Realizing Three-Electron Redox Reactions in NASICON-Structured Na$_3$MnTi(PO$_4$)$_3$ for Sodium-Ion Batteries

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Developing multielectron reaction electrode materials is essential for achieving high specific capacity and high energy density in secondary batteries; however, it remains a great challenge. Herein, Na$_3$MnTi(PO$_4$)$_3$/C hollow microspheres with an open and stable NASICON framework are synthesized by a spray-drying-assisted process. When applied as a cathode material for sodium-ion batteries, the resultant Na$_3$MnTi(PO$_4$)$_3$/C microspheres demonstrate fully reversible three-electron redox reactions, corresponding to the Ti$^{3+/4+}$ ($\approx$2.1 V), Mn$^{2+/3+}$ ($\approx$3.5 V), and Mn$^{3+/4+}$ ($\approx$4.0 V vs Na$^+/$Na) redox couples. In situ X-ray diffraction results reveal that both solid-solution and two-phase electrochemical reactions are involved in the sodiation/desodiation processes. The high specific capacity (160 mAh g$^{-1}$ at 0.2 C), outstanding cyclability ($\approx$92% capacity retention after 500 cycles at 2 C), and the facile synthesis make the Na$_3$MnTi(PO$_4$)$_3$/C a prospective cathode material for sodium-ion batteries.

The low cost and high abundance of sodium resources make sodium-ion batteries (SIBs) one of the most prospective choices for stationary energy storage.[11–10] However, the insertion/extraction of Na$^+$ with a radius of 95 pm is usually accompanied by a large volume change, making the development of stable SIB electrode materials a great challenge.[11–14] In addition, the solid-state diffusion of Na$^+$ with large radius in electrode materials usually suffers from sluggish kinetics.

NASICON-structured Na$_3$MnTi(PO$_4$)$_3$/C hollow microspheres by a spray-drying-assisted method. Interestingly, the resultant Na$_3$MnTi(PO$_4$)$_3$/C demonstrated fully reversible three-electron redox reactions at 2.1, 3.5, and 4.0 V vs Na$^+/Na$, corresponding to the Ti$^{3+/4+}$, Mn$^{2+/3+}$, and Mn$^{3+/4+}$ redox couples, respectively. The reversible three-electron redox reactions endow the Na$_3$MnTi(PO$_4$)$_3$/C with a high specific capacity of 160 mAh g$^{-1}$ at 0.2 C. The stable and open NASICON framework ensures the superior cycling stability of Na$_3$MnTi(PO$_4$)$_3$/C (90% capacity retention after 500 cycles at 2 C).

Herein, we produced Na$_3$MnTi(PO$_4$)$_3$/C (NMTP/C) hollow microspheres by a spray-drying-assisted method. Interestingly, the resultant NMTP/C demonstrates fully reversible three-electron redox reactions at 2.1, 3.5, and 4.0 V vs Na$^+/Na$, corresponding to the Ti$^{3+/4+}$, Mn$^{2+/3+}$, and Mn$^{3+/4+}$ redox couples, respectively. The reversible three-electron redox reactions endow the NMTP/C with a high specific capacity of 160 mAh g$^{-1}$ at 0.2 C. The stable and open NASICON framework ensures the superior cycling stability of NMTP/C (90% capacity retention after 500 cycles at 2 C).
data, and the unit cell parameters obtained from the structural refinement are $a = 8.8343$ Å and $c = 21.6654$ Å (Table S1, Supporting Information). The intense and sharp diffraction peaks indicate that the sample has a high crystallinity. The NMTP is constructed by isolated TiO$_6$ and MnO$_6$ octahedra sharing all the corners with PO$_4$ tetrahedra (Figure 1b,c). The polyanionic phosphate framework endows the Na$_3$MnTi(PO$_4$)$_3$ excellent structural stability and intrinsic safety.

Thermogravimetric analysis (TGA) is carried out in the air to determine the carbon content of the sample (Figure 1d). The total weight loss for NMTP/C-650 is 8.82 wt%. A slight mass increase happens at ≈520 °C, which is due to the oxidation of low-valence-state metal species. Considering the oxidation of the metal species during the combustion of carbon, the actual carbon contents of NMTP/C-650 should be slightly higher than the total weight loss (8.82 wt%). From the CHNS analysis, the carbon content of NMTP/C-650 is 8.85 wt%, which is consistent with the TGA result (Table S2, Supporting Information). Raman spectrum of NMTP/C-650 shows two characteristic peaks for carbon at 1350 cm$^{-1}$ (D-band) and 1594 cm$^{-1}$ (G-band) (Figure S3, Supporting Information). The $I_D/I_G$ ratio of NMTP/C-650 is 0.90, indicating that the carbon is partially graphitized.

The surface valence states of Mn and Ti are investigated by X-ray photoelectron spectroscopy (XPS) (Figure 1e,f). According to a recent publication, the Mn and Ti exist as Mn$^{2+}$ and Ti$^{4+}$ in the NASICON-structured Na$_3$MnTi(PO$_4$)$_3$. Interestingly, we find that a non-negligible fraction of Mn$^{3+}$ ([Mn$^{3+}$]/([Mn$^{2+}$] + [Mn$^{3+}$]) = 52.01%) exists in the sample. Accompanying the existence of Mn$^{3+}$, a significant fraction of Ti$^{3+}$ ([Ti$^{3+}$]/([Ti$^{4+}$] + [Ti$^{3+}$]) = 51.67%) is also observed.

Figure 2 shows the detailed microstructure of as-synthesized NMTP/C-650. The NMTP/C-650 is composed of microspheres with diameters ranging from 0.2 to 5 µm (Figure 2a,b). Transmission electron microscopy (TEM) image (Figure 2c) demonstrates that the NMTP/C-650 microspheres possess hollow interiors. Such a hollow structure with thin shell thickness would short the Na$^+$ diffusion distance when applied in SIBs. The high-resolution TEM (HRTEM) image shows the interplanar spacings of 0.44 nm, which matches well with the (104) planes of NMTP (Figure 2d). The energy-dispersive spectroscopy (EDS) mappings (Figure 2f) demonstrate that the Mn, Ti, C, Na, O, and P are homogeneously distributed in the NMTP/C-650 composite hollow spheres. For comparison, NMTP/C-600 and NMTP/C-700 (Figures S1–S8, Supporting Information) are also prepared by varying the annealing temperature.

To study the theoretical sodium storage capacity of NMTP/C-650, galvanostatic intermittent titration technique (GITT) measurement is conducted (Figure 3a). The cell is charged to 4.2 V at 50 mA g$^{-1}$ before GITT test. The NMTP/C-650 delivers a discharge capacity of 173 mAh g$^{-1}$ in GITT test, corresponding to ≈2.95 Na$^+$ intercalated into NMTP per formula (see Supporting Information). The discharge plateaus are located at 4.01, 3.52, and 2.12 V, corresponding to the reduction of Mn$^{4+}$ to Mn$^{3+}$, Mn$^{3+}$ to Mn$^{2+}$, and Ti$^{4+}$ to Ti$^{3+}$, respectively.

Cyclic voltammetry (CV) is also employed to study the sodium storage performance of NMTP/C-650. Three pairs of redox peaks located at 2.21/2.05, 3.75/3.44, and 4.15/3.94 V can be observed in the first cycle (Figure 3b), corresponding to the redox couples of Ti$^{3+}$/4+, Mn$^{2+}$/3+, and Mn$^{3+}$/4+, respectively. An additional pair of redox peaks with weak intensities can be observed at 2.43/2.33 V in the subsequent cycles. Unfortunately, these peaks cannot be assigned to any known redox couples at this stage.
Figure 3c presents the charge/discharge curves of NMTP/C-650 under various C-rates. Obvious plateaus can be discerned from the charge/discharge curves, which is consistent with the CV results. The NMTP/C-650 delivers discharge capacities of 160, 150, 141, and 129 mAh g\(^{-1}\) at 0.2, 0.5, 1, and 2 C, respectively (Figure 3c). In addition, the discharge capacity of NMTP/C-650 can be fully recovered when the C-rate is reduced back to 0.2 C after the high-rate test (Figure 3d). Obviously, the NMTP/C-650 outperforms the NMTP/C-600 and NMTP/C-700 in terms of specific discharge capacity and rate capability (Figure 3d; Figures S9 and S10, Supporting Information). When cycled at 2 C, the NMTP/C-650 exhibits a high discharge capacity of 119 mAh g\(^{-1}\), and \(\approx 92\%\) capacity retention can be observed after 500 cycles (Figure 3e,f). Under the same conditions, the NMTP/C-600 and NMTP/C-700 exhibit much lower discharge capacities and capacity retentions.

**Figure 2.** a,b) SEM, c) TEM, and d) HRTEM images of NMTP/C-650; e) HAADF-STEM image of NMTP/C-650 and f) the corresponding elemental mappings of manganese (green), titanium (orange), carbon (yellow), sodium (red), oxygen (purple), and phosphorus (blue).

**Figure 3.** a) The GITT curve of NMTP/C-650 at a current density of 13.3 mA g\(^{-1}\) in a discharged process. b) CV profiles of NMTP/C-650 at a scan rate of 0.1 mV s\(^{-1}\) in the electrochemical window of 1.5–4.2 V vs Na\(^+\)/Na. c) Charge/discharge curves of NMTP/C-650 at different rates. d) Rate performances of NMTP/C-600, NMTP/C-650, and NMTP/C-700. e) Representative charge/discharge curves of NMTP/C-650 at 2 C. f) Cycling performances of NMTP/C-600, NMTP/C-650, and NMTP/C-700 at 2 C.
To the best of our knowledge, the sodium storage performances of NMTP/C-650 are superior to most of the recently reported NASICON-structured SIB cathode materials (Table S3, Supporting Information). Electrochemical impedance spectroscopy (EIS) was used to study the electron/ion diffusion dynamics of the NMTP/C (Figure S11, Supporting Information). The equivalent electrical circuit for fitting the impedance data is shown in the inset of Figure S11 in the Supporting Information and the fitting results are summarized in Table S4 in the Supporting Information. The NMTP/C-650 manifests the lowest charge transfer resistance and the highest Na\(^{+}\) diffusion coefficient, which is responsible for its superior sodium storage performances.

To elucidate the structural change of NMTP/C-650 during the sodiation/desodiation processes, in situ XRD test is performed. In general, the diffraction peaks located at 20–21°, 23–24.5°, 27.5–29°, 30–33°, and 34–36° undergo a series of obvious and reversible changes during charge/discharge, demonstrating the highly reversible electrochemical reactions (Figure 4a). Specifically, the (211) (at ≈30.5°) and (116) (at ≈34.5°) diffractions shift rightward and then disappear during the desodiation process. Both peaks appear at the later stage of sodiation process and then shift leftward. The reversible peak shift indicates a solid-solution reaction, while the disappearance/appearance of diffraction peaks suggests a two-phase reaction. That is to say, both solid-solution and two-phase reactions are involved in the sodium storage process of NMTP/C-650. Based on the electrochemical characterizations, the structure evolution of NMTP during the sodium intercalation/deintercalation processes is proposed (Figure 4b). During the first desodiation process, two Na\(^{+}\) deintercalate from NMTP. Upon subsequent sodiation/desodiation, three Na\(^{+}\) reversibly intercalate into and deintercalate from the NMTP framework.

Na-ion full cells are also assembled based on the NMTP/C-650 cathode and a soft carbon anode (Figures S12–S14, Supporting Information). The full cell displays a specific capacity of 139 mAh g\(^{-1}\) (based on the mass of NMTP/C-650) at 0.5 C, retaining 117 mAh g\(^{-1}\) after 50 cycles (Figure S15, Supporting Information). The results demonstrate the practical applicability of NMTP/C-650 in sodium storage.

In summary, NMTP/C microspheres are produced by a spray-drying-assisted method. Unlike most NASICON-structured cathode materials, the NMTP/C demonstrates fully reversible three-electron redox reactions at 2.1, 3.5, and 4.0 V vs Na\(^+\)/Na, corresponding to the Ti\(^{3+}/4+\), Mn\(^{2+}/3+\), and Mn\(^{3+}/4+\) redox couples, respectively. The reversible three-electron redox reactions endow the NMTP/C a high specific capacity of 160 mAh g\(^{-1}\) at

![Figure 4.](image)

**Figure 4.** a) In situ XRD patterns of the NMTP/C-650 collected during galvanostatic charge/discharge at 50 mA g\(^{-1}\). b) Schematic illustration showing 2 Na\(^{+}\) deintercalating from Na\(_3\)MnTi(PO\(_4\))\(_3\) during the first charge process, and 3 Na\(^{+}\) intercalating into/deintercalating from the framework upon subsequent electrochemical discharge/charge processes.
0.2 C, and the highly stable NASICON framework ensures the
superior cycling stability of NMTP/C (≈92% capacity retention
after 500 cycles at 2 C). In situ XRD characterization reveals
that the sodium storage in NMTP/C involves both solid-
solution and two-phase reactions. This work sheds light on the
rational design of NASICON-structured cathode materials for
realizing multielectron redox reactions per transition metal.

**Experimental Section**

**Materials Synthesis:** The NMTP/C-650 microspheres were synthesized
by a facile spray-drying method with postannealing. In a typical
synthesis, NaH₂PO₄ (15 mmol), Mn(CH₃COO)₂·4H₂O (5 mmol),
dihydroxybis(ammonium lactato)titanium(IV) (C₁₂H₁₈N₂O₈Ti, 5 mmol),
and citric acid (10 mmol) were dissolved in deionized water and stirred at
room temperature for 30 min. Next, the solution was spray-dried using a
BUCHI Mini Spray Dryer B-290 to prepare the NMTP/C precursor.
The detailed conditions during spray drying were listed as follows: inlet
temperature 220 °C, aspirator rate 90%, rotameter setting 40 mm,
and pump rate 5%. The NMTP/C-650 was obtained after annealing
the precursor at 650 °C for 4 h in Ar. NMTP/C-600 and NMTP/C-700 were prepared by the same procedure, except the annealing temperatures
were set at 600 and 700 °C, respectively.

**Structure Characterization:** XRD measurements were performed on a
Bruker D8 Discover X-ray diffractometer with a nonmonochromated Co Kα X-ray source (λ = 1.5406 Å). TGA was performed on an STA-449C
thermobalance in the air with a temperature ramp of 5 °C min⁻¹. The CHNS
elemental analysis was performed with an elemental analyzer (Vario EL
cube, Elementar Analysensysteme, Germany). XPS analysis was performed
using a JEOL JEM-2100F STEM/EDS microscope working at 200 kV.

**Electrochemical Characterization:** The electrochemical properties were performed with 2016 coin-type cells in an Ar-filled glove box. The
cathode containing active material (60 wt%), acetylene black (30 wt%), and polytetrafluoroethylene (10 wt%) was cut into
1 cm² and a thickness of

**Supporting Information**

Supporting Information is available from the Wiley Online Library or
from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords
cathode materials, Na₃MnTi(PO₄)₃, NASICON structure, sodium-ion
batteries, three-electron redox reactions