrode equipped glass cell was assembled with sodium metal as the counter and reference

electrode, 1 mol/L NaClO₄ in EC:DEC (1:1 in volume) was used as electrolyte. Although the extracted Li⁺ during the first charge process was still residual in the battery system, it exerted little influence on the following Na⁺ insertion/extraction process due to the 2000 times of Na⁺ concentration compared with that of Li⁺. The charge/discharge profiles are shown in Fig. S2. The first charge process to 4.5 V corresponds to the extraction of Li from LiMn₂O₄, it is a typical charge profile of LiMn₂O₄/Li and a capacity of 114 mAh/g. In the following discharge process, Na⁺ ions were inserted into the cathode. The charge/discharge capacities gradually increase in the initial several cycles and reach the top value of over 150 mAh/g at the 5th cycle. The charge/discharge profiles show multi voltage steps which are similar with that of other layered manganese-based cathode of SIBs. The Jahn-Teller distortion seriously affected the charge/discharge profiles of the LiMn₂O₄/Na. In addition, the average charge/discharge potentials of LiMn₂O₄/Na is lower than that of the as-prepared CaFe₂O₄-type NaMn₂O₄ cathode. As shown in Fig. 2d, the capacity retentions increased gradually in the initial five cycles, and then decreased sharply in the following cycles. This behavior indicates that the structure instability of the spinel LiMn₂O₄ is caused by insertion of large radius Na⁺ into the smaller radius Li⁺ vacancy positions. Previous report also confirmed the phase transition of the spinel phase in SIBs.²³ On the contrary, the CaFe₂O₄-type NaMn₂O₄ show very stable cycle performance and the capacity retention of 94% even at the 200th cycle. This is mainly attributed to the ultrastable CaFe₂O₄-type structure of NaMn₂O₄.

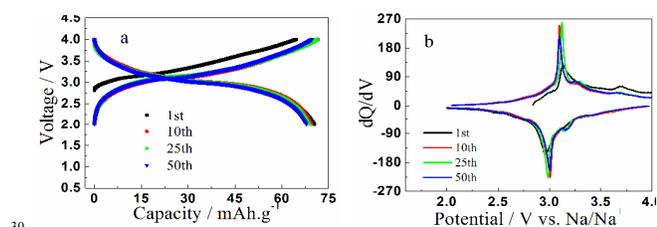


Fig. 3. Charge-discharge profiles of NaMn₂O₄ at 55 °C (a), the corresponding dQ/dV curves (b).

It is well known that the performance of manganese-based cathode deteriorates rapidly with increasing temperatures due to the Jahn-Teller distortion and seriously dissolution of Mn²⁺ from the electrode.²⁶ This has also been one of the key problems for the widely applications of spinel LiMn₂O₄. However, it has not been paid close attentions on manganese-based cathode in SIBs. In this work, we studied the charge/discharge profiles CaFe₂O₄-type structure of NaMn₂O₄ at different cycles at 55 °C (Fig. 3a). A smooth voltage profiles were obtained which is similar with that at room temperature. The capacity is a little higher which mainly due to the more activated Na⁺ in the CaFe₂O₄-type NaMn₂O₄ with the increased temperature. The discharge capacity fading is only 2.7 mAh/g from the first cycle (70.5 mAh/g) to the 50th cycle (67.8 mAh/g). This ultra-stable cycle performance at 55 °C let us further believe that the Jahn-Teller distortion has been suppressed to a large extent in the CaFe₂O₄-type NaMn₂O₄. To further understanding the voltage degradation process at 55 °C, the corresponding differential capacity versus voltage was

summarized in Fig. 3b). It shows a couple of the well-shaped redox peaks, a oxidation peak at 3.10 V and a reduction peak at 3.02 V, which demonstrates the high reversibility during the charge-discharge process. The shift of both peak positions during the 50 cycles is in the range of ± 0.02V in which agrees well with little structure changes. Very small shoulder peak was discovered in the first charge cycle, which might originate in the complicated reactions at the surface of the fresh electrode. All of the above combined results approve that the ultrastable cycle performance is due to the suppressed Jahn-Teller distortion and stable post spinel structure.²³

To further investigate the cathode material surface and structure evolutions after 50 charge/discharge cycles, the morphologies and structure of cycled samples were examined by SEM, TEM and XRD. Figure 4a shows the SEM image of cycled NaMn₂O₄. The microrods primarily particles experienced no obvious changes in size and morphology after cycles. The conductive agent and binder particles uniformly distribute in the microrod particles. There are no cracks or byproducts depositions on the particle surface. It also shows well crystalline from the TEM image in Fig. 4b. The material structure of cycled sample was carefully compared with that of pristine sample by XRD as shown in Fig. 4c. The main diffraction peaks shows good consistency and no peak shift or no new peaks can be detected in the cycled sample. The weakened diffraction peaks at high-angles might due to the blend with conductive agent and binder of cycled samples. The presented results indicate the stable characteristics of the post spinel structure during charge/discharge cycles. In contrast, the XRD patterns of LiMn₂O₄/Na after 50 cycles were also studied as shown in Fig. 4d. The patterns of cycled samples exhibit very different with that of the pristine spinel LiMn₂O₄. Obviously, the spinel structure cannot be maintained during the extraction/insertion of sodium ions. New peaks appeared and peak intensity contrast was changed to a great extent. The new patterns can be attributed to the structure changes from spinel to layered structure. This result is consistent with the previous report.²³ The stability of battery performance is well coincidence with the structure stability. Therefore, the high stable post spinel structure guaranteed the super performance of NaMn₂O₄ as cathode of SIBs.

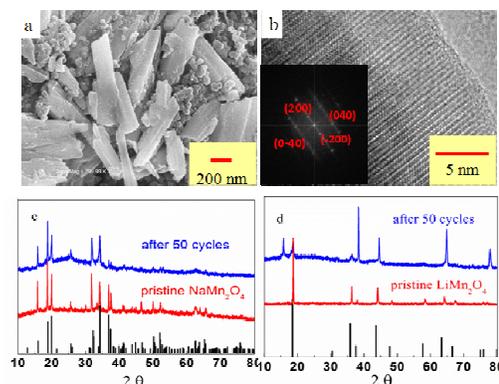


Fig. 4. Characterizations of samples after 50 charge-discharge cycles. SEM image (a), TEM image, the inset is an FFT (b), and XRD patterns of NaMn₂O₄ (c), XRD patterns of LiMn₂O₄ before and after cycles (d).

In summary, CaFe₂O₄-type NaMn₂O₄ has been synthesized under high pressure and used as cathode of SIBs for the first time. Both

the charge and discharge profiles show smooth plateaus and little polarization, which is rare in manganese-based cathode of SIBs. It shows an ultra-stable cycle performance both at room temperature and 55 °C. The capacity retention at the 200th cycle is 94% when cycled at room temperature. The Jahn-Teller distortion have been suppressed in this material due to the high barrier of rearrange MnO₆ octahedrons. Therefore, it presents a stable material structure during the charge/discharge process. The delivered capacity is less than the theoretical value due to the large particle size of NaMn₂O₄. The studies of synthesis of CaFe₂O₄-type NaMn₂O₄ with smaller size to enhance its capacity are under doing in our group. Although the capacity needs to be improved, the ultra-stable battery performance still encourage us for the future investigation of other post spinel cathode for SIBs.

Notes and references

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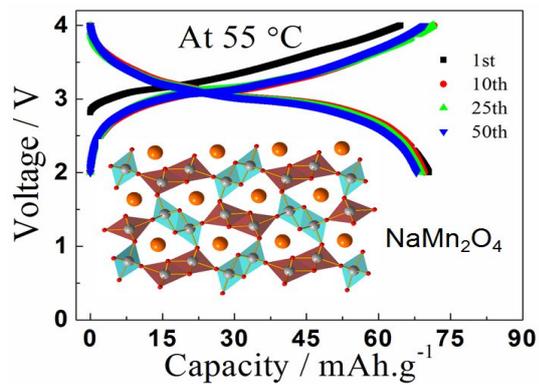
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† Electronic Supplementary Information (ESI) available: [IR, CV and detailed experiment method]. See DOI: 10.1039/b000000x/

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Table of Contents



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Keyword

CaFe_2O_4 -type, NaMn_2O_4 , sodium ion battery, Jahn-Teller distortion, stable cycle performance