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A Practical High-Energy Cathode for Sodium Ion Batteries Based on Uniform P2- $\text{Na}_{0.7}\text{CoO}_2$ Microspheres

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Abstract

Layered metal oxides have attracted increasing attention as cathode materials for sodium-ion batteries (SIBs). However, the application of such cathode materials is still hindered by their poor rate capability and cycling stability. Here, a facile self-templated strategy is developed to synthesize uniform P2- $\text{Na}_{0.7}\text{CoO}_2$ microspheres. Due to the unique microsphere structure, the contact area of the active material with electrolyte is minimized. As expected, the P2- $\text{Na}_{0.7}\text{CoO}_2$ microspheres exhibit enhanced electrochemical performance for sodium storage in terms of high reversible capacity (125 mAh g^{-1} at 5 mA g^{-1}), superior rate capability and long cycle life (86% capacity retention over 300 cycles). Importantly, the synthesis method can be easily extended to synthesize other layered metal oxide (P2- $\text{Na}_{0.7}\text{MnO}_2$ and O3- NaFeO_2) microspheres.

Keywords: P2- $\text{Na}_{0.7}\text{CoO}_2$, layered metal oxides, microsphere, cathode, sodium ion batteries

Rapid growth of renewable electric energy from solar, wind and other sources in the global energy markets has spurred the development of low-cost and effective energy storage systems.^[1-4] As lithium-ion batteries (LIBs) expand their territory from portable electronics to electric vehicles, a great concern arises about the widespread availability and rising price of lithium resources.^[5, 6] Therefore, exploration of alternatives to LIBs has been highlighted in recent years and a number of battery systems such as lithium-sulfur,^[7-9] lithium-air^[10-13] and rechargeable sodium-ion batteries (SIBs)^[14-17] have been revisited as possible candidates of post Li-ion technologies. Among them, SIBs have been considered as an ideal choice due to their similar chemical/electrochemical reaction mechanisms to LIBs, low cost and abundant sodium resources.^[16, 18, 19]

SIBs have attracted increasing attention in the past decade and many materials have been explored as electrodes for SIBs. However, due to the larger size of Na^+ ion compared to Li^+ ion, it is a more arduous challenge to explore suitable electrode materials with robust structure for stable reversible Na^+ ion extraction and insertion. As for the development of next-generation LIBs, the development of practical SIBs is also limited by the lack of suitable cathode materials. Among the potential cathode materials, phosphates,^[20-22] ferrocyanides^[23-25] and layered metal oxides^[26-29] have been intensively investigated, but their overall performance is still generally unsatisfactory for practical use of SIBs. Layered metal oxides have been considered as a class of promising cathode materials for SIBs, due to the rich family and various electrochemical active elements.^[14] The layered metal oxides can be catalogued into two main groups: O3 and P2 type structures, where Na^+ ions tend to locate at octahedral and prismatic sites, respectively.^[27] O3 type oxides possess a stable structure with reversible Na^+ ion insertion/deinsertion, but the reversible capacity can hardly exceed 120 mAh g^{-1} . Although P2 type oxides can deliver higher capacity, the cycling stability is usually less satisfactory due to the multi-phases transition during electrochemical reactions.^[30] Up to now, the investigation of layered metal oxides mainly focuses on the adjustment of the active metal center and ratio, determination of

reaction mechanisms and structural analysis. However, very few attention has been paid to the morphological effect on electrochemical performance for cathode materials of SIBs.^[15, 27] It is known that cathode materials with regular morphology and microsize could endow the electrodes with high capacity, long-term cyclability and high energy density for SIBs.^[31-34] For example, Hwang et al. have reported an O3 type layered compound with a radially aligned hierarchical columnar structure in spherical particles showing high specific capacity, good capacity retention and rate capability for SIBs.^[32] Zhang et al. have synthesized graphene decorated $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ microspheres, which enable high rate capability with long cycle life for sodium storage.^[31] These results indicate that cathode materials with microsphere structure indeed lead to enhanced sodium storage performance. On the other hand, microspheres can also improve the volumetric energy density of the electrodes and more importantly can be easily processed to obtain uniform electrode films, which are very favorable for practical batteries.

Herein we present a facile strategy to synthesize uniform $\text{P2-Na}_{0.7}\text{CoO}_2$ microspheres through a two-step self-templating method, as schematically illustrated in **Figure 1**. First, CoCO_3 microspheres synthesized via a modified solvothermal method are converted to Co_3O_4 microspheres by calcination in air. Then, the Co_3O_4 microspheres react with an appropriate amount of Na_2CO_3 under elevated temperature to obtain $\text{P2-Na}_{0.7}\text{CoO}_2$ microspheres. Although high calcination temperature is used during the synthesis process, the $\text{P2-Na}_{0.7}\text{CoO}_2$ particles can still maintain the spherical morphology. Impressively, the resultant $\text{P2-Na}_{0.7}\text{CoO}_2$ microspheres exhibit excellent sodium storage properties with high reversible capacity, superior rate capability and cycling stability. The synthesis method has been also successfully extended to synthesize $\text{P2-Na}_{0.7}\text{MnO}_2$ and O3-NaFeO_2 microspheres.

The panoramic field-emission scanning electron microscope (FESEM) image (Figure S1a, Supporting Information (SI)) shows that the as-synthesized CoCO_3 precursor consists of microspheres with an average diameter of about 5 μm . The magnified FESEM image (**Figure 2a**) reveals the rough

surface of the CoCO_3 microspheres. After being annealed in air, the CoCO_3 precursor microspheres are transformed into Co_3O_4 microspheres, as confirmed by FESEM (Figure S1b, SI) and powder X-ray diffraction (XRD) measurements (Figure S1c, SI). Compared with the CoCO_3 precursor, no obvious changes in structure and size can be observed for the Co_3O_4 microspheres (Figure 2b). After the second step calcination with Na_2CO_3 at elevated temperature, phase-pure $\text{Na}_{0.7}\text{CoO}_2$ with good crystallinity is obtained (Figure 2c). All the diffraction peaks of the XRD pattern can be indexed to a hexagonal P2-structure $\text{Na}_{0.7}\text{CoO}_2$ with P63/mmc space group (JCPDS card No. 87-0274).^[35] As demonstrated in the diagrammatic presentation (inset of Figure 2c), the P2 type layered structure exhibits an AB BA oxygen packing with Co ions in the octahedral sites and Na ions in the prismatic sites.^[36] The large-scale FESEM image of the product shows that the particles exhibit a morphology of well-maintained microspheres (Figure S2, SI). This sample of as-obtained $\text{Na}_{0.7}\text{CoO}_2$ microspheres is denoted as *s*-NCO. Clearly, the surface structure of *s*-NCO (Figure 2d,e) is different from that of the CoCO_3 and Co_3O_4 microspheres, which should originate from the recrystallization and crystal growth during the high temperature calcination. The high-resolution transmission electron microscope (HRTEM) image (Figure 2f) shows a clear lattice with a spacing of 0.541 nm, which matches well with the (002) plane of P2- $\text{Na}_{0.7}\text{CoO}_2$. The TEM image (**Figure 3a**) demonstrates that the surface of the microsphere is rather rough. The corresponding energy-dispersive X-ray spectroscopy (EDS) analysis (inset in Figure 3a) shows that the microsphere is composed of Na, Co and O elements with a Na/Co atomic ratio of ca. 0.71, further confirming the chemical composition of $\text{Na}_{0.7}\text{CoO}_2$. Elemental mapping of a part of the microsphere (Figure 3b-d) reveals that Na, Co and O elements are uniformly distributed in the particle. In addition, to understand the effect of morphology on the electrochemical performance of P2- $\text{Na}_{0.7}\text{CoO}_2$ material, P2- $\text{Na}_{0.7}\text{CoO}_2$ microparticles with irregular morphology (donated as *i*-NCO) are also synthesized and evaluated as cathode materials for SIBs (Figure S3, SI).

The sodium storage properties of *s*-NCO are first evaluated by cyclic voltammetry (CV). **Figure 4a** shows a typical CV curve of *s*-NCO at a scan rate of 0.1 mV s⁻¹ in the voltage range of 2.0 - 3.8 V (vs. Na/Na⁺). Similar to most P2 type oxides, the *s*-NCO cathode exhibits multiple pairs of redox peaks, indicating a series of complex phase transition reactions.^[27, 36, 37] The complicated phase transition comes from the changeable states of Na⁺/vacancy ordering and MO₂ layer gliding during Na⁺ ions insertion/deinsertion.^[36, 38] Figure 4b shows the representative charge/discharge voltage profiles of *s*-NCO between 2.0 and 3.8 V (vs. Na/Na⁺) at a current rate of 0.04 C (5 mA g⁻¹, 1 C = 125 mA g⁻¹). The discharge profiles exhibit multiple potential drops separated by either potential plateaus or sloping curves in good agreement with the CV result and reported literatures.^[36, 38-40] The voltage plateaus indicate the existence of biphasic domains which are the characteristic of first-order transitions during Na⁺ ions insertion/deinsertion. The sloping curves are related to the solid-solution behavior and potential drops are the signature of single-phase in a narrow sodium content range.^[36] Importantly, the *s*-NCO cathode can deliver a reversible discharge capacity of 125 mAh g⁻¹, which is higher than that of most of the P2-Na_{0.7}CoO₂ electrodes reported previously.^[35, 40-42] The improved specific capacity may result from the high crystallinity and phase purity of the Na_{0.7}CoO₂ microspheres.^[43, 44] Moreover, the *s*-NCO cathode offers an average discharge potential of 2.9 V, possessing a high energy density of 363 Wh kg⁻¹.

The rate performance of the *s*-NCO cathode is investigated by charging and discharging at various current rates ranging from 0.04 to 16 C (Figure 4c). As can be seen, the electrode can deliver an average reversible capacity of 125, 121, 119, 114, 112, 109, 106, 98 and 84 mAh g⁻¹ at 0.04, 0.08, 0.16, 0.4, 0.8, 0.16, 2.4, 4 and 8 C, respectively. Even at a high rate of 16 C (charge/discharge within about 2 min), a remarkable reversible and stable capacity of 64 mAh g⁻¹ can still be preserved. When the current density is reduced back to 0.16 C, a reversible capacity of 117 mAh g⁻¹ can be recovered, revealing the excellent cycling reversibility of *s*-NCO. Also shown in Figure 4c, the discharge capacity

of the *i*-NCO electrode fades rapidly as the current rate rises and the capacity drops to almost zero at the current rate of 4 C. The excellent rate capability of the *s*-NCO is also verified by the charge/discharge voltage profiles at various current rates (Figure 4d).

Moreover, the *s*-NCO electrode also exhibits excellent cycling stability. Specifically, a capacity retention of 86% over 300 cycles at a current rate of 0.4 C is observed (Figure 4e), corresponding to an average capacity loss of 0.046% per cycle. The Coulombic efficiency of the electrode remains around 100% during cycling. For comparison, the capacity of the *i*-NCO cathode drops rapidly with cycling and a capacity of only 40 mAh g⁻¹ is maintained after 200 cycles, corresponding to a low capacity retention of 46% (Figure 4e). Impressively, the *s*-NCO cathode also exhibits excellent cycling performance at other current rates (Figure S4, SI), retaining more than 88% of the initial capacity after 200 cycles (Table S1, SI). To the best of our knowledge, such superior rate capability and long cycling stability have not been reported before for P2-Na_{0.7}CoO₂ cathodes. The superior sodium storage properties of *s*-NCO may be attributed to its high crystallinity and uniform microsphere structure. The microsphere structure can effectively buffer the mechanical stress caused by Na⁺ ions insertion/deinsertion. It can also minimize the contact area of the electroactive materials with electrolyte, thus reducing unwanted side reactions and active materials dissolution and leading to high Coulombic efficiency.^[32] It is also worth mentioning that the measured tap density of *s*-NCO (1.8 g cm⁻³) is higher than that of *i*-NCO (1.45 g cm⁻³), which is expected to improve the volumetric energy density of SIBs.

Importantly, this self-templated synthesis method is quite general and can be also applied to prepare other layered metal oxide microspheres, such as P2-Na_{0.7}MnO₂ and O3-NaFeO₂ microspheres. All the Mn/Fe carbonates, Mn/Fe oxides, and as-derived Mn/Fe layered oxides show a similar microsphere structure (Figure S5, SI). The corresponding XRD patterns (Figure S6a,b, SI) confirm the successful synthesis of the P2-Na_{0.7}MnO₂ and O3-NaFeO₂ phases from corresponding metal carbonate

precursors. EDX analysis (Figure S6c,d, SI) confirms the elemental compositions of the P2-Na_{0.7}MnO₂ and O3-NaFeO₂ microspheres. The as-obtained P2-Na_{0.7}MnO₂ and O3-NaFeO₂ microspheres also exhibit enhanced reversible capacity (Figure S7, SI) compared to the materials in previous studies.^[45, 46] In addition, it can be seen that the P2-Na_{0.7}MnO₂ and O3-NaFeO₂ electrodes exhibit different charge/discharge profiles with the P2-Na_{0.7}CoO₂ electrode. This can be attributed to the different electron configurations of the active elements (Co, Mn, Fe), leading to different stable intermediates with complex changeable states of Na⁺/vacancy ordering, charge ordering and MO₂ layer gliding during Na⁺ ions insertion/deinsertion.

In summary, we have successfully developed a facile and self-templated method to synthesize Na_xMO₂ (M= Co, Mn, Fe) layered metal oxide microspheres. This method first involves the conversion of metal carbonates to metal oxide microspheres. Then the metal oxides are converted to Na_xMO₂ microspheres after reaction with Na₂CO₃ at elevated temperature. As an example, the P2-Na_{0.7}CoO₂ microspheres are thoroughly evaluated as a cathode material for sodium ion batteries (SIBs). Benefiting from their structural advantages, the P2-Na_{0.7}CoO₂ microspheres exhibit high specific capacity (125 mAh g⁻¹ at 5 mA g⁻¹), excellent rate capability and long-term cycling stability (86% retention in capacity over 300 cycles). This work might offer some inspiration for development of advanced cathode materials for practical deployment of SIBs.

Acknowledgements

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Figures and Captions

Figure 1. Schematic illustration of the two-step synthesis of P2-Na_{0.7}CoO₂ microspheres.

Figure 2. FESEM images of (a) CoCO₃ and (b) Co₃O₄ microspheres. (c) XRD pattern of P2-Na_{0.7}CoO₂ microspheres; inset is the corresponding crystal structure of P2-Na_{0.7}CoO₂. (d,e) FESEM images and (f) HRTEM image of P2-Na_{0.7}CoO₂ microspheres.

Figure 3. (a) Typical TEM image of P2-Na_{0.7}CoO₂ microspheres and corresponding elemental mapping of (b) sodium, (c) cobalt, and (d) oxygen elements. The inset in (a) is the EDX spectrum of P2-Na_{0.7}CoO₂ microspheres.

Figure 4. (a) A typical cyclic voltammogram of the *s*-NCO electrode at a scan rate of 0.1 mV s⁻¹. (b) Typical charge/discharge voltage profiles of the *s*-NCO electrode at a current rate of 0.04 C. (c) Rate performance of *s*-NCO and *i*-NCO, and (d) the corresponding charge-discharge voltage profiles of the *s*-NCO electrode at various current rates. (e) Cycling performance of *s*-NCO and *i*-NCO at a current rate of 0.4 C and the corresponding Coulombic efficiency of *s*-NCO. (Note: 1C = 125 mA g⁻¹)

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Layered metal oxide Na_xMO_2 ($\text{M} = \text{Co}, \text{Mn}, \text{Fe}$) microspheres have been synthesized via a facile self-templated method as advanced cathode materials for sodium ion batteries. As an example, the $\text{P2-Na}_{0.7}\text{CoO}_2$ microspheres exhibit greatly enhanced electrochemical sodium storage properties with high reversible capacity (125 mAh g^{-1} at 5 mA g^{-1}), superior rate capability and long-term cycle life (86% capacity retention over 300 cycles).