Rational Synthesis of Freestanding Na$_x$V$_2$O$_5$-rGO Paper as the Stable Cathode for Sodium Ion Batteries

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Flexible Na$_x$V$_2$O$_5$/rGO papers were successfully prepared via hydrothermal method followed by vacuum filtration as a high-performance cathode for SIBs. The as-prepared Na$_x$V$_2$O$_5$/rGO combined flexibility and high conductivity that can buffer stress and facilitate the fast transportation of electrons during the charge-discharge process. As a result, the as-prepared Na$_x$V$_2$O$_5$-rGO paper can exhibit a reversible Na-ion storage capacity of $\sim$197 mA h g$^{-1}$ at 100 mA g$^{-1}$ and a good cycling performance with 81% capacity retention for 400 cycles at a high current density of 500 mA g$^{-1}$, showing great potential in flexible energy storage devices.

Keywords: Na$_x$V2O5/rGO, flexibility, sodium ion batteries, cathode, freestanding

INTRODUCTION

With the increase in environmental concerns, people are eager to search for and develop safe and green energy storage systems (ESS). (Xu et al., 2017; Li et al., 2019). In recent years lithium-ion batteries (LIBs) have been applied to commercial electric vehicles (EVs) and provided a high energy density for large-scale energy storage systems (Xu et al., 2013; Huang et al., 2020), but the costs of lithium and the uneven global distribution of lithium resources gradually restrict their further applications. (Li et al., 2014). Therefore, safe and new cheap ESS that can partially replace LIBs need to be explored (Li et al., 2021). Among the new EES, sodium ion batteries (SIBs) have attracted increasing attention due to the rich potential sources of raw materials and suitable redox potentials (Jiang et al., 2014; Zhao et al., 2020). However, they have approximately 70% larger Na$^+$ than Li$^+$, which can bring sluggish diffusion kinetics to the solid state electrode materials, leading to the fast capacity decay and poor rate performance for SIBs (Liang et al., 2018; Huang et al., 2019). Thus, it is necessary to constantly study high-performance cathode materials that can meet the demands of both low cost and good electrochemical performance. (Wang et al., 2020). High-performance electrode materials should have several important traits including good electrical conductivity, abundant electrochemical active sites and desirable structure. (Lu et al., 2016; Pei et al., 2017). The above traits should be considered when designing and preparing high-performance sodium ion batteries.

To date, a large variety of sodium ion conductors such as pyrophosphates (Niu et al., 2019), fluorophosphates (Lim et al., 2014), sulfates (Wu et al., 2014), sodium transition-metal oxides (Liu et al., 2020a), polyanions (Senthilkumar et al., 2020), and the Prussian blue metalates (Liu et al., 2020b; Huang et al., 2021) have been proposed as SIB cathodes. Among these different types of SIB cathode materials, vanadium-based oxides have attracted significant attention due to their high Na-storage capacities, diverse structures, and high electrochemical activity. (Córdoba et al., 2019; Jo et al., 2020). In recent years, a variety of sodium vanadates including V$_2$O$_5$ polymorphs (Baddour-Hadjean...
of the 1D NaxV2O5 composite with the reduced graphene oxide (Zhou et al., 2019; Qu et al., 2021). If we can control fabrication and simultaneously acts as conductive network for strengthening carbon, can provide elastic matrix for loading cathode materials insertion/extraction reactions (Xu et al., 2020). In addition, the NaxV2O5 nanobelts and improve the conductivity of the whole rational introduction of rGO can reduce the aggregation of that can further improve electron transport (Xu et al., 2020). Freestanding electrode does not use non-conductive binders compared with the traditional cathodes, the as-prepared electrochemical performance of the electrode. Besides, graphene, as a typical two-dimensional structure and composition. A one dimensional (1D) structure can reduce ion diffusion path and promote the full use of active sites, which could endow cathode material with enhanced Na-ion storage performance (Zhu et al., 2019). In addition, the high electrochemical performance of NaxV2O5 is restricted by its low electron conductivity and large volume change. Design of a composite consisting of 1D NaV2O5-nH2O nanobelts and conductive carbon is a viable approach, which has both high electrochemical performance and good mechanical properties (Osman et al., 2021). Graphene, as a typical two-dimensional carbon, can provide elastic matrix for loading cathode materials and simultaneously acts as conductive network for strengthening the dynamical process both of electrons and ion transportation (Zhou et al., 2019; Qu et al., 2021). If we can control fabrication of the 1D NaV2O5 composite with the reduced graphene oxide (rGO), the freestanding NaV2O5/rGO composite cathode with enhanced electrochemical performance would be acquired.

In this work, a freestanding composite (denoted as NaxV2O5/rGO) consisting of δ-NaxV2O5 nanobelts and rGO was fabricated by a facile hydrothermal method combined with vacuum filtration. The freestanding composite composed of the δ-NaxV2O5 nanobelts and rGO offers several advantages. For instance, the bilayered δ-NaxV2O5 nanobelts with a large interlayer spacing and 1D belt-shaped morphology can reduce diffusion distance and provide a small diffusion for fast Na⁺ insertion/extraction reactions (Xu et al., 2020). In addition, the rational introduction of rGO can reduce the aggregation of NaxV2O5 nanobelts and improve the conductivity of the whole composite material (Ma et al., 2021), which can strengthen the mechanical integrity of the composite, thus improving the electrochemical performance of the electrode. Besides, compared with the traditional cathodes, the as-prepared freestanding electrode does not use non-conductive binders that can further improve electron transport (Xu et al., 2020). As a result, the as-prepared NaxV2O5/rGO electrode could exhibit a Na-storage capacity of ~197 mA h g⁻¹ and good cycling performance with 91% of capacity retention after 150 cycles at 100 mA g⁻¹, and high rate performance with ~91 mA h g⁻¹ at 500 mA g⁻¹. Moreover, a full Na-ion battery fabricated from the NaV2O5/rGO cathode and hard carbon anode can deliver a Na-storage capacity of 101 mA h g⁻¹ at 500 mA g⁻¹ and good cycling stability with a capacity retention of >75% over 100 cycles.

**EXPERIMENTAL DETAILS**

**Synthesis of the Ultra-Long NaₓV₂O₅ Nanobelts**

The NaₓV₂O₅ was synthesized by a hydrothermal reaction as follows: 3 mmol of sodiumiodide and 1.5 mmol of vanadium pentoxide were put into the 40 ml of 1 mol/L sodium chloride aqueous solution and constantly stirred for 8 h. Then, the mixture was put into a 40 ml Teflon-lined autoclave and placed into an electric oven at 200°C for 24 h. Finally, the obtained products were washed with deionized water and ethanol several times and dried at 80°C to obtain NaₓV₂O₅.

**Synthesis of the Free-Standing NaxV2O5/ rGO Paper**

The free-standing NaₓV₂O₅/rGO paper was prepared as follows: 120 mg of the NaₓV₂O₅ was synthesized by hydrothermal method and 60 mg of graphene oxide (GO) was synthesized via the modified Hummer’s method. The mixture of NaₓV₂O₅ and GO was ultrasonicated for 2 h followed by constantly stirring overnight until it became homogeneous. The mixed solution of NaₓV₂O₅ and GO was put into the Teflon-lined autoclave and placed at 180°C for 24 h. After the hydrothermal reaction, the product was re-dispersed in deionized water and subsequent vacuum filtration. The paper-like product via peeling was dried at 80°C for 24 h to obtain the free-standing NaₓV₂O₅/ rGO composite. The mass loading of the NaₓV₂O₅/rGO electrodes is ~3 mg/cm².

**Electrochemical Measurements**

**Fabrication of the Sodium Metal- NaxV₂O₅/rGO Half Cell**

The NaₓV₂O₅/rGO paper was directly cut into a round electrode with a diameter of 1 cm as the cathode and the active mass is ~1.2 mg. The homemade sodium sheets were used both as counter electrodes and reference electrodes. Whatman glass microfiber filters (GF/D) were used as the separator and 1 M NaClO₄ in ethylene carbonate (EC): propylene carbonate (PC) (1: 1 by v/v) with 5.0% fluoroethylene carbonate (FEC) as the electrolyte.

**Assembly of the Hard Carbon- NaxV₂O₅/rGO Full Cell**

The Na-ion full battery was fabricated in an argon-filled glove box composed of NaₓV₂O₅/rGO cathode and hard carbon anode. The hard carbon anode was prepared by mixing hard carbon, Super P, and polyvinylidene difluoride (8:1:1 wt%) in
N-Methylpyrrolidone, and then the slurry was spread onto Cu foil. We controlled the negative capacity/positive capacity ratio, which was ~1.1 to guarantee cell balance. The anode was firstly cycled between 0.01 and 1.5 V in a SIB half cell before preparing the full SIB cell.

RESULTS AND DISCUSSION

Figure 1 schematically illustrates the synthesis procedure of the Na$_x$V$_2$O$_5$/rGO paper. The mixture of the Na$_x$V$_2$O$_5$ and rGO was prepared by hydrothermal treatment of the Na$_x$V$_2$O$_5$ and GO. Then, the freestanding Na$_x$V$_2$O$_5$/rGO paper was obtained by facile vacuum filtration. The crystal structures of the as-synthesized samples (Na$_x$V$_2$O$_5$ and Na$_x$V$_2$O$_5$/rGO) are characterized by X-Ray diffraction (XRD). As shown in Figure 2, the XRD patterns of the synthesized Na$_x$V$_2$O$_5$ can be matched with a pure bilayer δ-Na$_x$V$_2$O$_5$ phase, which is consistent with previously reported results (Feng et al., 2018). Na$_x$V$_2$O$_5$/rGO exhibits similar diffraction patterns compared to that of the Na$_x$V$_2$O$_5$ sample, indicating Na$_x$V$_2$O$_5$ still exhibits high phase purity and GO has no effect on the formation of Na$_x$V$_2$O$_5$·nH$_2$O after the GO is added into the hydrothermal process. Then, the sodium to vanadium ratio was determined for the as-synthesized Na$_x$V$_2$O$_5$ sample by use of inductively coupled plasma optical emission spectroscopy (ICP-OES). The Na to V ratios in Na$_x$V$_2$O$_5$ samples were determined to be 0.16. When the vanadium level in each formula is set equal to 2.0, the corresponding sodium level in the Na$_x$V$_2$O$_5$ samples equals 0.32. (Supplementary Table S1). To confirm the morphology, SEM and TEM images were recorded on the as-synthesized Na$_x$V$_2$O$_5$ and Na$_x$V$_2$O$_5$/rGO paper. As shown in Figure 3A, one can see that the as-prepared Na$_x$V$_2$O$_5$ shows a long nanobelt morphology with a smooth surface and tens of micrometers in length and about 100–200 nm in width. The detailed crystal structures of Na$_x$V$_2$O$_5$ nanobelts were further characterized by a transmission electron microscope (TEM) (Figures 3B, C). The low-magnification TEM image (Figure 3B) further confirmed that the as-synthesized Na$_x$V$_2$O$_5$ nanobelts have a nanobelt structure, which is consistent with the observation in the SEM images. The high resolution (HR) TEM image demonstrates that these nanobelts are single crystals with an interplanar spacing of 0.36 nm, which corresponds to the (110) plane of the monoclinic phase Na$_x$V$_2$O$_5$ (Figure 3C). A typical scanning TEM image of a single Na$_x$V$_2$O$_5$ nanobelt and the corresponding element mapping images are recorded to further investigate the elemental distribution of the Na$_x$V$_2$O$_5$ nanobelt (Figure 3D). The elements Na, V, and O are homogeneously dispersed in the Na$_x$V$_2$O$_5$ nanobelt. Figures 3E, F exhibit the typical SEM images of Na$_x$V$_2$O$_5$/rGO paper. The interconnected Na$_x$V$_2$O$_5$ and rGO networks were observed, indicating the uniform intimate contact between Na$_x$V$_2$O$_5$ and rGO, which could increase the mechanical strength of freestanding Na$_x$V$_2$O$_5$/rGO hybrid paper to enhance cycling performance. Figures 3G–I shows optical images of freestanding Na$_x$V$_2$O$_5$/rGO paper, which can exhibit the excellent flexibility of Na$_x$V$_2$O$_5$/rGO paper and no obvious cracks were observed at the different bending states. Interestingly, based on the practical requirement, the
as-fabricated NaV₂O₅/rGO paper can be easily cut into the desired shapes to be directly used as the electrode of flexible SIBs.

To study the electrochemical performance of NaV₂O₅/rGO paper as cathode material for SIBs, the cyclic voltammetry (CV) test of NaV₂O₅/rGO nanocomposite electrode was first assessed during the initial three cycles at 0.1 mV s⁻¹. The CV curves of NaV₂O₅/rGO are overlapping, suggesting the highly reversible electrochemical behaviors. The slightly different shape between the first CV curve and subsequent CV curves may be caused by the electrode polarization. Furthermore, it exhibits six main anodic current peaks around 1.91, 2.75, 2.82, 3.01, 3.15, and 3.65 V (vs. Na⁺/Na), respectively, and six cathodic peaks around 1.65, 2.75, 2.91, 3.12, and 3.50 V (vs. Na⁺/Na). The multiple redox peaks correspond to the multi-step insertion/extraction of Na⁺ in the different available locations with energy differences. Two oxidation peaks (1.91 and 3.65 V) and reduction peaks (1.65 and 3.50 V) with high peak current demonstrate high Na⁺ diffusion kinetics of the NaV₂O₅/rGO paper electrode. The cycling profiles of the NaV₂O₅/rGO electrode at 100 mA g⁻¹ in the voltage range of 1.5–4.1 V are depicted in Figure 4B. The NaV₂O₅/rGO paper electrode shows analogous profiles corresponding well to the redox peaks of CV curves, indicating the good reversibility of the as-fabricated electrode. The dominated discharge/charge plateaus at about 3.6 V attributed to the reduction of V⁵⁺ to V⁴⁺ indicate a high electrochemical activity of V⁴⁺/V⁵⁺ (He et al., 2016; Feng et al., 2018).

The cycling performance of NaV₂O₅/rGO paper as cathode materials for SIBs is further studied, as shown in Figure 4C. The cyclability of the NaV₂O₅/rGO paper electrode was first tested at a low current density of 100 mA g⁻¹. It can deliver an initial charge/discharge capacity of 84 mAh g⁻¹. In the second and third cycles, the discharge capacity was almost no decay, demonstrating good Na-storage reversibility. After 150 cycles, a discharge specific capacity of 181 mAh g⁻¹ was retained with a high capacity retention of 91% compared with that in the 1st cycle (Figure 4C). On the contrary, the NaV₂O₅ electrode exhibit degraded electrochemical performance. The first discharge capacity of the NaV₂O₅ electrode could reach 185 mAh g⁻¹, but the discharge capacity was only retained at 131 mAh g⁻¹ after 150 cycles with a capacity retention of 70%. EIS tests are investigated to study the electrode reaction kinetics. Supplementary Figures S1A,B, the semicircle in high frequency (interfacial impedance, Rf) and middle frequency (charge transfer...
impedance, Rct) become larger after 10 cycles for Na$_x$V$_2$O$_5$ and Na$_x$V$_2$O$_5$/rGO. An equivalent circuit model was established, as shown in Supplementary Figure S1, where Rs is the internal resistance, Rf is the interfacial impedance, Rct represents the charge transfer resistance. As listed in Supplementary Table S2, the cycled Na$_x$V$_2$O$_5$/rGO shows lower Rf and Rct than those of Na$_x$V$_2$O$_5$, indicating faster reaction kinetics of Na$_x$V$_2$O$_5$/rGO.

From the above results, the Na$_x$V$_2$O$_5$/rGO paper electrochemical showed superior cycling stability and strengthened reaction kinetics compared with the rare Na$_x$V$_2$O$_5$ electrodes. The rate performance of the Na$_x$V$_2$O$_5$/rGO paper at different current densities is shown in Figure 4D. The Na$_x$V$_2$O$_5$/rGO paper cathodes could exhibit average specific discharge capacities of 200, 163, 129, 92, and 65 mAh g$^{-1}$ at current densities of 100, 200, 500, 1000, and 2000 mA g$^{-1}$, respectively. When the current density comes back to 100 mA g$^{-1}$, an average specific discharge capacity of 187 mAh g$^{-1}$ could be preserved, showing the excellent electrochemical performance of the Na$_x$V$_2$O$_5$/rGO paper electrode at the different current densities. Considering the high reversibility of the as-prepared Na$_x$V$_2$O$_5$/rGO paper electrodes, we further evaluated the Na$_x$V$_2$O$_5$/rGO electrode at 500 mA g$^{-1}$ for 400 cycles as shown in Figure 4E. A specific discharge capacity of 91 mAh g$^{-1}$ was retained after 400 cycles with a capacity retention of 81%. Therefore, we believe the as-prepared Na$_x$V$_2$O$_5$/rGO paper electrodes exhibited a high rate

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**FIGURE 4** (A) The initial three CV curves of the Na$_x$V$_2$O$_5$/rGO electrode at a scanning rate of 0.1 mV s$^{-1}$; (B) Initial three charge/discharge curves of the Na$_x$V$_2$O$_5$/rGO electrode at a current density of 100 mA g$^{-1}$. The electrochemical performance of Na$_x$V$_2$O$_5$/rGO electrode: (C) cycling performance; and (D) rate capability. (E) Cycling performance of Na$_x$V$_2$O$_5$/rGO electrode at a current density of 500 mA g$^{-1}$. 

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performance and good cycling stability, indicating the enhanced electrochemical performance of the freestanding electrodes in the present work. To confirm the benefits of the Na$_x$V$_2$O$_5$/rGO paper, a comparison of the Na-storage performance between the as-prepared Na$_x$V$_2$O$_5$/rGO and other vanadium-based cathode materials is listed in Table 1. The electrochemical performance of our synthesized Na$_x$V$_2$O$_5$/rGO is superior to the vanadium-based cathode materials of SIBs recently reported. The good electrochemical performance of our Na$_x$V$_2$O$_5$/rGO films may be due to the following reasons: first, the bilayered Na$_x$V$_2$O$_5$ nanobelts with a large interlayer spacing and 1D belt-shaped morphology can reduce diffusion distance and provide a small diffusion for fast Na’ ion insertion/extraction reactions.

The other is that the presence of rGO can reduce the aggregation of Na$_x$V$_2$O$_5$ nanobelts and improve the conductivity of the whole composite material, which can strengthen the mechanical integrity of the composite and thus improve the cycling stability of the electrode.

Due to the high chemical activity of Na metal, the metallic Na anode would be highly dangerous in practical application. Na-ion full batteries based on hard carbon and Na$_x$V$_2$O$_5$/rGO paper as the anode and cathode electrodes, respectively, were assembled to further study the electrochemical behavior of full SIBs. Figure 5A depicts the typical voltage profiles of the hard carbon anode and Na$_x$V$_2$O$_5$/rGO paper cathode measured in the Na half-cell. Both the Na$_x$V$_2$O$_5$/rGO and hard carbon could achieve...
reversible Na-ion transport from their respective skeleton structures. **Figure 5B** shows the charge–discharge profiles of the full battery at 500 mA g\(^{-1}\) with cut-off voltages of 3.8 and 1.0 V. The initial discharge–specific capacities could attain 109 mAh g\(^{-1}\). Charge-discharge specific capacities could also retain 134/135 mAh g\(^{-1}\) with a high Coulombic efficiency of 99% in the second cycle. As shown in **Figure 5C**, after 100 cycles, the full Na-ion battery retained a discharge specific capacity of 101 mAh g\(^{-1}\) with a capacity retention of >75%, showing the good cycling performance of SIBs based on Na\(_x\)V\(_2\)O\(_5\)/rGO paper electrode and hard carbon electrode. Importantly, the average Coulombic efficiency was higher than 98% during the 100 cycles, suggesting the highly reversible Na-ion storage behavior for the full Na-ion battery. Besides the high capacity retention, the full Na-ion battery also exhibited a good rate of performance. As shown in **Figure 5D**, the full Na-ion battery delivered average specific discharge capacities of 218, 197, 172, 137, 113, and 97 mAh g\(^{-1}\) at constant current densities of 50, 100, 200, 500, 1000, and 2000 mA g\(^{-1}\) respectively. When the current density was recovered to 50 mA g\(^{-1}\), the reversible capacity came back to 193 mAh g\(^{-1}\), indicating a good tolerance for the rapid Na-ion insertion/extraction cycles. The current work shows that the Na\(_x\)V\(_2\)O\(_5\)/rGO has great potential as the freestanding cathode material for stable sodium ion batteries.

**CONCLUSION**

In summary, a flexible Na\(_x\)V\(_2\)O\(_5\)/rGO paper was successfully prepared via the hydrothermal method followed by vacuum filtration as a high-performance cathode for SIBs. The as-prepared Na\(_x\)V\(_2\)O\(_5\)/rGO possessed flexibility and high conductivity that can buffer stress and facilitate the fast transportation of electrons during the charge-discharge process. As a result, the as-prepared Na\(_x\)V\(_2\)O\(_5\)/rGO paper can deliver a reversible Na-ion storage capacity of ~197 mA h g\(^{-1}\) at 100 mA g\(^{-1}\) and showed a good cycling performance with 81% capacity retention for 400 cycles at a high current density of 500 mA g\(^{-1}\), showing great potentials in flexible energy storage devices.

**DATA AVAILABILITY STATEMENT**

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding author.

**AUTHOR CONTRIBUTIONS**

JX conceived the concept and directed the research. QW and XL designed the project. QW and XL carried out material synthesis. YY and XYL performed material characterization. JX and XW wrote the paper. All authors discussed the results and commented on the paper.

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**SUPPLEMENTARY MATERIAL**

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fmats.2022.913804/full#supplementary-material

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