Single-phase P2-type layered oxide with Cu-substitution for sodium ion batteries

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Abstract

The development of high-performance layered oxide cathodes for sodium ion batteries (SIBs) continues to face being hindered by severe challenges to date. Herein, a single-phase P2-Na$_{0.65}$Mn$_{0.4}$Ni$_{0.3}$Co$_{0.1}$Cu$_{0.1}$O$_2$ (NMNCC) comprising multiple-layer-oriented stacked nanoflakes is designed and synthesized via a simple sol–gel method. The large lattice parameters ensure a large three-dimensional frame, which enables the diffusion of sodium ions. Owing to its optimal morphology structure modulation transition metal substitution strategy, the NMNCC electrode delivers a reversible capacity of 131.3 mAh g$^{-1}$ at 0.1 C with retention of 86.2% after 200 cycles. In addition, it provides an initial capacity of 86.7 mAh g$^{-1}$, and a retention of 80.0% after 500 cycles even at a current density of up to 1 A g$^{-1}$. The stable single-phase structure and slight volume shrinkage observed after Na$^+$ extraction further delay structural degradation. High Na$^+$ mobility and low Na$^+$ diffusion resistance are also guaranteed the excellent rate performance of the NMNCC electrode. Thus, we determine that the NMNCC cathode is significant in the advancement of promising novel layered oxide cathodes.

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1. Introduction

In the past few decades, the application of lithium ion batteries (LIBs) has been a major success in the secondary battery industry and has permitted its equipment with small electronic devices. However, the shortage of lithium resources challenges its application in large-scale electrical energy storage systems [1,2]. In this regard, sodium ion batteries (SIBs) have been considered as a promising alternative to LIBs due to the natural abundance of sodium [3,4]. Based on current studies, the cathode is the short board of the system; hence, the development of high performance cathode materials is key to improving the specific energy and promoting the applications of SIBs [5].

Therefore, various compounds have been explored as potential cathode materials for SIBs [6–11]. Layered oxides (Na$_x$TMO$_y$) are considered to be one of the most promising materials due to their large discharge specific capacity, high capacity density, and operating voltage [12,13]. In Na$_2$TMO$_2$, the most common structures are P2- and O3-types, where sodium ions occupy trigonal prismatic and octahedral sites, respectively [14]. Here, the following number denotes the number of sodium ions in the unit cell. P2-type Mn-rich layered oxides have been extensively studied because of their high structural stability [15–17]. However, the Jahn–Teller effect caused by Mn$^{2+}$ leads to rapid capacity decay [18]. Recently, a small substitution of transition metal elements into Mn-rich P2-type layered oxides were proposed to be an effective method to inhibit the Jahn–Teller effect [19–21]. Moreover, most P2-type materials undergo P2–O2 phase transitions at high voltage, which accelerates structural decay and shortens the life cycle [22,23]. One effective approach is to limit the cut-off voltage to below 4.1 V [15]. Therefore, it is critical to understand the factors that control the operating voltage.

In this contribution, we designed and synthesized P2-type Na$_{0.65}$Mn$_{0.4}$Ni$_{0.3}$Co$_{0.1}$O$_2$ (NMNCC) and NMNCC. After exploring the structure of the charge-discharge process, we found that a stable pure P2 phase structure is consistently maintained between 1.9 and 4.0 V. Meanwhile, the slight shrinkage of the cell volume during the charge process inhibits the phase transition. The introduction of copper not only reduces the charge transfer resistance, but also improves the mobility of Na$^+$. In addition, the phase transition

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can be prevented by controlling the cut-off voltage at 4.0 V, which is beneficial to the long-term cyclic stability and high rate performance of NMNCC cathodes. There is no doubt that this novel cathode is promising for the development of large-scale energy storage system in the future.

2. Experimental

2.1. Synthesis of P2-type Na$_{0.67}$Mn$_{0.6}$Ni$_{0.3}$Co$_{0.1}$Cu$_{0.1}$O$_2$

A simple sol–gel method was used to synthesize the P2-type NMNCC and NMNC cathode materials. Manganese (II) acetate tetrahydrate, nickel (II) acetate tetrahydrate, cobalt (II) acetate tetrahydrate, copper (II) acetate monohydrate and sodium carbonate anhydrous were dissolved into a citric acid solution with a corresponding stoichiometric ratio, then stirred for 30 min to form a uniform solution. The solution was heated at 80 °C in a water bath with constant stirring until a gel was obtained. Following this, it was transferred to an oven to thoroughly dry at 80 °C. The resulting powder was heated in a muffle furnace at 400 °C for 10 h and then slowly cooled to 25 °C. Finally, the powder was pressed into pellets and calcined at 900 °C for 10 h in a muffle furnace to form the target product. All the chemical reagents above were analytically pure.

2.2. Characterization

X-ray diffractometry (XRD) patterns were obtained with a Bruker Advance-D8 diffractometer using Cu–Kα radiation as the source. GSAS software was used to refine the cell parameter based on the Rietveld method. The content of metal elements was analyzed by the inductively coupled plasma (ICP) atomic emission spectrometry. The morphologies of the materials were examined by scanning electron microscopy (SEM) using a FEI Nova Nano STEM 230 equipment. Furthermore, transmission electron microscopy (TEM) images were collected using a JEOL-2100F electron microscope. The annular bright-field scanning TEM (ABF-STEM) images and energy-dispersive spectroscopy (EDS) mappings were collected at a Titan G2 electron microscope. The X-ray photoelectron spectroscopy (XPS) patterns were obtained with an ESCAJob 250 Xi electron spectrometer.

2.3. Electrochemical test

Coin-type (CR2016) cells were assembled to investigate the electrochemical properties of the fabricated cathode materials in a glove box filled with argon. The electrode was prepared by mixing the active material, acetylene black, and polyvinylidene fluoride with a weight ratio of 8:1:1 onto Al foils. The resulting electrodes were dried at 80 °C in vacuum oven for 24 h. The mass loading of the active materials was 1.5–2.5 mg cm$^{-2}$. The discharge and charge measurements were tested on a NEWARE battery test system. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were carried out on a CHI660a electrochemical workstation.

3. Results and discussion

The ICP result shown in Table S1 confirms the expected atomic ratio of Na:Mn:Ni:Co:Cu. The XRD patterns in Fig. S1 show the P2-type structure for the NMNCC sample, corresponding to the space group P6$_3$/mmc (no.194). To calculate the lattice parameters, the XRD result was refined by the Rietveld method, as shown in Figs. 1(a) and S2. $R_{wp}$ and $R_B$ are the weighted profile and profile $R$-factors, respectively, which can best reflect the deviation of fitting. Both the parameters $R_{wp}$ and $R_B$ were no more than 10%, indicating that the result of refinement is highly reliable. The detailed cell parameters are shown in Tables S2 and S3. Mn, Ni, Co and Cu ions were located at the octahedral 2a sites, combining with oxygen to form Mo$_2$ (transition metal oxide) layers. Sodium ions were inserted into two different locations and were distinguished as Na$_A$ and Na$_B$. This can also be observed from the model in Fig. 1(b). The lattice parameters of NMNCC were calculated to be $a = b = 2.8734(7)$ Å and $c = 11.1872(6)$ Å, which are larger than those of NMNC ($a = b = 2.8557(5)$ Å, $c = 11.1783(4)$ Å) and most materials previously reported [8,23–25]. The increase of the cell size is attributed to the introduction of Cu$^{2+}$, with a larger radius than Mn$^{4+}$, Ni$^{2+}$, and Co$^{2+}$ ($Cu^{2+} = 0.73 \ Å$, $Mn^{4+} = 0.53 \ Å$, $Ni^{2+} = 0.69 \ Å$, $Co^{3+} = 0.54 \ Å$). Large lattice parameters ensure a large three-dimensional framework, which is beneficial to the deintercalation and intercalation of sodium ions. The SEM images exhibits the particle size to be approximately 2 μm, as shown in Figs. 1(c) and S3. However, these particles can show multiple-layer-oriented stacked nanoflakes, which contributes to sodium ion migration by increasing the contact area of the electrode/electrolyte and shortening the diffusion distance. Fig. S4 shows the pore distribution of the NMNCC sample. As seen from the plot, NMNCC displays a pore width of 2–10 nm, which ensures a wider sodium transport channel.

The atomic-scale structural information of P2-NMNCC was further analyzed by the ABF-STEM images. As shown in Fig. 1(d) and (e), the structure is noticeably well-crystallized. The bright-dots at the [010] zone axis correspond with the Mo$_2$ layers, while the dark dots are in accordance with the sodium ion layers. The arrangement of the transition metal atoms (Mn, Ni, Co and Cu) is proven to have a hexagonal symmetry via the [001] zone axis, as shown in Fig. 1(e). All the ABF-STEM images demonstrate the P2-type structure of the as-synthesized sample with high crystallinity. Fig. 1(g)–(k) shows the EDS maps of Na, Mn, Ni, Co, and Cu elements. It is demonstrated that all the elements were uniformly distributed in the P2-type NMNCC.

Fig. 2 exhibits the ex-situ XPS patterns, revealing the valence states of the transition metals. According to the position of the bond energy for the pristine sample, it can be inferred that the Mn, Ni, Co, and Cu elements are tetravalent, divalent, trivalent and divalent, respectively. As the electrodes discharge to 1.9 V, the binding energy of Mn 2p$_{3/2}$ shifts to 641.5 eV due to the conversion of small quantities of Mn$^{3+}$/Mn$^{4+}$. In addition, the Co 2p$_{3/2}$ peaks decrease to 779.2 eV, indicating the generation of Co$^{3+}$. Meanwhile, when charged to 4.0 V, the Ni 2p$_{3/2}$ peaks approaching the higher binding energy demonstrates the oxidation of Ni$^{2+}$ to Ni$^{4+}$, which undergoes Ni$^{2+}$/Ni$^{3+}$ and Ni$^{3+}$/Ni$^{4+}$ reactions. The bonding energy of Co 2p$_{3/2}$ reaches 780.5 eV, demonstrating the existence of Co$^{4+}$. Furthermore, significant migration of the Cu 2p$_{3/2}$ peaks can be observed at 4.0 V, illustrating that Cu copper underwent a Cu$^{2+}$/Cu$^{3+}$ redox reaction between 1.9 and 4.0 V.

The CV curves of the NMNCC and NMNC electrodes at a scan rate of 0.2 mV/s between 1.9 and 4.0 V are displayed in Fig. 3(a). There are four groups of redox peaks that can be clearly observed in both curves and the introduction of copper does not increase the number of peaks. The reversible oxidation/reduction peaks at 3.39/3.29 V and 3.61/3.52 V were induced by the redox reactions of Ni$^{2+}$/Ni$^{3+}$, Ni$^{3+}$/Ni$^{4+}$, respectively, which ensure a high average operating voltage [26,27]. The peaks at 3.63/3.74 V correspond to the redox couples of Co$^{3+}$/Co$^{4+}$. Meanwhile, the redox peaks at 2.50/2.26 V are presumed to have originated from Co$^{2+}$/Co$^{3+}$ based on the results of XPS. With copper replacing part of the cobalt, the peak area of Co$^{3+}$/Co$^{4+}$ and Co$^{2+}$/Co$^{3+}$ decreased significantly. The redox voltage of copper Cu$^{2+}$/Cu$^{3+}$ was up to 3.82/3.87 V, and all the redox peaks slightly shifted to high voltage, indicating that
copper is beneficial to increasing the overall operating voltage. Besides this, the incomplete peaks below 2.1 V are the result of an amount of conversion of Mn$^{3+}$/Mn$^{4+}$, which can reduce the impact of the Jahn–Teller effect on the structure as much as possible and ensures a high reversible capacity. No significant peak attenuation was observed in P2-NMNCC after 5 cycles of scanning, indicating the high reversibility of the redox reactions. (Fig. S5) The galvanostatic discharge/charge curves of NMNCC at different cycle at 0.1 C between 1.9 and 4.0 V show high symmetry and reversibility (Fig. 3(b)). Even after 100 cycles, the platforms in the discharge curves only slightly attenuate. The rate capability at different current densities is displayed in Fig. 3(c). From the figure, the Cu-substituted NMNCC exhibits better rate performance than the NMNC. The reversible discharge capacities are 131.4, 127.3, 121.3, 112.8, 101.2, 80.4, and 65.0 mAh g$^{-1}$, respectively, at various rates from 0.1 C to 15 C. When the current returned to 0.1 C, the discharge capacity remained as 129.9 mAh g$^{-1}$. The discharge curves of NMNCC at different current densities in Fig. 3(d) exhibit the enhancement of the polarization of the electrodes with the increase of the current density, which leads to the weakening of discharge platforms. The platforms below 2.3 V even disappeared when the current density reached 10 C.

The cyclic performances at 0.1 C between 1.9 V and 4.0 V are displayed in Fig. 3(e). An initial reversible capacity of 131.3 mAh g$^{-1}$ at 0.1 C can be seen for the P2-NMNCC electrode, which maintained a retention of 86.7% after 200 cycles with an average Coulombic efficiency of approximately 99%. Whereas the P2-NMNCC electrode only had 71.9% initial capacity retention after 200 cycles at 0.1 C. Even when the current density reached 1 A g$^{-1}$, the reversible capacity of the MNNC electrode was 86.7 mAh g$^{-1}$, which is higher than that for the NMNCC (70.6 mAh g$^{-1}$ at 1 A g$^{-1}$). The capacity remained at 69.4 mA h g$^{-1}$ after 500 cycles, corresponding to a capacity retention of 80.0%. According to previous studies, Co$^{3+}$ plays an important role in improving electronic conductivity, which is favorable to enhance the rate performance [28]. Compared with other oxide cathode materials reported recently, NMNCC shows obvious superiority (Table S4).

To examine the mechanism of evolution and the Na$^+$ intercalation/deintercalation mechanism in the charge-discharge process, ex-situ XRD patterns of the electrodes were collected between 1.9 and 4.0 V, as shown in Fig. 4. The diffraction peaks of the Al foil appear at 44.4° and 65.0°. Besides this, small amounts of CuO impurities can be observed at 38.2°, which is due to the solubility limit in P2-type phases [29,30]. During the whole charge and discharge process, the MNNC electrodes maintained the P2-type structure without any Bragg diffraction peak disappearing or appearing between 35° and 70°. It is demonstrated that there was no phase transition during the process. With the increase of voltage, the
Bragg peaks [002] and [004] shifted to lower degrees, indicating that Na\(^+\) partly deintercalated from the unit cell. Moreover, when charged to 4.0 V, new peaks were observed at 16.9°, which were confirmed to be the Na/vacancies created by the release of sodium ions, as in a previous report [23]. Similarly, no phase transition was observed in NMNC when it was cycled between 1.9 and 4.0 V (Fig. S6), indicating that controlling the cut-off voltage below 4.0 V is effective to avoid phase transition.

The evolution of the lattice parameters of the P2-type NMNCC during the deintercalation and intercalation of Na\(^+\) is plotted in Fig. 5(a). The a lattice parameters gradually decreased with the deintercalation of Na\(^+\), which is attributed to the reduction of the transition metal ion radius in the MO\(_2\) layers as they enter higher oxidation states. Meanwhile, the c parameters increased during the charge process, indicating that the distance between the adjacent O\(^2-\) layers enlarged with Na\(^+\) removal [31,32]. Therefore, the overall cell volume shrunk during the removal of Na\(^+\). The volume change rate was approximately 1.27% after Na extraction. Such a small volume change is beneficial for stabilizing the structure and enhancing the cyclic performance. Even after 200 cycles at 0.1 C, the NMNCC electrode exhibited P2-type structure, and only a small NiO impurity peak at 43.0° was observed (Fig. 5(b)). Combined with the XPS results, the excellent structural stability may depend on the single-phase structure during the whole charge and discharge process, which also ensures that NMNCC exhibits outstanding cyclic performance and rate capability.

The Nyquist plots of the NMNC and MNCC electrodes are displayed in Fig. 5(c), and the fitting parameters for the equivalent circuit model are shown in Table S4 [33]. Cu-substituted P2-NMNC delivers lower charge transfer resistance \(R_{ct}\) and irreversible side reaction resistance \(R_i\), which proves from another aspect that the introduction of copper contributes to the diffusion of sodium ions. To further investigate the effect of copper doping on kinetics, galvanostatic intermittent titration technique (GITT) tests were conducted on the NMNC and MNCC electrodes, as shown in Fig. 6(a). The GITT test method followed that of a previous study [32]. A linear relationship can be observed between the voltage and \(t^{1/2}\) for both NMNC (Fig. S7) and MNCC (Fig. S8). The overall voltage plateau of the copper-doped NMNC is higher than that of NMNC. The diffusion coefficients of Na\(^+\) were calculated based on the GITT results (Fig. 6(b)), which are between 0.5 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1} to 2 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1} for both NMNCC and NMNC. Noticeably, the Na\(^+\) mobility of the NMNCC electrode was significantly higher when the Na content was less than 0.65, indicating that the introduction of copper improves the mobility of Na\(^+\) for a high voltage range.

Fig. 2. Ex situ XPS spectra of (a) Mn 2p, (b) Ni 2p, (c) Co 2p and (d) Cu 2p for NMNCC electrodes.
Fig. 3. Electrochemical performance: (a) CV curves at 0.2 mV/s; (b) Galvanostatic discharge/charge curves of NMNCC electrodes at 0.1 C (1 C = 175 mA g⁻¹); (c) rate capability between 0.1 and 15 C; (d) discharge curves of NMNCC at different current densities; cycling performance at (e) 0.1 C; and (f) high current density of 1 A g⁻¹.
4. Conclusions

In summary, a novel P2-type NMNCC cathode material consisting of multiple-layer oriented stacked nanoflakes was successfully designed and synthesized via a simple sol-gel method. The XRD and Rietveld refinement results confirm the structure as P2 phase. The Cu-substituted NMNCC electrodes exhibited excellent cyclic stability and rate performance, which are mainly attributed to the high stability of the pure P2 structure and enlarged lattice spacing. The outstanding structural stability was attributed to the single-phase structure and slight volume shrinkage after Na\(^+\) extraction, which further inhibited phase transition. The EIS results reflect the reduction of $R_D$ after the introduction of copper. Furthermore, the GITT tests show that the introduction of copper is beneficial to the improvement of Na\(^+\) mobility. We believe that such a cathode material with excellent cyclic stability and high rate performance could significantly contribute to the development of large-scale energy storage systems.
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Supplementary material

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