Encapsulation of Na$_4$MnV(PO$_4$)$_3$ in robust dual-carbon framework rendering high-energy, durable sodium storage

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Abstract

Na$_4$MnV(PO$_4$)$_3$ (NMVP) is a green, cheap, and high-energy cathode material for sodium-ion batteries. However, the low electrical conductivity severely limits its sodium storage performance. Herein, we report the spray-drying synthesis of robust and highly conductive reduced graphene oxide/amorphous carbon framework encapsulated NMVP (NMVP@rGO/AC) composite microspheres. The unique dual-carbon encapsulation architecture enables the NMVP@rGO/AC a high specific capacity (100 mAh g$^{-1}$ at 100 mA g$^{-1}$) with durable cyclability (capacity retention of 77.5% for 500 cycles). In situ XRD measurements reveal the reversible extraction/insertion of Na$^+$ via unique solid-solution and two-phase reactions during de-sodiation/sodiation processes. This work provides a versatile platform for the construction of rGO/AC dual-carbon encapsulated active materials for electrochemical energy storage.

1. Introduction

Sodium-ion batteries (SIBs) have attracted increasing research interest due to a number of advantages, such as the abundant resources, evenly geographical distribution, and low cost of Na[1–4]. They have been identified as a promising alternative to lithium-ion batteries for large scale energy storage[5]. However, the large ionic radius and sluggish diffusion kinetics of Na$^+$ make it difficult to develop suitable host materials with reversible and stable sodiation and de-sodiation behaviors[6, 7]. The cathode materials represent a key component affecting the performance of SIBs. The cathode materials for SIBs can be generally categorized to layered transition metal oxides[8–12], Prussian blue analogues[13–15], and polyanionic materials[16–18]. Among these materials, the NASICON (Na super ionic conductor) structured compounds are especially appealing due to their extremely stable structure as well as fast ion conductance[3, 19].

The NASICON-type Na$_5$V$_2$(PO$_4$)$_3$ represents a well-known SIB cathode material. It has an open three-dimensional (3D) structure composed of corner-sharing [VO$_6$] octahedra and [PO$_4$] tetrahedra, which produces large and fast Na$^+$ diffusion channels[20]. The Na$_5$V$_2$(PO$_4$)$_3$ exhibits a flat plateau at ~3.3 V versus Na$^+$/Na, which is associated with the V$^{4+}$/V$^{3+}$ redox couple[21]. Zhou et al substituted half of the V in Na$_5$V$_2$(PO$_4$)$_3$ with Mn, an element with lower cost and higher abundance, and obtained Na$_5$Mn$_2$V(PO$_4$)$_3$. The obtained Na$_5$Mn$_2$V(PO$_4$)$_3$/C exhibits two discharge plateaus at 3.3 and 3.6 V, corresponding to the V$^{4+}$/V$^{3+}$ and Mn$^{2+}$/Mn$^{3+}$, respectively[22]. When compared to Na$_5$V$_2$(PO$_4$)$_3$, the Na$_5$Mn$_2$V(PO$_4$)$_3$ demonstrates significantly enhanced theoretical energy density (383 Wh kg$^{-1}$ and 1233 Wh l$^{-1}$) owing to its high discharge plateaus. Just like other NASICON compounds, the Na$_5$Mn$_2$V(PO$_4$)$_3$ possesses poor electrical conductivity, which limits its Na storage performances[23]. To improve the electrical conductivity, compositing with
carbonaceous materials is an effective method [24–27]. Zhang and Jiao et al constructed a graphene aerogel supported Na$_4$MnV(PO$_4$)$_3$ with excellent rate capability and cyclability [28]. However, it is relatively difficult for aerogel-based materials to achieve space-efficient packing. From this standpoint, microspherical Na$_4$MnV(PO$_4$)$_3$/carbon based composites with high tap density are highly desirable.

Herein, we report the spray-drying synthesis of dual-carbon encapsulated Na$_4$MnV(PO$_4$)$_3$ microspheres (denoted as NMVP@rGO/AC). The NMVP nanoparticles are encapsulated in a robust, porous, and highly conductive reduced graphene oxide/amorphous carbon (rGO/AC) framework. Benefited from the open NASICON framework, porous structure, robust and highly conductive rGO/AC matrix as well as the nanoparticulate feature of NMVP, the resultant NMVP@rGO/AC demonstrates a high Na storage capacity (100 mAh g$^{-1}$ at 100 mA g$^{-1}$) and durable cyclability (77.5% capacity retention over 500 cycles at 1000 mA g$^{-1}$).

2. Experimental section

2.1. Materials synthesis

First, 10 mmol Na$_2$HPO$_4$·12H$_2$O, 5 mmol NH$_4$VO$_3$, and 5 mmol NH$_4$H$_2$PO$_4$ were dispersed into 150 ml deionized water by stirring. 5 mmol Mn(CH$_3$COO)$_2$·4H$_2$O was added into the suspension to obtain a yellow precipitate. Then, 10 mmol citric acid was added. After the solution became transparent, a well dispersed graphene oxide (GO) solution (5 mg ml$^{-1}$, 29.3 ml) was added. The slurry was spray-dried to form a microspherical precursor. The precursor was sintered at 750 °C for 6h in Ar to obtain the NMVP@rGO/AC microspheres. For comparison, NMVP@AC microspheres were also synthesized using the same procedure except no GO was introduced. To obtain the rGO/AC framework, the NMVP@rGO/AC (0.05 g) was added into 20 ml 4.0 M HCl with vigorous stirring for 12 h, centrifuged, washed with water and ethanol for three times.

2.2. Characterization

X-ray diffraction (XRD) measurements were performed on a Bruker D8 Advance x-ray diffractometer equipped with a Cu Kα x-ray source ($\lambda = 1.5418$ Å). Scanning electron microscopy (SEM) images were obtained using JEOL-7100F microscope. Transmission electron microscopic (TEM) and high-resolution TEM (HRTEM) images were collected using a JEOL JEM-2100F STEM/EDES microscope. Raman spectra were recorded using a Renishaw INVIA micro-Raman spectroscopy system. Brunauer–Emmett–Teller (BET) surface areas were measured using a Tristar II 3020 instrument by N$_2$ sorption at 77 K. Thermogravimetric analysis (TGA) was performed using a Netzsch STA 449C simultaneous analyzer. X-ray photoelectron spectroscopy (XPS) analysis was performed using a VG Multilab 2000.

2.3. Electrochemical measurements

The electrochemical performance was tested by assembling CR 2016 cells in a Ar-filled glove box. Na foil was used as both the counter and reference electrodes, 1.0 M NaClO$_4$ in propylene carbonate (PC) with 5% fluoroethylene carbonate (FEC) was used as the electrolyte. The cathodes were prepared by casting the slurry containing 70 wt% of active material, 20 wt% of acetylene black, and 10 wt% of polyvinylidene fluoride (PVDF) in N-methyl-2-pyrrolidone (NMP) onto aluminum foil and dried overnight at 70 °C in a vacuum oven. The mass loading of active materials was approximately 1.0–1.2 mg cm$^{-2}$. Galvanostatic charge/discharge measurements were performed with a multichannel battery testing system (LAND CT2001A) in the potential range of 2.5–3.8 V. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were conducted on electrochemical workstations (CHI600E and Autolab PGSTAT 302N).

3. Results and discussion

The synthesis of NMVP@rGO/AC microspheres are realized by a simple yet scalable spray-drying method (figure 1). First, a precursor suspension containing Na$_2$HPO$_4$, NH$_4$H$_2$PO$_4$, NH$_4$VO$_3$, Mn(CH$_3$COO)$_2$, C$_6$H$_8$O$_7$, and GO are spray-dried to obtain the intermediate microspheres. Among the precursors, the citric acid (C$_6$H$_8$O$_7$·H$_2$O) acts as both the carbon source and reductant for reducing V(III) to V(II). The intermediate is then annealed in Ar to obtain the NMVP@rGO/AC during which the citric acid and acetate ions are converted into amorphous carbon and the GO is reduced to rGO.

The morphological features of NMVP@rGO/AC are characterized by SEM and TEM. The NMVP@rGO/AC (figures 2(a), (b)) displays a well-defined morphological microsphere with sizes ranging from 0.5 to 2 μm. Such microspheres are highly desirable owing to their ability to achieve space-efficient packing in electrodes, which is beneficial for the volumetric energy density of batteries. The surface of NMVP@rGO/AC is relatively rough, indicating the microsphere may actually build up with primary nanoparticles. The TEM images of NMVP@rGO/AC (figures 2(c), (d)) reveal that each microsphere contains a solid nanoparticulate core (with
darker contrast) and a well-defined rGO/C shell (with lighter contrast). HRTEM of the NMVP@rGO/AC (figure 2(e)) shows clear lattice fringes of 0.38 nm, corresponding to the (113) interplanar distance of NASICON structured NMVP [29]. The nanoparticulate feature of NMVP, which would reduce the ion diffusion distance and render high rate capability, can be clearly confirmed from the high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image (figure 2(f)). The corresponding elemental mappings (figure 2(g)) show that the carbon signal overlaps with those of Na, Mn, V, O, and P. The homogeneous distribution of C throughout the entire microsphere suggests that the rGO/AC exist not only on the shell of the microsphere but also on the surfaces of the NMVP primary nanoparticles. This deduction is experimentally validated by etching the NMVP@rGO/AC microspheres with sufficient HCl (4.0 M). The etching of NMVP@rGO/AC with HCl leaves behind a highly porous 3D rGO/AC framework (figure S1 is available online at stacks.iop.org/JENERGY/2/025003/mmedia), rather than a hollow and thin rGO/AC shell. Such a 3D rGO/AC scaffold is highly favorable for enhancing the electrical conductivity of NMVP [30, 31]. The etching experiment also demonstrates the robustness of the rGO/AC dual-carbon framework.

As a control, NMVP@AC is also synthesized by a similar spray-drying process except that no GO is introduced during the synthesis. Just like the NMVP@rGO/AC, the NMVP@AC is also composed of microspheres (figure S2, supporting information) with uneven size distribution and a carbon shell can be clearly

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**Figure 1.** Schematic illustration for the spray-drying synthesis of NMVP@rGO/AC.

**Figure 2.** (a), (b) SEM, (c), (d) TEM, (e) HRTEM, (f) HAADF-STEM images and (g) EDS elemental mappings of NMVP@rGO/AC.
observed on the surface of each NMVP@AC microsphere. By etching the NMVP@AC with HCl, a highly crumpled, 3D porous carbon framework is left (figure S3, supporting information).

The NMVP@rGO/AC and NMVP@AC display almost identical XRD patterns (figure 3(a)). Both samples adopt a trigonal NASICON structure with a $R3c$ space group [29]. The sharp and intense diffraction peaks indicate the good crystallinity of the Na$_3$MnV(PO$_4$)$_2$. The carbon contents of NMVP@rGO/AC and NMVP@AC are determined by TG test. The mass loss associated with the combustion of rGO/AC mainly happens at 350 °C–500 °C. The slightly mass increase for both samples at ~500 °C is due to the oxidation of low valence state Mn and V. From the TGA curves, the carbon contents of NMVP@rGO/AC and NMVP@AC are measured to be 10.9 and 7.8 wt% (figure 3(b)), respectively. Owing to the higher carbon content of NMVP@rGO/AC, it exhibits a tap density (0.40 g cm$^{-3}$) slightly lower than that of NMVP@AC (0.47 g cm$^{-3}$).

The Raman spectra of NMVP@rGO/AC and NMVP@AC (figure 3(c)) feature two broad peaks located at ~1350 (D-band) and 1607 cm$^{-1}$ (G-band). The $I_d$/ $I_g$ intensity ratio of NMVP@rGO/AC and NMVP@AC is in the range of 1.17–1.24. The relatively high $I_d$/ $I_g$ ratio indicates the general amorphous characteristic of carbon in the samples.

XPS is performed to monitor the valence states of Mn and V in NMVP@rGO/AC and NMVP@AC. The survey spectra (figure S4, supporting information) show the existence of Na, Mn, V, P, O, and C elements in NMVP@rGO/AC and NMVP@AC, agreeing well with the EDS results. The Mn 2p spectrum (figure 3(d)) displays a dominant spin–orbit doublet for Mn$^{2+}$ (Mn 2p$_{3/2}$: 640.9 eV, Mn 2p$_{1/2}$: 653.0 eV), a spin–orbit doublet for Mn$^{3+}$ (Mn 2p$_{3/2}$: 642.3 eV, Mn 2p$_{1/2}$: 653.9 eV), and a shake-up satellite peak for Mn$^{2+}$ (646.5 eV), suggesting the co-existence of Mn$^{2+}$ and Mn$^{3+}$ in the NMVP@rGO/AC [32–35]. The XPS spectrum of V (figure 3(e)) shows the co-existence of both V$^{3+}$ (516.2 eV) and V$^{2+}$ (514.7 eV) in the sample [32, 36]. A similar phenomenon, that is the co-existence of Mn$^{2+}$ and Mn$^{3+}$ in NASICON compounds, has been observed in Na$_3$MnTi(PO$_4$)$_2$ [37].

Nitrogen sorption is employed to investigate the textual properties of NMVP@rGO/AC and NMVP@AC (figure 3(f)). Both samples manifest a typical type II isotherm with an H3 hysteresis loop, revealing their mesoporous feature. The mesopores are mainly distributed at 5–15 nm for NMVP@rGO/AC and 5–20 nm for NMVP@AC (figure S5, supporting information). It should be mentioned that the peak at ~3.8 nm might be an artifact caused by the capillary evaporation of N$_2$ at the lower end of hysteresis loop [38, 39]. Compared to NMVP@AC, the NMVP@rGO/AC possesses a much higher specific BET surface area (98 versus 47 m$^2$ g$^{-1}$) and total pore volume (0.22 cm$^3$ g$^{-1}$ versus 0.13 cm$^3$ g$^{-1}$ cm$^{-1}$ g$^{-1}$). When applied in SIBs, such highly porous feature would facilitate the diffusion of Na$^+$, contributing to rate performance.

The electrochemical performances of NMVP@rGO/AC and NMVP@AC are tested in half-cells in the potential window of 2.5–3.8 V versus Na$^+$/Na. The CV curves of NMVP@rGO/AC (figure 4(a)) show two pairs of anodic/cathodic peaks local at around 3.50/3.29 and 3.69/3.48 V, corresponding to the V$^{3+}$/V$^{2+}$ and Mn$^{2+}$/Mn$^{3+}$ redox couples, respectively. The first three consecutive CV profiles overlap quite well.

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**Figure 3.** (a) XRD patterns, (b) TGA curves, (c) Raman spectra of NMVP@rGO/AC and NMVP@AC. High-resolution (d) Mn 2p and (e) V 2p XPS spectra of NMVP@rGO/AC. (f) Nitrogen adsorption/desorption isotherms of NMVP@rGO/AC and NMVP@AC.
demonstrating the excellent reversibility of the electrochemical processes. Representative charge/discharge curves of NMVP@rGO/AC at 100 mA g$^{-1}$ show two well-defined plateaus at $\sim$3.3 V and $\sim$3.6 V, consistent with the CV results and previous literatures [24]. The NMVP@rGO/AC delivers a high initial discharge capacity of 100 mAh g$^{-1}$ and high-energy density of 343.4 Wh kg$^{-1}$, much higher than that of NMVP@AC (82 mAh g$^{-1}$ and 283.7 Wh kg$^{-1}$). Moreover, the NMVP@rGO/AC also demonstrates excellent cycling stability. A discharge capacity of 84.5 mAh g$^{-1}$ is retained after 70 cycles, corresponding to 84.5% of the initial discharge capacity. Under the same conditions, the discharge capacity of NMVP@AC decreases to 63.8 mAh g$^{-1}$, and the capacity retention is 77.8%. The long-term cycling performance of NMVP@rGO/AC at 1 A g$^{-1}$ is shown in Figure 4(d). The NMVP@rGO/AC delivers an initial discharge capacity of 81.4 mAh g$^{-1}$ and retains 63.1 mAh g$^{-1}$ after 500 cycles, corresponding to a capacity retention of 77.5%. In addition, the average Coulombic efficiency is close to 100%, which reveals the excellent reversibility of Na$^+$ insertion/extraction processes of NMVP@rGO/AC.

The rate performance and corresponding charge/discharge profiles of NMVP@rGO/AC are shown in Figures 4(e) and (f). The NMVP@rGO/AC delivers specific capacities of 105, 82.6, 59.2 and 45.1 mAh g$^{-1}$ at current densities of 100, 200, 500, and 1000 mA g$^{-1}$, respectively. When the current density turns back to 100 mA g$^{-1}$ from 1000 mA g$^{-1}$ gradually, the discharge capacity recovers to 94.3 mAh g$^{-1}$. However, the NMVP@AC delivers much lower capacities at various current densities; the capacity even drops to zero at 1000 mA g$^{-1}$. The significantly enhanced capacity and rate capability of NMVP@rGO/AC can be ascribed to the high conductivity of rGO/AC framework and the highly porous structure of NMVP@rGO/AC. The former enhances the electronic conductivity and the latter promotes Na$^+$ transport. EIS of NMVP@rGO/AC and NMVP@AC after the first cycle were collected (Figure S7). Both plots show a high-frequency semicircle followed by a low-frequency sloping line. The charge transfer resistance ($R_{ct}$) of NMVP@rGO/AC is calculated to be 322 $\Omega$, which is obviously lower than that of NMVP@AC (1510 $\Omega$), indicating its faster charge transfer on the electrode/electrolyte interface. In addition, the steeper line in the low-frequency region of NMVP@rGO/AC indicates the faster Na$^+$ diffusion in the bulk. The EIS results suggest that the largely improved electrochemical performance of NMVP@rGO/AC can be attributed to the rGO/AC dual-carbon framework, which enhances not only the electron transfer but also the Na$^+$ diffusion [40, 41].

Time-resolved in situ XRD is employed to monitor the structural evolution of NMVP@rGO/AC during Na$^+$ insertion/extraction processes. Figure 5 shows the in situ XRD pattern of the NMVP@rGO/AC as well as the corresponding charge/discharge profiles. The diffraction peaks experience obvious peak shifts and disappearance/reappearance during charging/discharging processes. Take the (113) diffraction originally centered at $\sim$23.1° as an example, the diffraction peak shifts to higher angles continuously during the initial charging (Na$^+$ extracting) to 3.6 V, suggesting a solid-solution reaction mechanism. Upon further charging to 3.8 V, the (113) diffraction peak disappears gradually; meanwhile, a new diffraction peak appears at $\sim$23.9°, indicating a two-phase reaction mechanism. Such changes are fully reversible, demonstrating the highly
reversible Na\(^{+}\) extraction/insertion in NMVP@rGO/AC during the de-sodiation/sodiation processes. To further investigate the oxidation states of V and Mn during de-sodiation process, \textit{ex situ} XPS spectra at different charge stages were recorded (figure S8, supporting information). Upon charge to 3.5 V, the binding energy of V 2p significantly improved, but the binding energy of Mn 2p showed little shifts, indicating only the oxidation of V\(^{3+}\) to V\(^{4+}\). After charging further to 3.8 V, the Mn 2p peaks shifted to higher binding energy with no obvious changes of V 2p, indicating the Mn\(^{2+}\) was oxidized to Mn\(^{3+}\). These results reveal that the Na\(^{+}\) extraction of NMVP@rGO/AC is two consecutive steps by the conversion of V\(^{3+}\)/V\(^{4+}\) and Mn\(^{2+}\)/Mn\(^{3+}\).

4. Conclusions

In summary, NMVP@rGO/AC microspheres are successfully synthesized by a facile and scalable spray-drying method. The NMVP nanoparticles are encapsulated in a 3D robust, porous, and highly conductive rGO/AC framework in the obtained NMVP@rGO/AC. Benefited from the open NASICON framework, porous structure, robust and highly conductive rGO/AC network as well as the nanoparticulate feature of NMVP, the obtained NMVP@rGO/AC microspheres demonstrate a high specific capacity (100 mA h g\(^{-1}\) at 100 mA g\(^{-1}\)) and superior long-term cycling stability (77.5% capacity retention for 500 cycles at 1000 mA g\(^{-1}\)). \textit{In situ} XRD measurement reveal the highly reversible Na\(^{+}\) extraction/insertion is realized through both solid solution and two-phase reaction mechanisms. This work provides a versatile platform for the mass production of rGO/AC dual-carbon encapsulated active materials for energy storage and conversion.

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