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Habit plane-driven P2-type manganese-based layered oxide as long cycling cathode for Na-ion batteries

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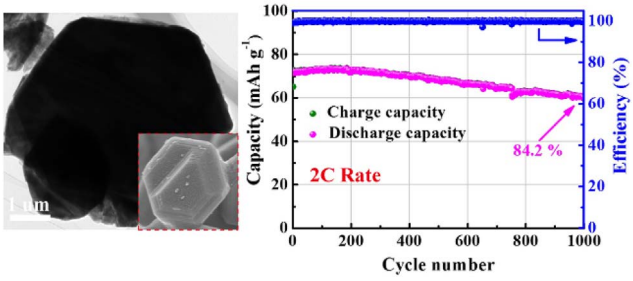
HIGHLIGHTS

- Layered P2-type transition oxides synthesized via a facile solid-state reaction.
- P2-NNM material exhibited a hexagons plate-like morphology.
- P2-NNM electrode exhibits superior rate capability and long cycle life.
- The electrode exhibits a quasi-solid-solution reaction during electrochemical reaction.

GRAPHICAL ABSTRACT



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ABSTRACT

Layered transition metal oxides are considered to be promising candidates as cathode materials for sodium-ion batteries. Herein, a facile solid-state reaction is developed to synthesize hexagons plate-like $Na_{0.67}Ni_{0.25}Mn_{0.75}O_{2+\delta}$ (denoted as P2-NNM) material with habit plane formed. The structure of this layered oxide is characterized by XRD, HR-TEM and SAED. The layered material delivers a high reversible capacity of 91.8 mAh g^{-1} at 0.2 C with a capacity retention of 94.4 % after 280 cycles, superior rate capability and long cycle life (84.2 % capacity retention after 1000 cycle). Ni^{2+} is an active ion and Ni doping alleviates the Jahn-Teller distortion, and Mn^{3+}/Mn^{4+} coexist as Mn^{4+} is desired from the stability perspective. Particularly, CV and XPS results confirm these results. Moreover, the electrode exhibits a quasi-solid-solution reaction during the sodium extraction and insertion. This contribution demonstrates that P2-NNM is a promising cathode electrode for rechargeable long-life sodium-ion batteries.

1. Introduction

Sodium-ion batteries (NIBs) have attracted considerable research attention since 2000s as well as in future which can fulfill the demand of the energy-storage market [1–3]. A lot of materials have been proposed for positive and negative electrodes of NIBs, including transition metal oxides, Prussian blue (PB), carbon based materials, alloy materials, and so on [4–7]. Among them, sodium transition metal oxides ($Na_{1-x}MO_2$, M: transition metal) are considered to be promising candidates as cathode materials. In particular, sodium manganese based layered oxides are a key family of these cathode materials due to the relatively low cost and environmentally friendly nature of the

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manganese [8,9]. The structures of the layered transition metal oxides can be classified into two groups: O3 type and P2 type (refer to different ways of oxygen layer stacking) [1,8,10]. The O3 type is stable when the x value is close to 0 in $Na_{1-x}MO_2$, while in the case of P2 type materials, the structure is stable when Na content is in the range of 0.3–0.7. P2 and O3-type layered materials have been extensively studied with electrochemical storage performances [2,11–14].

O3-type materials have higher reversible capacity but with poor cycling stability because Na^+ migration requires more energy [5,15,16]. On the other hand, P2-type materials seem to be more attractive as for a better structure stability and rate performances [12,17]. Very recently, multiple structure layered transition metal oxides contain both P-type and O-type structures are proposed for cathode materials. Minor O3 was successfully integrated into lithium-substituted P2-majority layered materials ($Na_{0.66}Li_{0.18}Mn_{0.71}Ni_{0.21}Co_{0.08}O_{2+\delta}$) toward a large-capacity approaching 200 mAh g^{-1}, and good rate capability of 134 mAh g^{-1} at 1 C [12]. Li-substituted layered P2/O3 biphasic $Na_{0.67}Mn_{0.55}Ni_{0.25}Ti_{0.2-x}Li_xO_2$ materials were designed for cathode, which can deliver an initial capacity of 158 mAh g^{-1} [13,18]. However, the extraction and insertion of large Na ions with an ionic radius of 1.02 Å could induce the phase transition such as O3-P3 [15] and P2-O2 [19]. As we all know, P2-$Na_{2/3}Ni_{1/3}Mn_{2/3}O_2$ delivers discharge capacity of 173 mAh g^{-1} within the voltage range of 1.5–4.5 V, but with poor cycle performance due to the P2-O2 transition at 4.2 V [20–22]. Moreover, this P2-$Na_{2/3}Ni_{1/3}Mn_{2/3}O_2$ is very stable against water [23]. The P2 phase is maintained in a wide desodiation range up to $Na_{0.46}MO_2$, and further extraction of Na^+ will lead to the P2↔O2 transition due to MO_6 gliding [1,13].

On the basis of above mentioned research, we propose a novel strategy to enhance the electrochemical performances of the P2-structure Mn-rich layered oxide with low nickel content ($Na_{0.67}Ni_{0.25}Mn_{0.75}O_{2+\delta}$, denoted as P2-NNM) as Ni containing layered oxides which exhibit promising Na storage performance such as high capacity and stable cycling performances. In addition, cut-off voltage of 3.9 V was adopted in order to obtain the high electrochemical performance. In this work, it exhibits a reversible capacity of 91.8 mAh g^{-1} at 0.2 C with capacity retention of 94.4 % and provides notable cyclic performance of discharge capacity of 71.5 mAh g^{-1} at 2 C with a capacity retention of 84.2 % after 1000 cycles. Thus, this new synthesized cathode material will undoubtedly contribute to the development of the NIBs and also broaden the design ideas for excellent NIBs electrode materials.

2. Experimental section

2.1. Material synthesis

The prepared layered material (denoted as P2-NNM throughout the manuscript) was synthesized by a solid-state reaction. A stoichiometric ratio of precursors of Na_2CO_3, NiO and Mn_2O_3 were completely mixed in a high energy ball mill for 6 h. The resulting material was then calcined twice at 900 °C for 16 h in air atmosphere with intermediate grinding to obtain object material. The heated powder were then ground and stored in an argon-filled glovebox until use.

The actual molar ratios of metal ions in the layered P2-NNM were analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, thermo ICAP ~ QC).

2.2. Characterization

The lattice structure of the material was characterized by X-ray diffraction (XRD), using a Rigaku diffractrometer with Cu Kα radiation (1.5405 Å) scanning in the 2θ range of 10–90° at a rate of 1.5° min^{-1} and a step size of 0.02°. The crystal structure was refined using Rietveld method. For in situ X-ray diffraction experiment during electrochemical cycling, a special cell was assembled using a beryllium window for X-ray penetration. The in situ cell was charged and discharged at current rate of 0.2 C. The morphology of the as-prepared P2-NNM was observed by FE-SEM (Field Emission Scanning Electron Microscopy, Zeiss, S-3500 N). High-resolution transmission electron microscope (HRTEM) was carried out on a Tecnai G2 F20 S-TWIN (200 KV) transmission electron microscope. The X-ray photoelectron spectroscopy (XPS) spectra were recorded with a spectrometer (Thermo escalab 250XI) having Al Kα radiation ($h\nu$ = 1486.6 eV). All binding energies were corrected using the signal of the carbon at 284.8 eV as an interval standard.

2.3. Electrochemical characterization

The working electrodes used for electrochemical testing were prepared by casting the slurry of the active material (75 wt%), acetylene black (15 wt%) and PVDF binder (10 wt%) on aluminum foil collector. All electrochemical tests were carried out using CR2032 coin cells. The coin cells were assembled with sodium metal as counter electrode, glass fiber as separator, and 1 M $NaPF_6$ in EC:DEC (1:1 in volume) as electrolyte in an argon-filled glove box. The galvanostatic charge/discharge tests were performed by Land instrument (Wuhan, China) at room temperature. Cyclic voltammograms (CV) were performed on a CHI660e electrochemical workstation (ChenHua Instrument Co., China) at a scan rate of 0.1 mV s^{-1}.

3. Results and discussion

The P2-NNM was successfully synthesized via high energy ball milling and the Na/Ni/Mn ratios performed by ICP-AES were determined to be 0.64:0.24:0.72. Fig. 1a shows the powder X-ray diffraction (XRD) pattern and the Rietveld refinement of the resulting material. All the diffraction lines can be indexed to a hexagonal lattice with space group $P63/mmc$, and the lattice parameters are refined to be $a = b$ = 2.8903 (1) Å, c = 11.1639 (1) Å with convergence R_p factor (9.64) and a χ^2 (3.763) using the GSAS + EXPGUI suite (detailed crystallographic data on refined P2-type are listed in Table S1). All of the diffraction peaks in the pattern clearly display the single phase of pure P2-phase structure as there is no peaks of impurities [22].

A schematic structure of the P2-NNM material is presented in Fig. 1b. In this structure, some of Na ions (0.26) is located in the trigonal prism of oxygen-ion (2b) and sharing faces with two MO_6 octahedrons while some of Na ions (0.46) is located at 2d site and combined with two MO_6 octahedrons edge-to-edge (According to refinement result shown in Table S1) [22,24]. Moreover, the d spacing of 5.5803 (6) Å can be deduced from the (002) peak. The large sodium Na slab can reduce the activation energy barrier of ion diffusion and accelerate the diffusion speed of sodium-ion in the crystal, which is beneficial for the high rate performance. Moreover, the structure is relatively stable as more Na ions located in the 2d site as Na2 site is considered to be more stable than the Na1 site according to previous research of P2-Na_xCoO_2 [25,26].

Detailed structure information obtained by High-resolution transmission electron microscope (HRTEM) image and scanning area electron diffraction (SAED) are presented in Fig. 1c and d. TEM images in Fig. 1c clearly show the layered structure of the P2-NNM material. The inset shows the interplanar distances between the neighboring lattice fringes, defined as 2.3 Å, is corresponding to (100) plane of the P2 phase. The bright spots projected along 001 direction in Fig. 1d correspond to a typical reflection originating from P2-structure lattice.

Fig. 2a and b shows the SEM images of the morphology of P2-NNM sample. The sample displays well-formed regular hexagons plate-like morphology with diameters of 1–3 μm and thickness of about 400 nm [22]. Moreover, the micro plate-like particle consisted of lamellar stacking of nanosheets was shown in Fig. 2b marked with green dotted circle, which was in line with published studies [27]. Fig. 2c further confirmed the hexagons morphology of P2-NNM sample. It should be noted that this is the apparent habit plane. Energy dispersive