Intercalation pseudocapacitance of FeVO$_4$-$n$H$_2$O nanowires anode for high-energy and high-power sodium-ion capacitor

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1. Introduction

Rechargeable sodium-ion storage devices, including sodium-ion batteries (SIBs) and capacitors (SICs), are considered as one of the most promising alternatives to those of lithium-ion counterparts for large-scale applications [1–4]. The low-cost sodium-based chemicals reduce the price of SIBs and SICs [5]. More importantly, the much abundant resources of sodium than those of lithium (23,000 vs. 17 ppm in earth’s crust) could make the promising widespread usages of SIBs and SICs [6–8].

The Nobel Prize in Chemistry 2019 is awarded to J.B. Goodenough, M.S. Whittingham and A. Yoshino for their contributions to the development of lithium-ion battery (LIB) [9]. Historically, the concept of electrochemical lithium-ion intercalation was firstly discovered in the 1970’s by Whittingham and co-workers [10–14]. Following the lithium-ion intercalation chemistry, sodium-ion intercalation has been demonstrated as well [15–19]. However, sodium-ion intercalation shows very different phase change behavior (e.g. coordination, lattice constant, crystal structure) and diffusion properties when compared to those of lithium-ion, owing to the larger ionic radius of Na$^+$ (1.02 Å vs. 0.76 Å for Li$^+$) [1]. The reduction potential of –2.71 V (vs. SHE) for Na$^+$ is higher than that of –3.04 V (vs. SHE) for Li$^+$ [20,21]. Generally, the storage capacity, operating voltage and energy density of SIBs/SICs are lower than those of lithium-ion counterparts [22]. But, it is worth noting that the larger Na$^+$ present a lower activation energy of ionic diffusion and smaller Stokes’ radius in solvent, resulting in higher mobility of [Na-solvent]$^+$ and ionic conductivity than that of Li$^+$ system [20,21]. Hence, it is proposed that the high-power SICs are very promising for sodium-ion applications.
replacing the present lithium-ion capacitors (LICs), since the rational use of low-cost sodium resources for large-scale applications. However, there are still some challenges for the development of SICs, including the design of high-rate sodium-ion storage electrode materials and their rapid charge-discharge mechanism [2, 23].

Pseudocapacitive materials store charge through battery-like Faradaic redox reactions but display rapid rates comparable to those of double-layer-capacitors [24]. Dunn and co-workers summarized the various transition metal oxides (TMOs) exhibiting pseudocapacitive behaviors [24]. Notably, the pseudocapacitive lithium-ion intercalation anode materials, such as T–Nb2O5 [25], TiO2(B) [26], MoS2 [16] and MoO3 [27], deliver ultrahigh-rate performance and are suitable for the development of high-energy and high-power hybrid LICs. Recently, Nb2O5 and TiO2 anode with pseudocapacitive behavior were also investigated for Na+ storage [28, 29]. However, their low initial coulombic efficiency results in an irreversible consumption of electrolyte, which is still unsatisfied [24]. It is assumed that developing the pseudocapacitive sodium-ion intercalation materials is promising for high-rate Na+ storage and high-performance SICs. However, it is rarely reported and remains largely unexplored.

The Faradaic reaction is highly depended on the redox of transition metals. Ferric vanadate is an attracting electrode owing to both Fe3+ and V5+ exhibiting electrochemical redox activity, resulting in multi-electrochemical reactions and high capacity [30–35]. FeVO4·nH2O nanowires for Li+ storage deliver a specific capacity of 1300 mAh g−1 in the potential range of 0.02–3.5 V (vs. Li+//Li), corresponding to about 9 Li+ ions per unit formula [31]. However, the Na+ storage mechanism and electrochemical behavior of FeVO4·nH2O have not been investigated yet. A deep understanding of the difference between the electrochemical reaction of Li+ and Na+ storage would help the design of high-performance energy storage devices. Herein, we systematically investigate the Na+ and Li+ storage behaviors of FeVO4·nH2O by electrochemical test, operando X-ray diffraction (XRD) and ex-situ TEM. It is found that the Na+ and Li+ intercalation reaction presents a pseudocapacitive behavior, which contributes to high initial coulombic efficiency (ICE), reversible cycling and high-rate capability. Based on the highly pseudocapacitive FeVO4·nH2O anode, we assemble a SIC without any additional pre-sodiation processes. The electrochemical behaviors of the SIC are intensively studied by three-electrode and two-electrode systems. The SIC delivers expected a maximum energy density up to 88 Wh kg−1 (at the power density of 95 W kg−1) and a high power density of 7.9 kW kg−1 (with the energy density of 35 Wh kg−1), and superior cycling stability (5000 cycles).

2. Experimental section

2.1. Experimental methods

2.1.1. Synthesis of FeVO4·nH2O nanowires

The FeVO4·nH2O nanowires were prepared by a facile hydrothermal method [36, 37]. Briefly, 4 mmol FeCl3·6H2O was dissolved in 20 mL deionized water under stirring. 4 mmol NH4VO3 was dissolved in another 20 mL deionized water at 80 °C. Then, the NH4VO3 solution was slowly added into the FeCl3·6H2O solution under stirring to form a suspension. After 10 min, the suspension was transferred into a 50 mL Teflon-lined stainless steel autoclave and heated at 180 °C for 4 h. The final precipitate was washed by centrifugation with deionized water and ethanol for each three times. Finally, the FeVO4·nH2O nanowires powders were obtained after drying under vacuum at 70 °C for 12 h.

2.1.2. Synthesis of Na2(VO2)(PO4)2/F/rGO composites

The Na2(VO2)(PO4)2/F/rGO (NVOPF/rGO) was synthesized by one-pot solvothermal method. Graphene oxide (GO) was prepared by the Hummers’ method [38]. Firstly, 2 mmol NH4VO3, 3 mmol NaF and 2 mmol NH4H2PO4 were dissolved in 20 mL GO dispersion (2 g L−1) under stirring. Then, 20 mL N,N-dimethylformamide (DMF) was slowly added to the above mixture with stirring for 1 h. The resulting solution was transferred into a 50 mL Teflon-lined stainless steel autoclave and heated at 180 °C for 24 h. Finally, the final precipitate was washed by deionized water and ethanol for three times, and then NVOPF/rGO powders were obtained after drying in a vacuum oven at 100 °C for 12 h.

2.2. Materials characterization

X-ray diffraction (XRD) measurements were conducted by using a D8 Advance X-ray diffractometer with a non-monochromated Cu Kα X-ray source at room temperature. Scanning electron microscopy (SEM) images were collected using a JEOLO-7100F microscope. Transmission electron microscopy and high-resolution TEM (HRTEM) images were collected by using a JEM-2100F STEM/EDS microscope. Thermogravimetric (TG) analysis was performed using NETZSCH-STA449F5 thermoanalyzer. The carbon content analyses were performed with CHNS elemental analyzer.

2.3. Electrochemical measurements

The coin cells (CR2016) and three-electrode device and operando cells were assembled in an Ar-filled glove box. The working electrode of FeVO4·0.6H2O was prepared by mixing 80% active materials, 12% conductive carbon and 8% carboxymethyl cellulose (CMC). Then, the slurries were coated onto the carbon coated Al foil or Cu foil for Na+ or Li+ storage test, respectively. The NVOPF/rGO electrode was made by mixing 70% active materials, 20% conductive carbon and 10% polyvinylidene fluoridie (PVDF). Then, the homogeneous slurries were coated onto the carbon coated Al foil and dried in a vacuum oven at 70 °C for 12 h. The mass loading of FeVO4·0.6H2O and NVOPF/rGO was ~1 and ~2 mg cm−2, respectively. To assemble the sodium-ion coin cell, the working electrode was a disk with a diameter of 10 mm; sodium disk (a diameter of 14 mm) was used as the counter and reference electrode; Celgard-2350 film was used as separator, and 1 M NaPF6 in diethylene glycol dimethyl ether was used as the electrolyte. To assemble the three-electrode device, the assembling diagram was presented in Fig. 4a, in which sodium ring (inner diameter of 17 mm, outer diameter of 24 mm) was used as the reference electrode. To assemble lithium-ion coin cell, lithium disk (a diameter of 14 mm) was used as the counter and reference electrode; Celgard-2400 separator was used; 1 M lithium hexafluorophosphate (LiPF6) solution in ethylene carbon–dimethyl carbonate (1:1 vol/ vol) was used as electrolyte. Galvanostatic charge-discharge rate performance and cyclic voltammetry were performed by using Bio-Logic VMP3 potentiostat at room temperature. The long-term cycling performance was performed by using NEWARE battery testing system.

3. Results and discussion

3.1. Characteristics of FeVO4·nH2O nanowires

The FeVO4·nH2O nanowires powder is in yellow (inset of Fig. S1a) [36]. The powder XRD of the product is shown in Fig. S1a. All the diffractions are indexed to Fervanite (FeVO4·nH2O, JCPDS card No. 27–0257) [34, 36]. Fourier transform infrared (FTIR) spectrum further characterizes the Fe–O, V–O, V–O–Fe and V–O–Fe stretching modes and demonstrates the existence of crystal water (Fig. S1b). The number of water molecules in FeVO4·nH2O is 0.6, depicted by thermal gravity analysis (Fig. S1c). The chemical formula of the obtained product is FeVO4·0.6H2O. The scanning electron microscope (SEM) image (Fig. S1d) displays nanowire morphology of FeVO4·0.6H2O. Transmission electron microscopy (TEM) image (Fig. S1e) shows the nanowire with a width of about 100 nm and a length of several micrometers. Fig. S1f shows the high-resolution TEM (HRTEM) image of FeVO4·0.6H2O nanowire. The measured 8.1 Å inter distance is in agreement with (100) plane of FeVO4·0.6H2O lattice [32].
3.2. Lithium-ion and sodium-ion storage mechanism

The electrochemical performance and storage mechanism of FeVO$_4\cdot$0.6H$_2$O were investigated by assembling half cell (2016-type and operando XRD measurement cell), in which the lithium or sodium foil was used as the counter and reference electrode. At first, we investigated the lithium-ion intercalation behavior, then parallelly compared to that of sodium-ion intercalation. Fig. 1a shows the cyclic voltammetry (CV) curves in the potential range of 1–3 V vs. Li$^+$/Li. The CV curves show a broad cathodic peak at ~2.3 V and a sharp cathodic peak at ~1.6 V. All the peaks disappeared at the following de-lithiation process and 2nd repeated cycle. The galvanostatic (GV) discharge-charge profiles at 0.1 A g$^{-1}$ (Fig. 1b) shows the same result to CV curves. The lithiation process from an initial state to 2 V displays a linear-like capacitive slop curve, corresponding to the intercalation numbers of 1.3 Li$^+$ ions per formula unit. Then continuous discharging, an obvious plateau at ~1.6 V vs. Li$^+$/Li was observed. The lithiation numbers are 3.4 Li$^+$ ions per formula when discharged to 1 V. When it is charged to 3 V, the de-lithiation process is quite different, indicating an irreversible process. The reversible Li$^+$ storage number of FeVO$_4\cdot$0.6H$_2$O anode is 2.2 Li$^+$ ions per formula unit. Operando XRD patterns were used to investigate the Li$^+$ storage mechanism, as shown in Fig. 1c. The diffraction peaks at 27.7°, 30.4° and 34.2° are indexed to FeVO$_4\cdot$0.6H$_2$O. The first lithiation process can be separated into three steps. The corresponding schematic is displayed in Fig. 1k. At the first step, the diffraction peaks continuously shift toward a lower angle, from 27.7° to 27.0°, 30.4° to 30.2° and 34.2° to 34.0°, respectively. This step is the lithium intercalation into the FeVO$_4\cdot$0.6H$_2$O under a single-phase reaction. At the second step, it occurs at the plateau reaction of ~1.6 V, the intensity of diffraction peaks gradually weakens even to totally disappear, corresponding to an irreversible transformation from crystalline FeVO$_4\cdot$0.6H$_2$O into amorphous state. The third step is continuous lithiation of amorphous sample, accompanied with no peaks observed in XRD patterns. During charging back to 3 V, all diffraction peaks remain disappearance. The linear-like charge profile is quite different from the initial discharge curve, corresponding to an irreversible process. The FeVO$_4\cdot$0.6H$_2$O nanowires at the

![Fig. 1. Lithium-ion and sodium-ion storage mechanism of FeVO$_4\cdot$0.6H$_2$O. For Li$^+$ storage in 1–3 V vs. Li$^+$/Li, CV curves (a) and potential vs. composition profiles (b) of FeVO$_4\cdot$0.6H$_2$O nanowires, respectively; (c) operando XRD pattern during galvanostatic test at 0.1 A g$^{-1}$; (d, e) ex-situ HRTEM images of FeVO$_4\cdot$0.6H$_2$O nanowires when discharged to 1 V vs. Li$^+$/Li and charged to 3 V vs. Li$^+$/Li, respectively. For Na$^+$ storage in 0.05–3 V vs. Na$^+$/Na, CV curves (f) and potential vs. composition profiles (g) of FeVO$_4\cdot$0.6H$_2$O nanowires, respectively; (h) operando XRD pattern during galvanostatic test at 0.1 A g$^{-1}$; (i, j) ex-situ HRTEM images of FeVO$_4\cdot$0.6H$_2$O nanowires when discharged to 0.05 V vs. Na$^+$/Na and charged to 3 V vs. Na$^+$/Na, respectively. (k) A schematic diagram of the similarity and difference in FeVO$_4\cdot$0.6H$_2$O for Li$^+$ and Na$^+$ storage mechanism after deep-lithiation/sodiation.](image-url)
discharged state (Fig. S2a and Fig. 1d) and charged state (Fig. S2b and Fig. 1e) were characterized by TEM and HRTEM, respectively. The results show that the FeVO$_4$·0.6H$_2$O maintains the nanowires morphology but turns to amorphous state, which are consistent with the observation by operando XRD. Owing to the irreversible amorphous transformation occurred below 2 V vs. Li$^+$/Li, a potential range of 2–3 V vs. Li$^+$/Li is selected to investigate the Li$^+$ intercalation behaviors of FeVO$_4$·0.6H$_2$O (Fig. S3), which delivers much reversible storage of 1.12 Li$^+$ ions per formula unit and a high ICE of 89%.

Subsequently, the electrochemical Na$^+$ storage behavior and mechanism were investigated systematically. Fig. 1f shows the CV curves in the potential range of 0.05–3 V vs. Na$^+$/Na. There are broad cathodic peak at ~1.65 V and sharp cathodic peak at ~0.6 V, and broad anodic peak at ~1.7 V in the 1st cycle. Then, the cathodic peak current decreases in the next cycle, indicating an irreversible redox process. The CV charge-discharge profiles when initial discharged to 1 V displays a linear slop curve, which is a typical capacitive behavior, as shown in Fig. 1g. The intercalation numbers are 1.3 Na$^+$ ions per formula unit. Then continuous discharging to 0.05 V, an obvious plateau at ~0.6 V vs. Na$^+$/Na is observed and the related amount of Na$^+$ storage corresponds to 4.1 Na$^+$ ions per formula unit. When charged to 3 V, the de-sodiation plateau is at ~1.7 V. Approximately 3.7 Na$^+$ ions per formula unit are de-sodiated, thus the amount of irreversible Na$^+$ ions is ~0.4. The operando XRD patterns are collected as well to figure out the Na$^+$ storage mechanism of FeVO$_4$·0.6H$_2$O (Fig. 1h). Different from the lithiation process as discussed above, the initial sodiation process only includes two steps. From initial state to 1 V, the discharge peaks continuously shift toward lower angle, from 27.6° to 26.6°, 30.4° to 29.3° and 34.2° to 33.6°, respectively, indicating a single-phase sodium-ion intercalation behavior. The lower angle shifts are related to the enlarging volume of crystal structure during sodium-ion intercalation. At the second step, the discharge peaks almost disappear at the beginning of discharge potential at 1 V vs. Na$^+$/Na, corresponding to irreversible transformation from crystalline into amorphous state. The discharge plateau at ~0.6 V is the sodiation of amorphous Na$_x$-Fe-V-O phase. After charging back to 3 V, no discharge peaks are recovered. Amorphous FeVO$_4$·0.6H$_2$O nanowires were observed by TEM (Figs. S2c and d) and HRTEM (Fig. 1i and j) images at the sodiated and desodiated states, respectively, which were consistent with the results of operando XRD.

Based on the above results, the detailed charge storage mechanism of FeVO$_4$·0.6H$_2$O for both Li$^+$ and Na$^+$ is schematically shown in Fig. 1k. FeVO$_4$·0.6H$_2$O electrode for the Li$^+$ and Na$^+$ storage undergoes similar reaction processes, including intercalation of Na$^+$ (or Li$^+$) into FeVO$_4$·0.6H$_2$O through single-phase reaction and the amorphous transformation of crystalline FeVO$_4$·0.6H$_2$O after deep reaction. However, there are some differences between the Li$^+$ and Na$^+$ storage processes. At the intercalation process, the intercalation amount of Li$^+$ and Na$^+$ ions are similar, but the XRD peaks of FeVO$_4$·0.6H$_2$O present a larger shift for Na$^+$ storage than those for Li$^+$ storage (Fig. 1c and h). This difference indicates slightly enlarged lattice expansion by Na$^+$ intercalation, which is possibly caused by a larger ionic radius of Na$^+$ than that of Li$^+$. Interestingly, the amorphous transformation step is also quite different between the Li$^+$ and Na$^+$ storage. The amorphous transformation for lithiation accompanies with a discharge plateau (namely conversion reaction [32,39]), while the operando XRD peaks gradually weaken during the plateau reaction and then totally disappear. However, the amorphous transformation caused by sodiation directly occurs after the sodium-ion intercalation step that is before the plateau reaction, which may be due to excessive volume expansion caused by the over number of Na$^+$ intercalation. The related cycling stabilities are extremely poor after irreversible amorphous transformation taking place (Figs. S4a and b). The capacity retention is only 20% for Li$^+$ storage and 18% for Na$^+$ storage after 100 cycles, respectively.

3.3. Pseudocapacitive sodium-ion intercalation behavior of FeVO$_4$·0.6H$_2$O

Inhibiting the irreversible amorphous transformation is a key measure for optimizing the electrochemical performance [40,41]. According to above investigation, the potential window is set in the range of 1–3 V vs. Na$^+$/Na, while only sodium-ion intercalation process is involved. Fig. 2a shows the first and second CV curves in the potential range of 1–3 V vs. Na$^+$/Na, which only displays a pseudo-rectangular shape. Fig. 2b shows the potential vs. composition profiles of FeVO$_4$·0.6H$_2$O nanowires in 1–3 V vs. Na$^+$/Na. The charge-discharge curves display a capacitive-like voltage response, consistent with the result of CV test. The total amount of Na$^+$ storage is 1.3 per formula unit, and the amount of reversible Na$^+$ is 1.08, corresponding to an ICE of 83%. Besides, the operando XRD patterns are tested at the current density of 0.1 A g$^{-1}$ in the potential range of 1–3 V (Fig. 2e). The diffusion peaks of FeVO$_4$·0.6H$_2$O shift towards lower angle (from 27.6° to 26.6°, 30.4° to 29.3° and 34.2° to 33.6°) and then returns to its original position during sodiation and de-sodiation processes, indicating the highly reversible (de)intercalation processes. The different (de)sodiated states of FeVO$_4$·0.6H$_2$O nanowires were characterized by TEM (Figs. S5a and b, respectively) and HRTEM (Fig. 2d and e, respectively), which showed the crystalline nanowire morphology. Compared to the HRTEM image of initial FeVO$_4$·0.6H$_2$O nanowires (Fig. S1d), the spacing of (100) plane at the discharged state of 1 V is slightly increased from 8.1 to 8.3 Å (Fig. 2d). Then, the spacing of (100) plane recovers to the original value at the re-charged state of 3 V (Fig. 2e), indicating the reversible (de) intercalation processes confirmed by operando XRD as well.

Based on the above results, the pseudo-rectangular current response and pseudo-linear voltage response were realized based on the Na$^+$ (de) intercalations. Thus, the electrochemical kinetics analysis was used to investigate the relation of measured current (i) and sweep rate (v). A series of CV for Na$^+$ storage were measured at various rates from 0.2 to 10 mV s$^{-1}$ (Figs. 2f and S6a). The CV shape is pseudo-rectangular, indicating capacitive behavior. CV curves for Li$^+$ intercalation storage at various sweep rates from 0.2 to 1 mV s$^{-1}$ also show a similar capacitive behavior (Fig. S6b). The relation of measured current (i) and sweep rate (v) can be presented by the following Equation (1):

$$i = v^{b}\quad (1)$$

Where the b is the slope of log (i) vs. log (v) plots at a specific potential. A b-value of 0.5 indicates diffusion-controlled process, whereas b-value of 1 indicates surface-controlled process. Figs. 2g and S6c show the change of b-value about Na$^+$ and Li$^+$ storage, respectively. For Na$^+$ storage, all of b-value are very close to 1 rather than 0.5, which suggests the domination of pseudocapacitive charge storage process. Especially, the b-value for Na$^+$ storage is higher than that for Li$^+$ storage, indicating highly capacitive Na$^+$ storage property.

The total current responses (i) can be divided into two parts: capacitive responds (k$V$) and diffusion-controlled responds (k$V^{1/2}$), which can be presented by the following Equation (2):

$$i(V) = k_{V} + k_{V^{1/2}}\quad (2)$$

The quantitative analysis is firstly calculated at the sweep rate of 1 mV s$^{-1}$. The capacitive contribution of CV curve is 93% and 83% for Na$^+$ and Li$^+$ storage, respectively (Fig. 2h and Fig. S6d). As shown in Fig. S6e, the value of capacitive contribution enhances with the increase of the sweep rate. These results confirm that the sodium-ion intercalation process of FeVO$_4$·0.6H$_2$O in 1–3 V vs. Na$^+$/Na exhibit exceptional pseudocapacitive features. The detailed charge storage mechanism of FeVO$_4$·0.6H$_2$O for Na$^+$ storage in 1–3 V vs. Na$^+$/Na is schematically shown in Fig. 2i. Different from the traditional battery-type intercalation anode, FeVO$_4$·0.6H$_2$O presents reversible Na$^+$ intercalation pseudocapacitance behavior.
3.4. Rate capability and long-term cycling stability of Na\(^+\) intercalation reaction

The electrochemical performance for Li\(^+\) and Na\(^+\) storage is compared and analyzed based on intercalation reaction. The rate capacity of FeVO\(_4\)·0.6H\(_2\)O anode from 0.1 to 10 A g\(^{-1}\) is shown in Fig. 3a. At the current density of 0.1 A g\(^{-1}\), the sodiation capacity is 169 mAh g\(^{-1}\), which is similar to the lithiation capacity (158 mAh g\(^{-1}\)). At a higher current density of 6 A g\(^{-1}\), the sodiation capacity is 60 mAh g\(^{-1}\), which is lower than lithiation capacity of 21 mAh g\(^{-1}\). At 10 A g\(^{-1}\), the sodiation capacity remains 40 mAh g\(^{-1}\). A better rate performance of FeVO\(_4\)·0.6H\(_2\)O for Na\(^+\) storage is probably due to that a larger Na\(^+\) presents a lower activation energy of ionic diffusion and smaller Stokes’ radius in solvent, resulting in higher mobility of [Na-solvent]\(^+\) and ionic conductivity than those of Li\(^+\) [20, 21]. The related GV curves at different currents present a typical capacitive-like shape (Fig. 3b).

The cycling performance was tested at the current density of 2 A g\(^{-1}\) (Fig. 3c). The sodiation capacity is 86 mAh g\(^{-1}\) after 2000 cycles, corresponding to a capacity retention of 83% (calculated based on the capacity at second cycle), which is higher than the result of Li\(^+\) storage (40 mAh g\(^{-1}\) after 2000 cycles with a capacity retention of 36%). Interestingly, the FeVO\(_4\)·0.6H\(_2\)O exhibits better cycling performance for Na\(^+\) storage. This comparison indicates that the (de)intercalation of Na\(^+\) is much reversible that those of Li\(^+\), although the former leads to larger volume expansion but the lattice is highly recoverable (Fig. 2c). The related charge-discharge curves at different cycles are presented in Fig. S7a, all of which show the linear slops in 1–3 V vs. Na\(^+\)/Na. Especially, the lithiation and sodiation capacity show an increasing trend in the first 70 cycles and then gradually decrease during (de)intercalation process. For explaining the phenomena, the ex-situ XRD patterns in 1–3 V vs. Na\(^+\)/Na, CV curves (a) and potential vs. composition profiles (b) of FeVO\(_4\)·0.6H\(_2\)O nanowires, respectively. (c) Operando XRD pattern during galvanostatic test at 0.1 A g\(^{-1}\). (d, e) Ex-situ HRTEM images of FeVO\(_4\)·0.6H\(_2\)O nanowires when discharged to 1 V vs. Na\(^+\)/Na and charged to 3 V vs. Na\(^+\)/Na, respectively. (f) CV curves of FeVO\(_4\)·0.6H\(_2\) nanowires in 1–3 V vs. Na\(^+\)/Na at different sweep rates from 0.2 to 1 mV s\(^{-1}\). (g) Analysis of b-value at different potential. (h) Separation of the capacitive and diffusion contribution at a sweep rate of 1 mV s\(^{-1}\). (i) A schematic diagram of pseudocapacitive Na\(^+\) intercalation mechanism for FeVO\(_4\)·0.6H\(_2\)O nanowires.
V vs. Na⁺/Na are presented in Fig. S7b. All of the diffraction peaks of FeVO₄·0.6H₂O after 50 cycles still exist, but they partially widen or disappear after 1000 cycles, indicating that FeVO₄·0.6H₂O would have the trend of partly amorphous transformation after long-term cycles. The result shows that the increase of capacity during the initial cycles may be an activation process and the followed capacity decay is related to the slightly amorphous transformation. The realization of pseudocapacitive intercalation reaction greatly enhances the rate and cycling performance of Na⁺ storage, which is very promising for developing high-performance SICs.

3.5. Hybrid sodium-ion capacitor based on pseudocapacitive intercalation FeVO₄·0.6H₂O anode

To further demonstrate the potential of FeVO₄·0.6H₂O anode in SIC, a SIC was assembled by Na₃(VO)₂(PO₄)₂/rGO (NVOPF/rGO) cathode and FeVO₄·0.6H₂O anode. The phase of the prepared NVOPF/rGO material is confirmed by XRD (Fig. S8a). The SEM image (Fig. S8b) displays nanorod morphology of NVOPF. Determined by the CHNS elemental analysis, the carbon content of NVOPF/rGO is 6.28 wt%. NVOPF/rGO is a Na-rich battery-type cathode with high-rate capability (Fig. S9) [42–44]. The NVOPF/rGO can provide the de-intercalated Na⁺ into the FeVO₄·0.6H₂O anode which delivers high ICE and excellent pseudocapacitive performance. In this case, the very complex and unsafe pre-sodiation treatment on the anode side is avoided, which could largely reduce the manufacturing processes and cost. Based on the capacity balance, the weight ratio of cathode: anode is 2:1. The total capacity and energy density of SICs are based on both mass of positive and negative materials. At first, as schematically shown in Fig. 4a, the three-electrode device by using sodium as reference (which is not involved in the electrochemical reaction) is used to record the electrochemical operation potential of each anode and cathode, respectively. This method is very important and useful to deeply investigate the operation function and mechanism of a whole device. The GV charge-discharge curves of the three-electrode device (Fig. 4b) at 1 C (1 C is defined as the current density of a full-discharge for 1 h) show the typical capacitor-like triangular shapes. The voltage windows of both electrodes barely change after cycling for 40 h, indicating that the full cells show high reversibility. Fig. 4c shows the charge-discharge profiles and actual potential (vs. Na⁺/Na) of cathode and anode at high rates. The charge or discharge potential of cathode and anode shifts with the increase of current density, owing to their different rate behavior and the internal resistance of the SIC. Thanks to the three-electrode device, it clearly proves that the potential shifts of cathode and anode are within the range of just 0.05 V. The actual operating potential of NVOPF/rGO cathode is within 3.5–4.1 V (vs. Na⁺/Na), and FeVO₄·0.6H₂O anode safely works in 0.9–3.1 V (vs. Na⁺/Na), indicating the excellent safety and stability of the SIC even at high rates. The assembled SIC makes full use of the two plateaus of the NVOPF/rGO cathode and the pseudocapacitive intercalation of FeVO₄·0.6H₂O, maximizing energy density of the devices even without any pre-sodiation treatments.

The two-electrode cell was assembled to confirm actual application. The operation mechanism of SIC is shown in Fig. 5a. During charge process, the Na⁺ ions de-intercalate from NVOPF/rGO cathode and then intercalate into the FeVO₄·0.6H₂O anode. At the discharge process, the Na⁺ ions move on the contrary. The charge-discharge curves at 0.06 A g⁻¹ (Fig. 5b) display a pseudo-linear voltage response. The ICE of the SIC is 83%, which mainly depends on the ICE of FeVO₄·0.6H₂O anode. The SIC is assembled without any pre-sodiation on the anode material, highlighting the significance of high ICE of anode materials. The electrochemical impedance spectra (EIS) of SIC (Fig. S10) shows small high-frequency semicircles, referred to the low charge transfer resistance (Rct) of ~5 Ohm, indicating a fast charge transfer process. Subsequently, the rate performance of the SIC was tested based on two-electrode systems (Fig. 5c), which was basically consistent with the result of the three-electrode results. The SIC delivers a high discharge capacity of ~54
mAh g\(^{-1}\) at 0.06 A g\(^{-1}\) (1 C). The SIC displays excellent high-rate performance: a reversible capacity of \(\sim 42\) mAh g\(^{-1}\) at 0.6 A g\(^{-1}\) (15 C), 31 mAh g\(^{-1}\) at 2.4 A g\(^{-1}\) (90 C) and 25 mAh g\(^{-1}\) at 4.8 A g\(^{-1}\) (260 C). Long-term stability of the SIC at the high rate of 1 A g\(^{-1}\) (24 C) is shown in Fig. 5d, after initial cycling at low current density (Fig. S11). The capacity retention maintains at 70%, 65%, 60% after 1000, 2000 and 5000 cycles. The related charge-discharge curves of the SIC (Fig. 5e) remain similar during the long-term cycles.

Energy density and average power density of the SIC were calculated based on the results of rate performance, as shown in the Ragone plots (Fig. 5f). The SIC exhibits a maximum energy density of \(88\) Wh kg\(^{-1}\) at a power density of \(95\) W kg\(^{-1}\). At the high power of 0.9, 1.7 and 3.4 kW kg\(^{-1}\), the delivered energy density is 63, 55, 45 Wh kg\(^{-1}\), respectively. When the output power ability is much enlarged to 7.9 kW kg\(^{-1}\), the energy density is 35 Wh kg\(^{-1}\). Comparing to the reported state-of-the-art SICs, even those anodes had additional electrochemical presodiation treatment [28,45–47], our assembled SIC delivers much better high energy and power density, as well as ultra-long cycling stability.

Fig. 5. Electrochemical performance of the SIC based on two-electrode systems. (a) Schematic diagram of FeVO\(_4\) -0.6H\(_2\)O//NVOPF/rGO SIC. The charge-discharge curves at 0.06 A g\(^{-1}\) (b) and the rate capacity (c) of the SIC. (d, e) Long-term cycling performance of the SIC and the related charge-discharge curves at different cycles at 1 A g\(^{-1}\). (f) Ragone plots of FeVO\(_4\) -0.6H\(_2\)O//NVOPF/rGO SIC, and the comparisons with the reported state-of-the-art SIC: V\(_2\)O\(_5\)//AC [45], TiO\(_2\)//AC [46], Nb\(_2\)O\(_5\)//AC [28], Ti\(_2\)CT\(_x\)//Na\(_2\)Fe\(_2\)(SO\(_4\))\(_3\) [47].
4. Conclusion

In conclusion, pseudocapacitive sodium-ion intercalation of FeVO$_2$⋅0.6H$_2$O nanowires is demonstrated and successfully applied in the assembly of a novel SIC. The deep sodiation (or lithiation) reaction of FeVO$_2$⋅0.6H$_2$O anode is separated into two steps: ion intercalation and amorphization transformation. Especially, it is proved that Na⁺ intercalation reaction of FeVO$_2$⋅0.6H$_2$O presents a pseudocapacitive behavior. The pseudocapacitive sodium-ion storage behavior (93% of capacity from the pseudocapacitance at a sweep rate of 1 mV s$^{-1}$) naturally enables the high-rate ability. In addition, the pseudocapacitive sodium-ion intercalation of FeVO$_2$⋅0.6H$_2$O anode delivers high capacity, high ICE, remarkable rate capability and cycling stability. We have demonstrated the FeVO$_2$⋅0.6H$_2$O as an effective anode for developing a new prototype of SIC. In this case, previous complex and unsafe pre-processing steps are waived. Based on the intuitive evaluation of three-electrode system, the electrode in FeVO$_2$⋅0.6H$_2$O/NVOPF/rGO SIC shows a tiny potential drift (0.05 V), which is conductive to realize the long-term cycles and high safety of SIC. The FeVO$_2$⋅0.6H$_2$O/NVOPF/rGO SIC delivers a high specific energy of 88 Wh kg$^{-1}$, high energy density of 35 Wh kg$^{-1}$, and power density of 7.9 kW kg$^{-1}$ (with an energy density of 35 Wh kg$^{-1}$), as well as stable 5000 cycles. This work presents the significant advantages of intercalation pseudocapacitance for obtaining both high energy and high power SICs.

Declaration of competing interest

The authors declare that they have no known competing interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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