RAPID COMMUNICATION

New layered metal oxides as positive electrode materials for room-temperature sodium-ion batteries*

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In order to achieve better Na storage performance, most layered oxide positive electrode materials contain toxic and expensive transition metals Ni and/or Co, which are also widely used for lithium-ion batteries. Here we report a new quaternary layered oxide consisting of Cu, Fe, Mn, and Ti transition metals with O3-type oxygen stacking as a positive electrode for room-temperature sodium-ion batteries. The material can be simply prepared by a high-temperature solid-state reaction route and delivers a reversible capacity of 94 mAh/g with an average storage voltage of 3.2 V. This paves the way for cheaper and non-toxic batteries with high Na storage performance.

Keywords: layered oxides, positive electrode, sodium-ion battery, energy storage

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1. Introduction

The rapid development of renewable and sustainable energies requires large scale energy storage systems due to their characteristics of intermittence, randomness, and instability.[1,2] Sodium-ion batteries operated at room-temperature have been attracting increasing interest for such applications because of the abundance of Na resources and the potential low cost compared to lithium-ion batteries, which are more suitable for portable electronic devices and electric vehicles.[3–6] Up to now, numerous positive electrode materials with different crystal structures have been investigated for Na extraction/insertion.[7–14] Among them, layered metal oxides have long been exploited as an important class of hosts for rechargeable batteries.[13,15–35] For instance, $LiCoO_2$ is one of the most famous and successful positive electrode materials for lithium-ion batteries.[1] Since the discovery of Na_xCoO_2, which is able to store Na,[15] many other layered oxides have been extensively studied. However, in order to achieve better Na storage performance, most of them contain toxic and expensive transition metals of Ni and/or Co,[15,16,18,21,23–25,28–35] which are also commonly and widely used for lithium-ion batteries. This will limit their large-scale application. Therefore, it is essential to explore new layered oxides with cheaper and environmentally-benign transition metals. For example, we recently found that the Cu^{2+}/Cu^{3+} redox couple is highly reversible in Na-containing layered oxides with high operation voltage.[36] This important finding reveals that we can use cheaper, non-toxic Cu instead of Ni or Co as a building block for the layered oxides. In this work, we further demonstrate that we can incorporate Cu and Fe into an O3-type layered oxide to form quaternary $Na_{0.9}Cu_{1/4}Fe_{1/4}Mn_{1/4}Ti_{1/4}O_2$, which shows a good Na storage performance in terms of both high storage capacity and high operating voltage.

2. Experiment

The $Na_{0.9}Cu_{1/4}Fe_{1/4}Mn_{1/4}Ti_{1/4}O_2$ material was synthesized by a simple solid-state reaction using precursors of Na_2CO_3 (99%), CuO (99.8%), Fe_2O_3 (99.5%), Mn_2O_3 (99%), and TiO_2(99.8%). They were ground uniformly in stoichiometric proportion and heated in air at 850 °C for 15 h to form the final products. Powder X-ray diffraction (XRD) was performed on a Bruker D8 Advance diffractometer equipped with a Cu $K\alpha$ radiation source ($\lambda_1 = 1.54060$ Å, $\lambda_2 = 1.54439$ Å). The morphologies and elemental mapping of the materials were investigated by a scanning electron microscope (SEM) (Hitachi S-4800).

The working electrode was prepared by spreading the slurry of the active material of $Na_{0.9}Cu_{1/4}Fe_{1/4}Mn_{1/4}Ti_{1/4}O_2$ (80 wt.%), acetylene black (15 wt.%), and the polyvinylidene fluoride (PVdF) (5 wt.%) binder on an Al foil. The working electrodes were dried at 110 °C under a vacuum for 10 h. The electrolyte was 1 M $NaClO_4$ in propylene carbonate. The coin-type (CR2032) cells were assembled with a pure sodium foil as the counter electrode and a glass fiber as the separator in an argon-filled glove box. The charge and discharge measurements were carried out on a Land BT2000 battery test system (Wuhan, China) in the voltage range of 2.5–4.0 V at room temperature.

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3. Results and discussion

Typically, layered metal oxides Na_xMO_2 (M: transition metal) can be mainly categorized as either O3 or P2 according to the definitions by Delmas *et al.*[37] The letters O and P represent the Na coordination environments of octahedral and prismatic sites, while the numbers refer to the number of repeating MO_2 slabs in the unit cell. The formation of O3- or P2-type depends on the sodium content and the synthetic conditions. Figure 1 shows the XRD pattern of the $Na_{0.9}Cu_{1/4}Fe_{1/4}Mn_{1/4}Ti_{1/4}O_2$ sample synthesized at 850 °C in air. For comparison, the standard XRD pattern of O3-$NaFeO_2$ is also displayed in Fig. 1. It can be seen that all of the diffraction peaks of the resulting sample are in good agreement with those of $NaFeO_2$, indicating a typical O3 phase material with no impurity. By careful examination, some peaks such as (003) and (006) are found to shift slightly to lower angles compared with those of $NaFeO_2$. This observation is related to the Na content in this Na-deficient material. In general, in $NaMO_2$, when a small amount of Na is extracted from the layered structure, the c axis expands slightly, leading to a downshift of the (00l) peaks.

Figure 2(a) shows a typical SEM image of the quaternary $Na_{0.9}Cu_{1/4}Fe_{1/4}Mn_{1/4}Ti_{1/4}O_2$ sample. The particle sizes are in the range from 2 μm to 5 μm. The surface morphology of the sample is revealed as steps in Fig. 2(b), which is a typical feature of the layered oxides. In order to check the rough distribution of four transition metals, energy dispersive spectroscopy (EDS) was performed. The EDS elemental mapping results in Fig. 3 reveal a homogeneous distribution of Cu, Fe, Mn, and Ti elements in the material. No aggregation of any single element was observed.

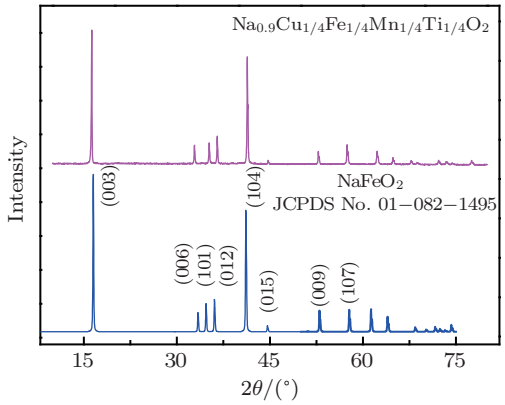


Fig. 1. XRD pattern of as-synthesized $Na_{0.9}Cu_{1/4}Fe_{1/4}Mn_{1/4}Ti_{1/4}O_2$ sample and the standard JCPDS of α-$NaFeO_2$.

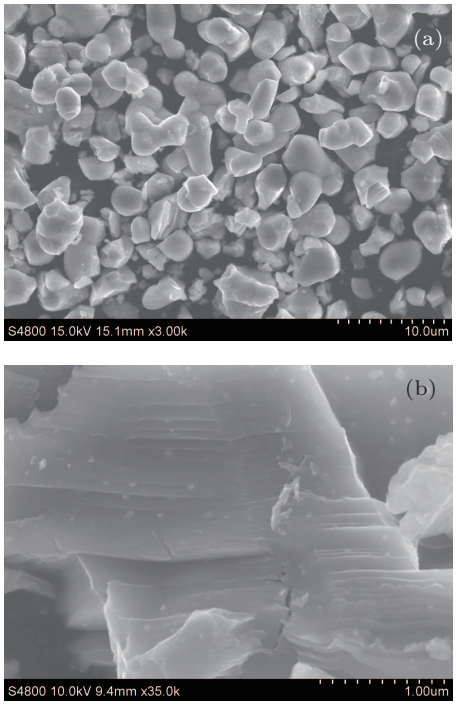


Fig. 2. Typical SEM images with different magnifications of the $Na_{0.9}Cu_{1/4}Fe_{1/4}Mn_{1/4}Ti_{1/4}O_2$ sample.

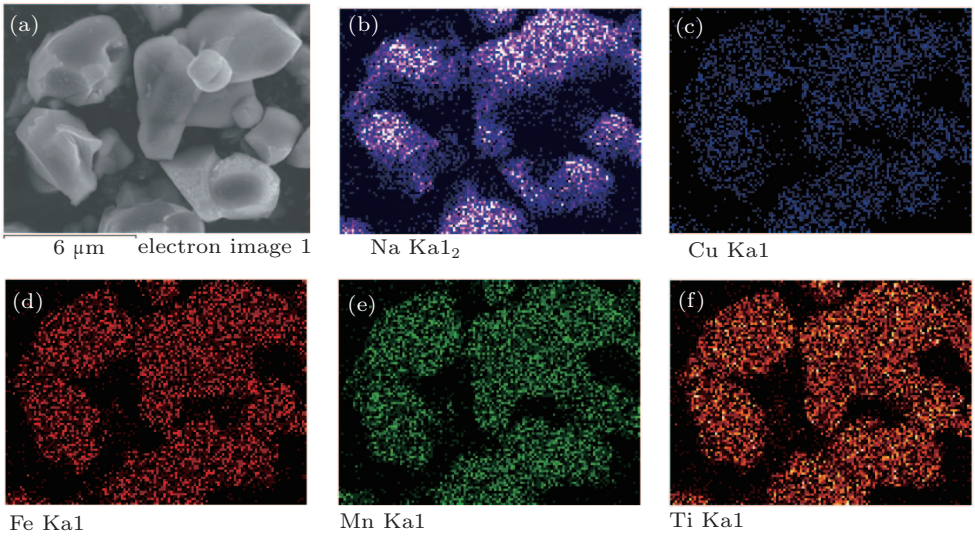


Fig. 3. EDS elemental mapping of the $Na_{0.9}Cu_{1/4}Fe_{1/4}Mn_{1/4}Ti_{1/4}O_2$ sample: (a) SEM image, (b)–(f) the corresponding elemental mapping of Na, Cu, Fe, Mn, and Ti, respectively.

To investigate the Na de-intercalation/intercalation behavior in the layered $Na_{0.9}Cu_{1/4}Fe_{1/4}Mn_{1/4}Ti_{1/4}O_2$ electrode, galvanostatic charge and discharge at a current rate of C/10 (10 mA/g) were carried out in sodium half cells. The results are shown in Fig. 4(a). In the first charge process, a short plateau at ca. 3.2 V was observed followed by a long slope until 4.0 V. This short plateau indicates a two-phase reaction with a phase transition from O3 to P3, which is a common characteristic of O3-type materials. The other feature, at the end of the discharge profile, is a short plateau at ca. 3.0 V, which is much higher than that of other O3-type materials such as O3-$NaFe_{1/3}Ni_{1/3}Mn_{1/3}O_2$, O3-$NaNi_{0.5}Mn_{0.5}O_2$, $Na_xFe_{0.5}Mn_{0.5}O_2$, $Na[Ni_{0.4}\ Fe_{0.2}Mn_{0.2}Ti_{0.2}]O_2$.[23,24,26,30,33] This could be due to the incorporation of Cu and/or Ti elements into the transition metal layer.

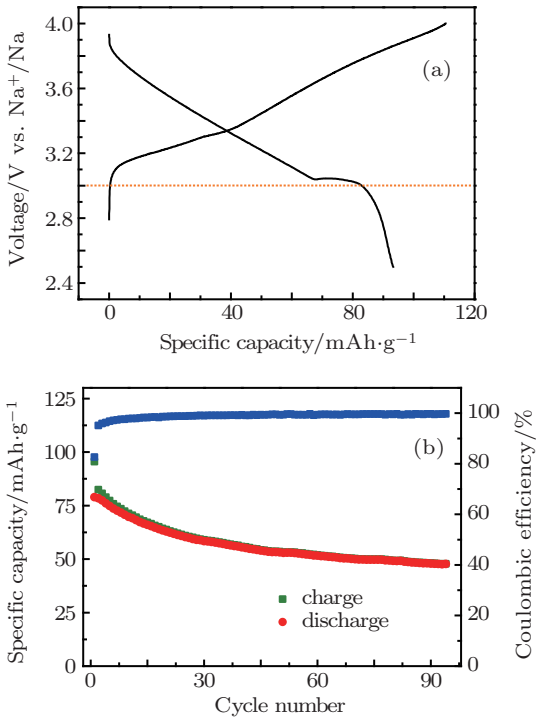


Fig. 4. (a) The typical first galvanostatic charge and discharge profiles of the $Na_{0.9}Cu_{1/4}Fe_{1/4}Mn_{1/4}Ti_{1/4}O_2$ electrode cycled between 2.5 V and 4.0 V at a current rate of C/10. (b) Cycle performance of the $Na_{0.9}Cu_{1/4}Fe_{1/4}Mn_{1/4}Ti_{1/4}O_2$ electrode cycled between 2.5 V and 4.0 V at a current rate of 1C.

The first charge and discharge capacities are 110 mAh/g and 94 mAh/g, respectively, corresponding to a Coulombic efficiency of 85%. The average discharge voltage is ca. 3.2 V. This high operation voltage could be attributed to the coexistence of Cu^{2+}/Cu^{3+} and Fe^{3+}/Fe^{4+} redox couples with a relatively high voltage in the transition metal layer. The resulting quaternary $Na_{0.9}Cu_{1/4}Fe_{1/4}Mn_{1/4}Ti_{1/4}O_2$ also exhibits moderate rate capability and cyclic performance as shown in Fig. 4(b). The charge and discharge capacities at a current rate of 1C are 95.5 mAh/g and 78 mAh/g, respectively. After 90 cycles, capacity retention of 60% was achieved.

4. Conclusion

In this work, following our first discovery of the high reversibility of the Cu^{2+}/Cu^{3+} redox couple in Na-containing layered positive electrode materials, we further demonstrate that Cu and Fe can be incorporated into an O3-type layered oxide to form $Na_{0.9}Cu_{1/4}Fe_{1/4}Mn_{1/4}Ti_{1/4}O_2$, which was prepared by a simple solid-state reaction method. The resulting material is able to deliver a reversible capacity of 94 mAh/g with moderate rate capability and cyclic stability. We believe that the Na storage performance can be further improved in this series of new layered oxides through tuning the compositions of $Na_aCu_{1-x-y-z-d}Fe_xMn_yTi_zD_dO_2$ (D: dopant, e.g., Li, Mg, Al, etc., $0 < x < 1$, $0 < y < 1$, $0 \leq z < 1$, $0 \leq d < 1$, $0.6 < a \leq 1$) and controlling how oxygen stacks to form O3, P2, O′3, P3 , etc., which will show great promise for practical application in sodium-ion batteries.

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