**O3-type Na(Mn₀.25Fe₀.25Co₀.25Ni₀.25)O₂**: A quaternary layered cathode compound for rechargeable Na ion batteries.

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Short communication

O3-type Na(Mn0.25Fe0.25Co0.25Ni0.25)O2: A quaternary layered cathode compound for rechargeable Na ion batteries

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Abstract

We report a new layered Na(Mn0.25Fe0.25Co0.25Ni0.25)O2 compound with O3 oxygen stacking. It delivers 180 mAh/g initial discharge capacity and 578 Wh/kg specific energy density with good cycling capability at high cutoff voltage. In situ X-ray diffraction (XRD) shows a reversible structure evolution of O3-P3-O3–O3–O3′–O3″ upon Na de-intercalation. The excellent capacity and cycling performance at high cutoff voltage make it an important model system for studying the general issue of capacity fading in layered Na cathode compounds.

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1. Introduction

Layered sodium metal oxides have attracted considerable interest as cathodes for Na-ion batteries partly due to the fact that all seven layered NaTMO2 with the O3-structure, where TM is a single oxidizable 3d transition metal ion from Ti, V, Cr, Mn, Fe, Co, Ni [1], can be easily synthesized, and showed the capability to intercalate Na ions reversibly [2–7]. This is very different from their Li analogues, where only LiCoO2 and LiNiO2 reversibly intercalate Li ions [8]. Furthermore, different transition metal ions can be easily mixed in the TM layer to make new NaTMO2 compounds [9–15]. Among them, O3-Na(Fe0.5Co0.5)O2 (denoted hereafter as FC) shows a capacity around 160 mAh/g with excellent capacity retention when cycled below 4.0 V and an average voltage of 3.14 V [11]. O3-Na(Ni0.5Mn0.5)O2 (denoted hereafter as NM) shows an initial discharge capacity of 185 mAh/g and average voltage of 3.22 V, partly due to a long high voltage plateau around 4.0 V [12,16]. But capacity retention of NM is poor if the 4.0 V plateau is included in the galvanostatic cycling.

We report here in this communication a new quaternary O3-structured compound with composition Na(Mn0.25Fe0.25Co0.25Ni0.25)O2 (denoted hereafter as MFCN), with theoretical capacity of 239 mAh/g and initial discharge capacity of 180 mAh/g over an average discharge voltage of 3.21 V. More importantly, its capacity retention is significantly improved over NM and FC even when cycled with high charge voltage cutoff. In-situ lab X-ray diffraction (XRD) to reveal the structure evolution of MFCN in the first electrochemical cycle shows a reversible O3-P3-O3–O3–O3′–O3″ phase transformation. Our result shows the opportunity to further improve the electrochemical performance of layered NaTMO2 compounds by designing new combinations of transition metal ions in the TM layer.

2. Experimental

Stoichiometric amounts of Na2CO3 (99.95% Alfa Aesar), Mn2O3 (99.99% Sigma-Aldrich), Fe2O3 (99.99% Alfa Aesar), Co3O4 (99.7% Alfa Aesar), and NiO (99.99% Sigma-Aldrich) powder were mixed and pressed into a pellet. MFCN was synthesized by sintering the pellet at 900 °C in an oxygen gas flow for 12 h. The pellet was quenched to room temperature and transferred immediately into an Ar-filled glovebox. An XRD sample was sealed with Kapton film inside the glovebox and then scanned from 10° to 85° 2θ angle on a PANalytical X’pert PRO diffractometer equipped with a Cu Kα radiation source. Structure analysis using the Rietveld method was carried out using Highscore Plus.

The X-ray absorption spectroscopy (XAS) at the Mn, Fe, Co and Ni K-edge were collected in a transmission mode at beamline X18A of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. Energy calibration was carried out using the first inflection point of the reference spectrum of Mn, Fe, Co and Ni-metallic foils.
which were simultaneously collected during each measurement. The X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectra were processed using the Athena and Artemis software package [17,18]. The cathode film was made by mixing MFCN powder, Super P carbon black (Timcal) and dry PTFE (DuPont) with the weight ratio of 80:15:5. A Swagelok battery was assembled using glass fiber (Whatman GF/F) as a separator, Na metal (99.95% Sigma-Aldrich) as an anode and 1 M NaPF6 (98%, Sigma-Aldrich) in EC:DEC (anhydrous, 1:1 volume ratio) as an electrolyte with the moisture level less than 3 ppm. The galvanostatic cycling was tested on Solartron 1470E at C/10 rate between 1.9–4.3 V on the cathode film with the loading of 2.2 mg/cm².

Fig. 1. (a) The powder XRD refinement of O3-Na(Mn0.25Fe0.25Co0.25Ni0.25)O2 (MFCN) using R-3 m symmetry. The goodness of fit is 4.35 and Rwp is 2.18. The inset table shows the refined lattice parameters. The background from 10 to 30° is from the Kapton film used to seal the XRD sample. The electron diffraction pattern in the inset is taken along the [003] zone axis, which is perpendicular to the ab plane. (b) XANES spectra at the Mn, Fe, Co, Ni K-edges of pristine MFCN and different transition metal oxide samples with standard valence states, including MnO (Mn2+), Mn2O3 (Mn3+), MnO2 (Mn4+), FeO (Fe2+), Fe2O3 (Fe3+), CoO (Co2+), LiCoO2 (Co3+), LiNi1/3Co1/3Mn1/3O2 (Ni2+), LiNiO2 (Ni3+), Li0.2Ni1/3Co1/3Mn1/3O2 (Ni4+).

Table 1 Mn, Fe, Co and Ni K-edge EXAFS structure parameters of pristine MFCN.

<table>
<thead>
<tr>
<th>TM in MFCN</th>
<th>Path</th>
<th>r/Å</th>
<th>σ²/10⁻³ Å²</th>
<th>ΔE/eV</th>
<th>R</th>
</tr>
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<tbody>
<tr>
<td>Mn−O</td>
<td>1.92(8) ± 0.014</td>
<td>3.56 ± 1.72</td>
<td>0.70 ± 2.53</td>
<td>0.003</td>
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<tr>
<td>Mn−TM</td>
<td>2.94(7) ± 0.005</td>
<td>2.95 ± 1.03</td>
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<td>Mn−Na</td>
<td>3.03(1) ± 0.122</td>
<td>17.65 ± 11.48</td>
<td>0.001</td>
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<tr>
<td>Fe−O</td>
<td>2.01(1) ± 0.006</td>
<td>6.10 ± 10.70</td>
<td>0.12 ± 1.62</td>
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<tr>
<td>Fe−TM</td>
<td>2.94(9) ± 0.004</td>
<td>3.89 ± 0.69</td>
<td></td>
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</tr>
<tr>
<td>Fe−Na</td>
<td>3.21(1) ± 0.059</td>
<td>58.65 ± 42.42</td>
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<tr>
<td>Co−O</td>
<td>1.94(5) ± 0.010</td>
<td>4.18 ± 1.36</td>
<td>0.47 ± 1.97</td>
<td>0.002</td>
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</tr>
<tr>
<td>Co−TM</td>
<td>2.91(8) ± 0.009</td>
<td>4.62 ± 0.87</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Co−Na</td>
<td>3.03(3) ± 0.046</td>
<td>40.30 ± 24.19</td>
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<tr>
<td>Ni−O</td>
<td>2.05(4) ± 0.007</td>
<td>6.81 ± 1.23</td>
<td>1.56 ± 0.88</td>
<td>0.001</td>
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</tr>
<tr>
<td>Ni−TM</td>
<td>2.94(9) ± 0.005</td>
<td>4.11 ± 0.70</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni−Na</td>
<td>3.31(4) ± 0.036</td>
<td>13.24 ± 5.65</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

r: bond length; σ²: Debye–Waller factor (disorder); ΔE: inner shell potential shift; R: R-factor.

Fig. 2. (a) Galvanostatic charge and discharge profiles at 1st, 2nd, 5th and 10th cycles for MFCN. (b) Discharge capacity of MFCN cycled between 1.9–4.3 V at different cycles compared with NM cycled between 1.9–3.8 V and FC cycled between 1.9–4.0 V, all at C/10 rate. (c) Discharge capacity of MFCN cycled between 1.9–4.3 V at different cycles compared with NM and FC cycled between 1.9–4.2 V, all at C/10 rate.
performance of MFCN between 1.9 and 4.3 V compared with NM cycled
ing the specified 180 mAh/g occurs over an average discharge voltage of 3.21 V, mak-
MFCN between 1.9 V
FC.

systems, indicating that MFCN is not a simple combination of NM and

The phase transition processes are reversible upon discharge as shown in Fig. 3.

One feature of the structural evolution of MFCN is that no monoclinic
distortion is observed during Na de-intercalation. This is very different
from the NM system where multiple phase transitions between hexagonal and monoclinic phases are observed [12,16]. Monoclinic
distortions usually arise from anisotropic Na ordering such as the stripe ordering [19], Jahn–Teller distortion of the TM ions, or the coupling between them [19]. The absence of anisotropic Na ordering in MFCN may be a result of Na site disorder caused by the perturbations of the TM disorder. The particular TM composition in MFCN also reduces the amount of active Jahn–Teller ions, with only 25% Ni in the TM layer compared with 50% in the NM system. These factors may largely suppress any monoclinicity, giving a much smoother electrochemical profile for MFCN compared with the more stepwise-like profile in the NM system.

Although FC shows excellent cycling performance when cycled below 4.0 V cutoff voltage [11], our result shows that the cyclability drops significantly when the cutoff voltage is increased to 4.2 V, which may indicate some structural instability and irreversibility of FC at high voltage and/or very low Na composition. On the contrary, our in-situ XRD of MFCN shows that the high voltage O3′ and O3″ phases are reversible in the initial cycle, consistent with the reversible features observed in the first charge and discharge electrochemical profiles. However, we also notice that the O3′ phase region of MFCN above 4.25 V is not fully reversible in the following cycles as observed in Fig. 2a. It is thus also important to understand the mechanism of capacity fading in the O3′ phase of MFCN in future studies.

4. Conclusion

A new Na ion battery cathode material with composition Na(Mn0.25Fe0.25Co0.25Ni0.25)O2 is synthesized by the solid state reaction and shows an initial discharge capacity of 180 mAh/g and specific energy density of 578 Wh/kg. At high cutoff voltage the cycling performance of MFCN is noticeably better than that for the Na(Fe2/3Co1/3)O2 and Na(Ni2/3Mn1/3)O2, indicating a difference in the intrinsic properties of these compounds. The structural evolution in MFCN shows reversible phase transitions in the high voltage range and the absence of monoclinic distortions. The results show that MFCN is a high capacity cathode material and an important model system to investigate the general issue of capacity limits and fading of layered Na-TM cathodes for Na-ion batteries.

Conflict of interest

The authors declare that there is no conflict of interest.

Acknowledgments

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References