Research Article

Large Scale One-Pot Synthesis of Monodispersed $\text{Na}_3(\text{VOPO}_4)_2\text{F}$ Cathode for Na-Ion Batteries

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Received 23 November 2021; Accepted 31 December 2021; Published 8 February 2022

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Na-ion batteries (NIBs) have received significant interest as potential candidates for large-scale energy storage owing to the widespread distribution of sodium and superior low-temperature performance. However, their commercial application is usually hindered by the high production cost and inadequate performance for electrode materials, particularly for cathodes. $\text{Na}_3(\text{VOPO}_4)_2\text{F}$ (NVOPF) has been recognized as one of the most promising cathodes for high-energy NIBs owing to the high working voltage and energy density. Here, we report a facile highly efficient room-temperature solution protocol for large-scale synthesis of NVOPF cathode for NIBs. By simply regulating pH, NVOPF can be obtained, which delivered a discharge capacity of 120.2 mAh g^{-1} at 0.1 C and 72% capacity retention over 8000 cycles at 25 C . Besides, the kilogram-level NVOPF products have been synthesized, and 26650 cylindrical cells were fabricated, which exhibit excellent cycling stabilities, remarkable low-temperature performance with comparable safety features. We hope our findings could provide insights on the industrial application of NVOPF in NIBs.

1. Introduction

Rechargeable Na-ion batteries (NIBs) have attracted extensive attention owing to the outstanding virtues, including abundant sodium resources, low cost, and similar working principle to lithium-ion batteries (LIBs), making NIBs the promising candidate for highly efficient and large-scale energy storage systems (ESSs) [1–4]. The cathode, as the critical component determining the energy density of NIBs, has accordingly captured comprehensive attention [5–7]. Up to now, substantial efforts have been devoted to the development of high-performance cathode materials including layered oxides, Prussian blue analogues, and polyanionic materials, which show distinguishable electrochemical behavior owing to the varied intrinsic structure characteristics [8–11]. Among them, V-based polyanionic compounds usually exhibit superior long-term cycling stability due to

their open 3D host skeleton and strong inductive effects, such as $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ [12, 13], NaVOPO_4 [14], $\text{Na}_3(\text{VPO}_4)_2\text{F}_3$ [15], $\text{Na}_3(\text{VOPO}_4)_2\text{F}$ [16], and $\text{Na}_7\text{V}_3(\text{P}_2\text{O}_7)_4$ [17] [18–20]. In particular, the series compounds $\text{Na}_3(\text{VO}_{1-x}\text{PO}_4)_2\text{F}_{1+2x}$ ($0 \leq x \leq 1$, NVPFs) have been extensively investigated because they could offer high capacity ($128\text{--}130 \text{ mAh g}^{-1}$) with a two-electron transfer and high operating voltage ($3.6\text{--}4.1 \text{ V}$) [21–30]. Besides, they often present high ionic-conductivity property and stable crystal structure, which is suitable well for the high-energy NIBs [26, 31–34]. However, the high preparation cost rooted in the synthetic strategy limits the scale-up production for sodium vanadium fluorophosphates.

Up to now, various methods for the preparation of NVPFs have been reported. Among them, the solid-state approach based on high temperature was typically adopted in the synthesis of NVPFs. There is no doubt that high

energy consumption from the solid-state method will increase the cost of ESSs. Meanwhile, the products usually show irregular morphologies or even heterogeneous compositions accompanied by impurity derived from the severe volatilization of VF_3 , leading to poor electrochemical performance [30, 32, 35–37]. Furthermore, HF would corrode the equipment at high temperature. Beyond that, liquid-phase syntheses were developed rapidly in recent years, to reduce energy consumption and rationally regulate the morphologies for better electrochemical performance. As an example, Goodenough et al. synthesized NVOPF via solvothermal method, which marks the evolution from high temperature to mild condition [38]. In 2015, Qi et al. developed a solvothermal low-temperature strategy for NVOPFs and firstly reported the room temperature preparation within dozens of days [39]. Very recently, our group developed a facile large-scale room-temperature controllable synthesis of NVOPF via a solution-phase method, which can remarkably reduce the manufacturing cost of the cathode materials within 6 days to get nearly 100% yield [30]. However, the long reaction cycle restricts the conversion rate of space and equipment, leading to a low production efficiency. Besides, like many other phosphate electrode materials, NVOPFs showed a low intrinsic electronic conductivity due to the separation of V atoms by $[\text{PO}_4]$ tetrahedral [40], which affects the Na^+ ion diffusion and then hinders its rate capabilities. To solve this problem, different strategies, such as coating with carbon [26, 36, 41–43] and doping with heteroatoms [44, 45], have been energetically developed and proven to have positive effects on improving the apparent and intrinsic electronic conductivity. While these modification methods always rely on the complicated high-temperature synthesis, which is not suitable for the common solution-based syntheses. Accordingly, to achieve high-performance polyanionic cathode via a simple low-cost approach requires precise regulation in the size and morphology of products, which offers shortened ion/electron transport pathways and sufficient prerequisites for high tap density NIBs.

In this work, a facile and highly efficient room-temperature solution-phase strategy for the fabrication of NVOPF was investigated. And the high-purity monodispersed NVOPF submicron-cuboids have been prepared by precisely regulating the solution's pH and substrate concentration. More importantly, the one-pot synthesis provided in this study can be easily scaled up to kilogram-level preparation of NVOPF to construct commercial cylindrical batteries. The potential mechanism for morphology formation and superior electrochemical performance has also been investigated by multidimensional experimental characterizations. Thus, the proposed room-temperature large-scale synthesis provides essential reference significance for the industrial application of NVOPFs in NIBs.

2. Experimental

2.1. Materials. Vanadylsulfate hydrate ($\text{VOSO}_4 \cdot x\text{H}_2\text{O}$, 99.9%, Alfa), sodium phosphate monobasic dihydrate ($\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$, 99%, Sigma), sodium fluoride (NaF , 99.99%, Aladdin), ammonium hydroxide ($\text{NH}_3 \cdot \text{H}_2\text{O}$, 28–

30 wt% solution of NH_3 in water, Acros), sodium perchlorate (NaClO_4 , 98–102%, Alfa), propylene carbonate (PC, 99.7%, Sigma-Aldrich), 4-fluoro-1,3-dioxolan-2-one (FEC, 98%, Alfa), and sodium metal (Na , 99%, Alfa). All above reagents were used as received without further treatment.

2.2. Synthesis of the $\text{Na}_3(\text{VOPO}_4)_2\text{F}$ (NVOPF). Firstly, a certain amount of $\text{VOSO}_4 \cdot x\text{H}_2\text{O}$ was dissolved in deionized water to form a homogeneous solution labeled as S1, and a certain $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$, NaF , and $\text{NH}_3 \cdot \text{H}_2\text{O}$ were dissolved in deionized water to form a homogeneous solution labeled as S2. Then, S1 and S2 were rapidly mixed to get solution S3 at 30°C , and the molar ratio of V: P: F in S3 was maintained at 1:3:1.7. Finally, the products were collected by filtration and washed several times with deionized water and ethanol and dried at 100°C for 6 h to obtain the final product.

2.3. Material Characterization. X-ray powder diffraction (XRD) was performed on a D8 advanced X-ray diffractometer (Bruker, Germany) using Cu K_α radiation ($\lambda = 1.5405 \text{ \AA}$). Scanning electron microscopy (SEM) images were acquired on a Hitachi S-4800 equipped with EDS (energy dispersive X-ray spectrometry) (Hitachi, Japan). Transmission electron microscopy (TEM) was conducted on a JEM-2100Plus (JEOL, Japan). Fourier transform infrared (FTIR) spectra were carried out on a VERTEX 70v Bruker spectrometer (Bruker, Germany). UV-vis absorption spectra (UV) were measured on a U-4100 spectrometer (Hitachi, Japan). X-ray photoelectron spectroscopy (XPS) was recorded using Thermo Scientific ESCLAB 250Xi (Thermo Fisher Scientific, America) equipped with monochromic Al K_α radiation. All spectra were calibrated for the charging effect with the C1s peak at 284.8 eV . Cyclic voltammetry (CV) was conducted on the CHI800D electrochemical workstation (Chenhua, China). Inductively coupled plasma atomic emission spectrometry (ICP-OES) was used to analyze the concentration of vanadium in the aqueous phase, conducted on Optima 7000DV (PerkinElmer, America).

2.4. Electrochemical Measurements. All the galvanostatic measurements of NVOPF were conducted with a 2032-type coin cell on a Land BT2000 battery test system (LANHE, China). The cathode sheets were prepared by mixing NVOPF, KB, and polytetrafluoroethylene (PTFE) in a mass ratio of 7:2:1 followed by rolling the composite to square thin slices subsequently dried at 120°C under high vacuum overnight, with the thickness of 0.1 mm . The active material loading is about $5\text{--}8 \text{ mg cm}^{-2}$ in the size of $6 \times 6 \text{ mm}$. Coin cells were assembled in a glove box under Ar. The liquid electrolyte ($200 \mu\text{L}$) used here was 1 M NaClO_4 in PC with 3 wt.% FEC as a functional additive. Na metal was adopted as an anode. The Whatman glass fiber was employed as the separator. During the charge and discharge process, the same current rate was used ($1 \text{ C} = 130 \text{ mA g}^{-1}$). The specific capacity is based on the mass of active material. The 26650 cylindrical cells using NVOPF as the cathode with hard carbon as the anode were manufactured at HiNa Battery Technology Co., Ltd.

3. Results and Discussion

For the room-temperature solution-phase synthesis of NVOPF particles, it is vital to balance different parameters, including raw materials, reaction time, additives, and pH. According to our previous experiments, VOSO_4 and $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ are ideal vanadium sources and phosphorus sources, respectively [36, 46]. NaF is widely used as a fluorine source for the synthesis of F-containing compounds. And the reaction of the three salts above has been written as below [36]:

We expect that the chemical reaction will go to the right following the chemical reaction balance if the by-product H_2SO_4 is removed from the reaction system. Furthermore, it has been reported that NVOPF would be dissolved in a strongly acidic solution. Therefore, we intentionally introduce $\text{NH}_3 \cdot \text{H}_2\text{O}$ into the reaction system to eliminate H_2SO_4 and predict that NVOPF can precipitate rapidly at room-temperature under an appropriate pH value.

Beyond our expectation, NVOPF particles form immediately as the solution of VOSO_4 was poured into the mixed solution of Na, P, and F sources with $\text{NH}_3 \cdot \text{H}_2\text{O}$, as recorded in Supplementary 2 Video S1. The XRD pattern of as-prepared samples was shown in Figure S1, which is well-indexed to the standard card (PDF# 97-041-1950). In this case, the reaction time has been greatly saved compared to the reported room-temperature synthetic process [30]. According to our previous work, pH value acts as an important role in the preparation of the objective products^{16,30,36,37}. Thus, we prepared different-pH solutions where the concentrations of V, P, and F were 0.07 mol L^{-1} , 0.21 mol L^{-1} , and 0.119 mol L^{-1} , respectively, and the pH values ranged from 3 to 8 were adjusted through adding different amounts of $\text{NH}_3 \cdot \text{H}_2\text{O}$. As expected, the highest yield of 99.2% can be reached at the pH of 6 with a fixed static time of 1 day. The vary of yields with increasing pH was listed in Table S1, resulting from ICP-OES tests.

Generally speaking, for a solution-based strategy, the particle size and microstructure can be rationally adjusted by regulating the concentration of the reactants. Herein, the concentrations of the raw materials were monitored with the invariant pH value at 6 (the as-prepared samples were marked as C1, C2, C3, C4, and C5), whose details and yields have been listed in Table S2. It can be seen that the yields have been slightly enhanced with the increasing concentration of precursors. The XRD profiles of products were recorded in Figure S2a, from which pure NVOPF has been obtained. And the microscopic morphologies of corresponding products were also recorded in Figure S2b-f, from which the particle size becomes smaller and smaller with increasing concentration. Although high reactant concentration favors the high yield, the small particle size will induce severe side reactions that consume electrolytes and reduce cycling stabilities. Therefore, we choose the concentration of C5 (Table S2) for further optimization, from which uniform

cuboids in modest submicron-size successfully achieved. Besides, we investigated the effect of aging time on the yield of NVOPF, as seen in Table S3. Results show that it could get a 98.7% yield at the moment of reactant mixing, and it slightly rises to 99.2% with a static time of 1 day. After 2 days' aging, it could achieve the complete conversion of V with the yield of ~100%. However, aging time benefits the crystallinity of as-prepared samples, as demonstrated in Figure S1. Based on the higher yield and better crystallinity, the 2 days' aging sample was chosen as the referral target to be further explored.

The typical morphologies of as-synthesized NVOPF were precisely observed by combining SEM and TEM, as shown in Figure 1. Monodispersed cuboids in size about 800 nm have been obtained from Figures 1(a)–1(c) from SEM. The lattice finger marked in Figure 1(d) from HR-TEM corresponds to the (101) plane of NVOPF. Figures 1(e) and 1(f) show the low-resolution images obtained from TEM, which further confirms the morphology observed from SEM. Considering the dynamic performance of NVOPF, the monodispersed submicron-cuboids could remarkably shorten transportation lengths for Na^+ and electrons, resulting in fast desodiation/sodiation transfer kinetics [41]. More importantly, differing from tens of submicron-sized particles that will consume lots of liquid electrolytes resulting in low Coulombic efficiencies and active materials utilization, the monodisperse 800 nm cuboids can efficiently reduce the consumption of liquid electrolyte and construct a uniform CEI on their surfaces. Furthermore, the uniform morphologies could efficiently homogenize current distribution and hence inhibit locally overcharge or overdischarge, contributing to utilizing the capacity of active materials sufficiently and holding the long-cycling stability. Besides, the EDS from SEM corroborates the uniform distribution of all containing elements in NVOPF, as shown in Figure S3.

Since NVOPF was first reported in 2002, there exists a debate about its crystal structure. In 2002, Massa showed a tetragonal NVOPF with $I4/mmm$ space group, while in 2011, Tsirlin et al. presented a tetragonal NVOPF with $P4_2/mnm$ space group [47, 48]. Up to now, some of the groups have believed NVOPF to be $I4/mmm$ space group [26, 30–33, 36, 39, 41, 42, 44, 46, 49–51], while others followed the $P4_2/mnm$ space group [52–55]. Herein, two Rietveld structural refinements for NVOPF have been carried out based on the $I4/mmm$ space group and $P4_2/mnm$ space group, respectively. The Rietveld refinement data of NVOPF have been listed in Table S4, from which it can be seen that better reliability factor values ($R_{wp} = 5.85\%$ and $R_p = 4.5\%$) for $I4/mmm$ space group have been obtained than those ($R_{wp} = 11.96\%$ and $R_p = 8.12\%$) for $P4_2/mnm$. Hence, we believe that our synthesized NVOPF belongs to the $I4/mmm$ space group whose crystallographic data were listed in Table S5. It has been reported that Na atoms show the more disordered distribution in $I4/mmm$, which will lead to superior dynamic properties [30]. The XRD profile and the Rietveld-refined results were shown in Figure 2(a). No traces of impurities and intermediate phases are detected, indicating the high purity of the as-

FIGURE 1: Material synthesis. (a)–(c) SEM images of NVOPF in different magnifications. (d) HR-TEM image of NVOPF. (e) and (f) TEM morphologies of NVOPF in different magnifications.

synthesized NVOPF. Figure S4 provides the tetragonal crystal structure diagram of NVOPF with a pseudolayered framework formed by a repeating unit parallel to the *ab* plane. The repeating unit is composed of $[\text{V}_2\text{O}_{10}\text{F}]$ bioctahedra and $[\text{PO}_4]$ tetrahedra connected by sharing O vertices. Along the *c* axis, in the $[\text{V}_2\text{O}_{10}\text{F}]$ bioctahedra, $[\text{VO}_5\text{F}]$ octahedra are bridged by F vertices located in the same *ab* plane as the disordered Na atoms. It has been proved that Na^+ diffuses in 2D channels between these pseudolayers, which contribute to the rapid desodiation/sodiation during the charge/discharge processes [33, 42, 56].

FTIR spectra were widely conducted in investigating the molecular structure of $\text{Na}_3(\text{VO}_{1-x}\text{PO}_4)_2\text{F}_{1+2x}$ ($0 \leq x \leq 1$) compounds. As shown in Figure 2(b), the FTIR spectrum of the synthesized product is highly consistent with the previously reported that of $\text{Na}_3(\text{VOPO}_4)_2\text{F}$ [27, 37]. The strong broad band ranging from 1000 cm^{-1} to 1200 cm^{-1} represents the asymmetric stretching vibration of the PO_4^{3-} group. The bands at 670 cm^{-1} and 555 cm^{-1} correspond to the P-O symmetric stretching vibration and bending vibration. More importantly, the V-O stretching vibration (916 cm^{-1}) is remarkably stronger than the V-F vibration (947 cm^{-1}), which is due to the more numbers of the V-O bonds than that of V-F bonds in the $\text{Na}_3(\text{VOPO}_4)_2\text{F}$ lattice [27, 30, 32, 37, 50]. In addition, UV-vis spectrum is a valuable tool to characterize the valence of V [30, 57]. Herein, the UV-vis spectra of the as-synthesized product, standard VCl_3 , and VOSO_4 samples were obtained in Figure 2(c). It can be identified that the absorption peaks of the synthesized product are similar to those of VOSO_4 but very different from those of VCl_3 . A maximum adsorption peak at 764 nm and a shoulder peak at 630 nm indicate V^{4+} in the synthesized product [36].

The electrochemical Na^+ -storage properties of as-synthesized NVOPF cuboids were gauged in coin half cells with sodium metal as the counter/reference electrode. The typical charge-discharge profiles of NVOPF at various cur-

rent densities are displayed in Figure 3(a). For the current density of 0.1 C, it presented two prominent charge-discharge plateaus located at around 3.6 V and 4.0 V with small polarizations, which can be described as a typical two-step reaction as follows:

Plateau at around 3.6 V:

Plateau at around 4.0 V:

As the current density increases, all the charge-discharge curves still exhibit two distinct plateaus accompanied by the increment of voltage hysteresis due to the increasing ohmic polarization, concentration polarization, and electrochemical polarization. The discharge capacities recorded at 0.1 C, 1 C, 2 C, 5 C, 10 C, 15 C, 20 C, and 25 C are 120.2 mAh g^{-1} , 119.5 mAh g^{-1} , 117.5 mAh g^{-1} , 116.3 mAh g^{-1} , 109.7 mAh g^{-1} , 103.4 mAh g^{-1} , 93.5 mAh g^{-1} , and 74.1 mAh g^{-1} , respectively, suggesting superior rate capability. Furthermore, the discharge capacity at 0.1 C could almost restore to its initial value of 118.2 mAh g^{-1} after the rate tests of 70 cycles as shown in Figure 3(b), only 1.7% capacity loss, indicating that NVOPF could operate at arbitrarily varied current densities.

To manifest the potential of NVOPF in high-power and long-life applications, we measured the ultrafast long-term charge-discharge performance at 25 C, as shown in Figure 3(c), respectively. As a result, the batteries exhibit ultralong cycling stability with 72% retention after 8,000 cycles, and the first discharge capacity reaches 75.7 mAh g^{-1} . Besides, a series of batteries operating at lower rates of 1 C, 2 C, 5 C, 10 C, 15 C, and 20 C, respectively, were

FIGURE 2: Crystal and electronic structure characterizations. (a) Rietveld-refined profiles of as-synthesized NVOPF from the proposed $I4/mmm$ space group according to Ref.2002. (b) FTIR spectrum of NVOPF. (c) UV-vis spectra of NVOPF, VCl_3 , and VOSO_4 .

recorded in Figure S5. As a result, all batteries exhibit excellent cycling stabilities, suggesting the outstanding electrochemical performance of the as-synthesized NVOPF. In terms of preparation cost and Na-storage performance, the current work shows the comparable comprehensive properties in contrast to the reported NVOPF cathodes for NIBs, as listed in Table S6. Besides, the half and full cell performances of the typical cathode materials prepared by room-temperature routes were summarized in Table S7. Compared to other materials, the current cathode exhibits the decent electrochemical performances.

Notably, the method proposed in this study can be easily scaled up. The synthesized kilogram-level NVOPF was shown in Figure 4(a) and made into large sheets on the coating production line, as shown in Figure S6a-b. Afterward, the prepared NVOPF cathode sheets were assembled into NVOPF-26650 cylindrical cells with the hard carbon as anodes, as shown in Figure 4(b). The 0.2C charge and

discharge results show that the prepared NVOPF-26650 cylindrical cell has a capacity of 1.78 Ah, as shown in Figure S6c, when cycled at 5C, the initial discharge capacity decreased to 0.99 Ah. And the capacity retention reaches up to 95.2% after 2000 cycles at 5C with high average Coulombic efficiency of near 100%, as shown in Figure 4(d), demonstrating the remarkable electrochemical performance and the practicability of the current strategy. Furthermore, the low-temperature performance of the prepared NVOPF-26650 cylindrical cell is tested at 25°C, -20°C, and -30°C, respectively, as shown in Figure 4(c). Before discharge, the charging process is conducted first at 0.2C at 25°C, and then discharging the cell at 0.2C at different temperatures. Taking the discharge capacity at 25°C as 100%, it can be seen that the discharge capacity retention rate is 78% at -20°C and 63.5% at -30°C, demonstrating the glorious low-temperature characteristic of the NVOPF-26650 cylindrical cell, superior to the LiFePO_4 -based cell shown in Figure 4(c).

FIGURE 3: Na-storage performance of half cell. (a) Charge-discharge profiles of NVOPF electrodes at different rates from 0.1 C to 25 C, and corresponding rate capability (b). Cycling performance of NVOPF electrodes at (c) 25 C.

The safety of the battery is the most crucial parameter of the battery. As shown in Figure S7a-d, we performed a nail penetration experiment on a fully charged NVOPF-26650 cylindrical cell. It can be seen that there is no fire or explosion in the cylindrical cell during the nail penetration process. Figure S7e shows the cylindrical cell after the nail penetration test, indicating that the NVOPF-26650 cylindrical cell has an excellent safety characteristic.

To elucidate the evolution process of NVOPF crystal structure during desodiation/sodiation and understand the underlying reasons for the outstanding electrochemical performance of the as-synthesized NVOPF, we carried out the in situ XRD measurement of the NVOPF electrode for the first two cycles at 0.1 C, as presented in Figure 5(a). For the new electrode, the XRD pattern is similar to that of the orig-

inal NVOPF powder, except for several diffraction peaks of the Al current collector (38.6° (111), 44.8° (200)). The detailed structural evolutions during cycling are monitored by the changes of selected peaks of 27.9° (200), 28.8° (103), 32.7° (202), 39.9° (220), 40.5° (213), 43.3° (301), 49.9° (303), 51.5° (006), 53.2° (224), 57.7° (400), 60.5° (402), and 61.6° (330). During the desodiation process, the (200) peak at 27.9° weakens gradually while shifts to higher degrees and finally merges with the (103) peak at 28.8° . Inversely, the (103) peak shifts to lower degrees with diminished intensity. The variations in the same trend are also detected for several other couples of adjacent peaks during the desodiation process, such as 39.9° (220)- 40.5° (213), 49.9° (303)- 51.5° (006), and 60.5° (402)- 61.6° (330). Besides, several other peaks at 32.7° (202), 43.3° (301), 53.2° (224), and 57.7° (400) also

FIGURE 4: Electrochemical properties of 26650 cylindrical cell. (a) Mass production of NVOF, (b) NVOF||carbon 26650 cylindrical cells, (c) low-temperature performance, and (d) cycling performance of 26650 cylindrical cells at 5 C.

exhibit lower and lower intensity when moved to higher degrees. As a result, two-Na extractions are achieved through the transformation from $\text{Na}_3(\text{VOPO}_4)_2\text{F}$ to $\text{Na}_2(\text{VOPO}_4)_2\text{F}$ and final $\text{Na}(\text{VOPO}_4)_2\text{F}$, as presented in equations (2) and (3). As expected, the XRD patterns change in the opposite direction and return to the pristine state during the subsequent sodiation process, demonstrating the excellent reversibility of NVOF during electrochemical cycling. Furthermore, the second desodiation/sodiation cycling of NVOF shows an entirely consistent trend of XRD patterns with that of the first cycling. Similar to earlier reports, no new phase appears during desodiation/sodiation, indicating the characteristics of a single-phase solid solution [27, 30, 31, 33, 55]. According to Bragg's law, we can evaluate the changes in lattice parameters a and c values with the Na content in the NVOF electrodes during desodiation, as shown in Figure S8. The a value decreases continuously with extracting Na^+ from the crystal lattice, originating from the increasing positive electricity and decreasing cationic radius of V. In contrast, the c value constantly increases due to the rising repulsive force between the pseudolayers. The volume change is only 2.7% at the end of desodiation by calculating the volume of unit cells, suggesting a

minimal lattice strain during the desodiation/sodiation processes. Accordingly, this explains that the high cycling stability of NVOF is due to the high structural reversibility and minor lattice strain during the desodiation/sodiation.

To illuminate the root cause of the high-rate electrochemical capabilities of NVOF, we conducted CV measurement at various scan rates to explore the Na^+ -migration kinetics in NVOF crystal lattice, as shown in Figures 5(b)–5(d). The CV profile recorded at 0.03 mV s^{-1} equaling to 0.1 C reveals two couples of redox peaks (O1/R1 and O2/R2) as presented in Figure 5(b). The first couple centered at 3.65/3.56 V corresponds to the activity of $\text{V}^{4+}/\text{V}^{5+}$ attributed to the reversible $\text{Na}^+(2)$ extraction and insertion. The second couple centered at 4.07/3.97 V corresponds to the activity of $\text{V}^{4+}/\text{V}^{5+}$ attributed to the reversible $\text{Na}^+(1)$ extraction and insertion [26]. The good linear relationships for plots of I_p vs. $\nu^{1/2}$ have been obtained as shown in Figure 5(d), resulting from CV curves at different scan rates as presented in Figure 5(c). The excellent fitting results imply that the electrochemical desodiation/sodiation processes are diffusion-controlled [26, 35, 43, 50, 58]. Therefore, the Na^+ -diffusion coefficient (D_{Na^+}) is calculated on the basis

FIGURE 5: Structure evolution and Na⁺ diffusion characteristic. (a) In situ XRD patterns and corresponding charge-discharge curves for NVOPF in the first two cycles. (b) The CV curve at a scan rate of 0.03 mV s⁻¹. (c) CV curves at different scan rates for NVOPF. (d) A linear relation between I_p and $v^{1/2}$ for NVOPF.

of Randles-Sevcik equation [29, 35]:

$$I_p = 2.69 \times 10^5 n^{3/2} A C_0^* D_{Na^+}^{1/2} v^{1/2}, \quad (4)$$

where I_p is the peak current (A), n stands for the number of transferred electrons, A is the area between electrode and electrolyte, C_0^* is Na⁺ concentration in the electrode, D_{Na^+} is Na⁺ diffusion coefficient (cm² s⁻¹), and v is the scan rate (V s⁻¹). For simplification, here, A is approximated to be the electrode area (0.64 cm²), and C_0^* is estimated from the crystallographic cell parameter of NVOPF.

Accordingly, a series of D_{Na^+} values can be calculated as 7.8×10^{-9} cm² s⁻¹ (O1), 2.6×10^{-9} cm² s⁻¹ (R1), 1.1×10^{-8} cm² s⁻¹ (O2), and 5.8×10^{-9} cm² s⁻¹ (R2). The high D_{Na^+} values at different reaction stages indicate that as-synthesized NVOPF would have superior rate performance. Besides, O2/R2 redox pair displays higher D_{Na^+} values than

those of the O1/R1 redox pair, suggesting that the desodiation/sodiation process kinetic at around 4.0 V is superior to that at about 3.6 V, and the charge/discharge profiles at low temperatures further confirm this point.

Furthermore, ex situ XPS spectra were conducted to examine the changes of the V oxidation state during the desodiation/sodiation process. Figure S9 shows that the binding energy in the original powder is 517.12 eV/524.62 eV, corresponding to V⁴⁺. During the desodiation process, the characteristic peaks of V gradually moved towards high binding energies. Generally, in the same crystal structure, the binding energies of elements will increase with increasing the oxidation state of elements. Hence, the oxidation state of V in the NVOPF electrode gradually increased with increasing the charging depth from the original V⁴⁺ to fully charged-state V⁵⁺. More importantly, the binding energies changed in the opposite direction and almost returned to the pristine state before desodiation

during the subsequent sodiation process. The binding energy values of V in the NVOPF electrode at different charge-discharge voltage were listed in Table S8. During desodiation/sodiation, the slight difference of binding energies at the same voltage is due to the electrochemical polarization. Therefore, the XPS spectra confirm the reversible transformation of the V oxidation state between V^{4+} and V^{5+} in the NVOPF electrode during desodiation/sodiation, indicating the electrochemical activity of the NVOPF is highly reversible. Besides, the XPS results agree well with the results of in situ XRD.

To further understand why capacity fading after cycles and provide valuable references for further enhancement of electrochemical performance, a simple analysis of battery failure was carried out. After cycled for 8,000 cycles, the coin cell has been disassembled, as shown in Figure S10a, from which it can be seen that the electrolyte is almost dry. The XRD patterns of original and cycled electrode sheets were compared, where there is little change, as shown in Figure S10b. Besides, SEM characterization was carried out to observe the change in morphology of NVOPF as presented in Figure S11; the submicron-cuboids morphology is maintained, indicating the excellent structure stability of NVOPF. Therefore, the fade of capacity could be ascribed to the degradation of the electrolyte. Consequently, we believed that the electrochemical performance of NIBs based on NVOPF would be further improved by optimizing the electrolyte.

4. Conclusions

In summary, a facile and room-temperature strategy for the large-scale fabrication of NVOPF submicron-cuboids has been developed for the first time. Besides, the controllable synthesis of monodispersed NVOPF particles can be realized through regulating pH value and reactant concentration. The as-prepared NVOPF cuboids present superior rate capability and excellent cycling performance of 72% capacity retention at 25 C over 8000 cycles, which can be attributed to the specific submicron-sized morphology with shortened diffusion path, and the reversible crystal structural evolution with small volume change. More importantly, kilogram-grade NVOPF product can be easily obtained via such a facile one-pot strategy. To demonstrate the practical application of NVOPF product, commercial 26650 cylindrical batteries were conducted to exhibit impressive cycling stabilities at 5 C, remarkable low-temperature performance at -30°C , and great safety characteristics during nail penetration. The facile and high-efficient room-temperature strategy and commercial tests referred in the current work provide a critical reference to the future industrial manufacture of NVOPF.

Data Availability

The data and materials used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare no conflicts of interest.

Authors' Contributions

Q.Q.Z., X.S., and Q. Z contributed equally to this work. J.M.Z and Y.S.H. proposed and designed the project. Q.Q.Z., X.S., and Q. Z performed the experiments. K.X.L prepared the 26650 cylindrical cells, and F.X.D carried out the in situ XRD characterization. All the authors contributed to the write-up of the article. Qiangqiang Zhang, Xing Shen, and Quan Zhou contributed equally to this work.

Acknowledgments

This work was supported by the National Natural Science Foundation (NSFC) of China (51725206, 52122214, and 52072403), Beijing Natural Science Foundation (2222078), the Science and Technology Project of Inner Mongolia (2021GG0162), the Strategic Priority Research Program of the Chinese Academy of Sciences (XDA21070500), Youth Innovation Promotion Association of the Chinese Academy of Sciences (2020006), Beijing Municipal Natural Science Foundation (2212022), and Innovation Academy for Green Manufacture, CAS (IAGM2020C07).

Supplementary Materials

Supplementary 1. Figure S1: the XRD pattern of as-prepared sample with varied aging time. Figure S2: (a) XRD patterns of as-synthesized NVOPF in different salts concentration. SEM images of as-synthesized NVOPF in different salts concentration (b) C1, (c) C2, (d) C3, (e) C4, and (f) C5. Figure S3: SEM-EDX elements mapping of NVOPF. Figure S4: crystal structure diagram of NVOPF with the $I4/mmm$ group. Figure S5: cycling performance of NVOPF at 1 C, 2 C, 5 C, 10 C, 15 C, and 20 C current rates, respectively. Figure S6: NVOPF-26650 cylindrical cell. (a) NVOPF electrode paste, (b) NVOPF sheet, and (c) charge-discharge curves at 0.2 C and 5 C. Figure S7: NVOPF-26650 cylindrical cell safety test: nail penetration. Figure S8: the evaluation of unit cell parameters a and c in the process of desodiation. Figure S9: ex situ XPS spectra at different charge-discharge states of NVOPF. Figure S10: (a) optical photograph of the disassembled cell after cycled for 8,000 cycles. (b) XRD patterns of original and cycled electrode sheets. Figure S11: SEM images of NVOPF after 8,000 cycles. Table S1: yields of NVOPF in different pH values with fixing salt concentration and aging time. Table S2: yields of NVOPF in different salts concentration with fixing pH = 6 and aging time. Table S3: yields of NVOPF in different aging time with fixing pH = 6 and salts concentration of C5. Table S4: crystallographic and Rietveld refinement data of as-synthesized $\text{Na}_3(\text{VOPO}_4)_2\text{F}$. Table S5: atomic coordinates, cation, and anion occupancies of $\text{Na}_3(\text{VOPO}_4)_2\text{F}$. Table S6: the comparison of synthesis and electrochemical performance for $\text{Na}_3(\text{VOPO}_4)_2\text{F}$ between the present literatures and this work. Table S7: the performance comparison for the recent-developed cathode materials obtained by room-temperature routes for

NIBs. Table S8: binding energy values of V in the NVOFP electrode at different charge-discharge voltage. *Supplementary 2*. Video S1: the video of the moment for the synthesis of NVOFP particles as the solution of VOSO_4 was poured into the mixed solution of Na, P, and F sources with $\text{NH}_3\cdot\text{H}_2\text{O}$. (*Supplementary Materials*)

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