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A Novel Process for the Synthesis of NaV₂O₅ Mesocrystals from Alkaline-Stripped Vanadium Solution via the Hydrothermal Hydrogen Reduction Method

Guobin Zhang ^{1,*}, Yimin Zhang ^{1,2,*}, Shenxu Bao ¹ and Liuhong Zhang ²

- School of Resources and Environmental Engineering, Hubei Key Laboratory of Mineral Resources Processing and Environment, Wuhan University of Technology, 122 Luoshi Road, Wuhan 430070, China; sxbao@whut.edu.cn
- ² State Environmental Protection Key Laboratory of Mineral Metallurgical Resources Utilization and Pollution Control, Hubei Collaborative Innovation Center for High Efficient Utilization of Vanadium Resources, Wuhan University of Science and Technology, 947 Heping Road, Wuhan 430081, China; zhangliuhong1994@163.com
- * Correspondence: zgb@whut.edu.cn (G.Z.); zym126135@126.com (Y.Z.); Tel.: +86-027-6886-2876 (Y.Z.)

Received: 27 March 2019; Accepted: 29 April 2019; Published: 1 May 2019



Abstract: NaV₂O₅ mesocrystals were successfully synthesized from an alkaline-stripped pentavalent vanadium solution through a novel hydrothermal hydrogen reduction process. The optimal conditions for the hydrogen partial pressure, reaction temperature, initial solution pH value, and reaction time for the pure-phase NaV₂O₅ synthesis were ascertained to be 4 MPa, 200 °C, 4.0, and 2 h, respectively. The synthesis time (only 2 h) was greatly shortened, by nine times, compared with the most time-saving (18 h) hydrothermal process at present. X-ray diffraction (XRD) analysis revealed that the as-prepared powders demonstrated a typical layered orthorhombic structure of NaV_2O_5 . The purity of the as-prepared NaV_2O_5 reached up to 99.98%. An electrochemical test showed that the as-prepared NaV_2O_5 has a potential application in sodium ion batteries. According to scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analyses, the as-prepared NaV_2O_5 powders were identified to have rod-like mesocrystals consisting of small rods which preferentially grow along the (010) direction. Furthermore, the phase transformation mechanism and crystal growth mechanism in NaV₂O₅ preparation were discussed systematically, based on which the synthesis mechanism of NaV_2O_5 was proposed as pentavalent vanadates pre-sedimentation, hydrogen reduction with dehydration, sodium ions insertion, and finally self-assembly oriented attachment. The synthesis process is characterized as time-saving and low-cost, and thus it may have great application prospects.

Keywords: NaV2O5; hydrothermal; hydrogen reduction; vanadium

1. Introduction

Vanadium (V) and its compounds have been widely used in many fields such as electrode materials, catalysts, steel alloys, V redox flow battery, advanced materials, and the chemical industry [1–4]. NaV₂O₅ is one of the typical layered alkali vanadates of orthorhombic structure. In the NaV₂O₅ structure, Na-ions are located in the interlayer space [5–7]. NaV₂O₅ initially drew much attention for its spin-Peierls property [8–15]. In recent years, NaV₂O₅ has been considered to have a potential application as the cathode material in lithium ion batteries or sodium ion batteries owing to its layered orthorhombic structure [16–19]. Therefore, the preparation of NaV₂O₅ has been attracting increasing attention.



NaV₂O₅ can be prepared by a solid-state reaction process, but this process requires a reaction temperature of 650 °C and a long reaction time (more than two days) [20–23]. In order to lower the reaction temperature, some hydrothermal methods have been developed [5,6,16–18,24]. In the hydrothermal methods, V₂O₅, NH₄VO₃, and NaVO₃ are usually used as vanadium resources, NaOH and Na₂CO₃ are usually used as sodium resources, and NH₂OH·HCl, ethylene diamine tetraacetic acid (EDTA), H₂C₂O₄, and Na₂C₂O₄ are usually used as reducing agents. Through hydrothermal methods, the reaction temperature for the preparation of NaV₂O₅ can be lowered to about 200 °C, while the reaction time still must be at least 18 h. Moreover, reducing agents such as NH₂OH·HCl and EDTA are very expensive. The long reaction time and the high price of the agents are disadvantages for the large-scale preparation and application of NaV₂O₅. Therefore, there is high demand for the development of a time-saving and low-cost process to prepare NaV₂O₅.

Vanadium-bearing shale is a unique and a strategic vanadium resource that is used in China. Vanadium-bearing shale is also an important raw material for the preparation of V_2O_5 , NH₄VO₃, NaVO₃, and other vanadium compounds through various vanadium extraction processes [25]. Alkaline-stripped pentavalent vanadium solution (ASPVS) is a vanadium-enriched solution obtained in the vanadium extraction process. The typical flowsheet for ASPVS formation is shown in Figure 1 [26]. The extraction agent for pentavalent vanadium (V(V)) ions enrichment is trialkylamine and the stripping agent is sodium hydroxide solution. After the formation process, the ASPVS containing vanadium (V) and sodium (Na) with high concentrations as well as trace impurity ions is prepared [26]. Hence, ASPVS may be expected to be both a sodium resource and a vanadium resource for the preparation of NaV₂O₅.



Figure 1. Typical flowsheet for alkaline stripped pentavalent vanadium solution formation.

In previous research, a vanadium precipitation process of hydrothermal hydrogen reduction (HHR) for synthesizing V_2O_3 from ASPVS was first developed [27,28]. In the research, it was found that V(V) ions in the solution could be reduced to trivalent vanadium (V(III)) compounds or tetravalent vanadium (V(IV)) compounds by hydrogen (H₂). In the HHR reaction, the thermodynamic feasibility of the reaction increases as the solution pH value decreases, while the activity of hydrogen (H₂) and the solubility of hydrogen increase as the reaction temperature and the hydrogen partial pressure increase, respectively. Therefore, the degree of the reduction of the product obtained by this method is related to the solution pH value, reaction temperature, hydrogen (H₂) gas partial pressure, and reaction time. Additionally, it was found that NaV₂O₅ was first precipitated from ASPVS in the HHR process, which was further transformed to VO₂(H₂O)_{0.5} and finally reduced to V₂O₃. Therefore, it is reasonable to prepare pure-phase NaV₂O₅ through the HHR method by controlling reaction conditions. If so, the synthesis process can be low-cost, because ASPVS and H₂ are much cheaper than the raw materials

and reducing agents used in the previous processes. Moreover, it will be more exciting if the synthesis time can be greatly shortened.

In this paper, the HHR method for preparing pure-phase NaV_2O_5 from ASPVS is proposed. Through controlling the reaction temperature, solution pH value, H₂ consumption, and reaction time, the pure-phase NaV_2O_5 was successfully synthesized. The effects of different synthesis conditions on the vanadium precipitation percentage and the phase composition of the as-prepared product were investigated in detail. Importantly, the reaction time was shortened to 2 h. Furthermore, the synthesis mechanism of NaV_2O_5 was revealed in detail.

2. Materials and Methods

2.1. Materials and Reagents

Alkaline stripped pentavalent vanadium solution was prepared from vanadium-bearing shale by a typical vanadium extraction process [26]. H₂ gas (99.9% purity) and N₂ gas (99.9% purity) were used as the reducing agent and flushing gas, respectively, in the experiment. Distilled water was used in the whole process.

2.2. Synthesis Methods

For NaV_2O_5 synthesis, ASPVS (150 mL) was first adjusted to a certain pH value by sulfuric acid to prepare the feed solution. The feed solution was then poured into a 250 mL autoclave. The autoclave was flushed by N_2 gas three times. After this was done, it took 1 h to heat the solution to the reaction temperature, following which H_2 gas was transferred into the autoclave. After the hydrothermal reaction had taken place for a certain period of time, the heating procedure was turned down to cool the autoclave. The collected powder was first washed by distilled water and then dried at 90 °C for 10 h to obtain the final product.

2.3. Characterization

The phase composition of the as-prepared product was analyzed by X-ray diffraction (XRD, D/MAX 2500PC, Rigaku, Tokyo, Japan) using Cu Kα radiation. The micro morphology of the product was investigated by scanning electron microscopy (SEM, JSM-IT300, JEOL Ltd., Tokyo, Japan) and transmission electron microscopy (TEM, JEM-2100F, JEOL Ltd., Tokyo, Japan). The elemental analysis was conducted on an energy-dispersive spectrometer (EDS, X-Act, Oxford Instruments, Oxford, UK). The concentration of the solution and the chemical composition of the product were detected through inductively coupled plasma–atomic emission spectroscopy (ICP–AES, Optima-4300DV, Perkin Elmer, Waltham, MA, USA).

2.4. Electrochemical Testing

The electrochemical performance of the obtained NaV₂O₅ was characterized by coin cell assembly (2016-type). The obtained NaV₂O₅, acetylene black, and polyvinylidene difluoride (10 wt.%) were mixed well in weight ratios of 8:1:1, dissolved in N-methyl pyrrolidone solution to obtain a slurry. The obtained slurry was coated uniformly onto aluminum foil, and then dried at 90 °C for 12 h. The dried aluminum foil was punched into round discs with a diameter of 8 mm. The surface density of active materials was about 2 mg·cm⁻². The coin cell (2025) was assembled in an argon-filled glove box with sodium metal as the counter electrode and Grade GF/D (Whatman, Maitstone, UK) as the separator. NaPF₆ (1.0 mol/L) dissolved in ethylene carbonate/ethyl methyl carbonate (weight ratio of 3:7) was used as the electrolyte solution. Galvanostatic charge/discharge measurement was performed by a multichannel battery testing system (LAND CT2001A, 5V10Ma-K, Wuhan Blue Electronic Co. Ltd., Wuhan, China) at a current density of 100 mA·g⁻¹ with a voltage region between 0.01 and 3.0 V.

2.5. Data Treatment

Equation (1) was used to calculate the V precipitation percentage:

$$\gamma = [1 - (\alpha V_{\alpha} / \beta V_{\beta})] \times 100\% \tag{1}$$

where γ stands for the V precipitation percentage (%), α stands for the V concentration (mg/L) of the filtrate, β stands for the V concentration of the feed solution, V_{α} stands for the volume (L) of the filtrate, and V_{β} stands for the volume (L) of the feed solution.

3. Results and Discussion

The concentrations of the main elements in the alkaline-stripped pentavalent vanadium solution are listed in Table 1. As shown in Table 1, the concentrations of V and Na in the solution reached up to 20.5 g/L and 23.1 g/L, respectively, while the concentrations of other elements were very low. Thus, the solution can be used to prepare NaV₂O₅.

Table 1. Concentrations of the main elements in the alkaline-stripped pentavalent vanadium solution (ASPVS).

Items	V	Na	Р	Al	Fe	Si	Mg
Concentration (g/L)	20.5	23.1	0.013	0.009	0.007	0.012	0.008

3.1. Effect of Initial Solution pH Value

To investigate the effects of the initial solution pH value during NaV_2O_5 preparation, several experiments at different initial solution pH values were conducted. The reaction temperature, H_2 gas partial pressure, and reaction time were fixed at 200 °C, 4 MPa, and 2 h, respectively.

Figure 2 shows that V precipitation percentage decreased from 99% to 11% when the initial solution pH value increased from 4.0 to 12.0. This result indicates that the increase of the initial solution pH value can hinder the reaction proceeding efficiency, because the increase of the initial solution pH can cause the decrease of the thermodynamic driving force of the reaction during the HHR process for vanadium precipitation [27]. Therefore, the initial pH of the solution should be kept at a relatively low value in order to obtain a high recovery.



Figure 2. The effect of initial solution pH value on vanadium precipitation percentage.

As shown in Figure 3a,d,e, the diffraction peaks of the products prepared from solutions with initial pH values of 4.0, 7.0, and 8.0 were all attributed to NaV_2O_5 , indicating that the as-prepared powders were pure-phase NaV_2O_5 . The phase compositions of the products prepared from solutions with initial pH values of 5.0, 6.0, and 9.0 were identified as NaV_2O_5 mixed with $VO_2(H_2O)_{0.5}$ (Figure 3b,c,f). When the initial pH value was increased above 10.0, the phase of NaV_2O_5 could not be detected in the product and the as-prepared products were ascertained as $VO_2(H_2O)_{0.5}$ (Figure 3g,h,i).



Figure 3. The phase compositions of the products prepared from solutions with different initial pH values of (a) 4.0, (b) 5.0, (c) 6.0, (d) 7.0, (e) 8.0, (f) 9.0, (g) 10.0, (h) 11.0, and (i) 12.0 under a reaction temperature of 200 °C, a H₂ gas partial pressure of 4 MPa, and a reaction time of 2 h.

As shown in Figure 4, the increasing trend of the final pH value was not the same as the increase of the initial pH value. Unexpectedly, the final pH values from initial pH values of 7, 8, and 9 were lower than the final pH values from initial pH values of 5 or 6. However, it was common for the final pH value to be higher than the initial pH value, which indicated that the reaction could consume hydrogen ions. So, the final pH value of the solution during the reaction depends on the percentage of the vanadium precipitation. As the vanadium percentages at initial pH values of 7, 8, and 9 were much lower than the vanadium percentage at an initial pH of 6 (Figure 2), the final pH values at initial pH of 7, 8 and 9 were lower than the final pH values at initial pH values of 5 or 6.

Combining the results shown in Figure 3 with the results shown in Figure 4, when the final solution pH value was below 8.6 (the corresponding initial pH values were 4, 7, and 8), the product obtained was identified as the pure-phase NaV₂O₅. When the final solution pH value was between 8.6 and 10.6 (the corresponding initial pH values were 5, 6, and 9), the phase of the prepared product was identified as NaV₂O₅ mixed with VO₂(H₂O)_{0.5}. As the final pH value of the solution was above 10.7 (the corresponding initial pH values were 10, 11, and 12), the product obtained was ascertained to be VO₂(H₂O)_{0.5}. Some researchers found that the solubility of NaV₂O₅ dropped sharply when the solution pH value was above 9.0 [24]. Hereby, it is rational to conclude that some V(IV) in the reduced solution would preferentially precipitate from the solution in the form of VO₂(H₂O)_{0.5} instead of NaV₂O₅ cannot precipitate from the solution and all the V(IV) in the reduced solution will form the VO₂(H₂O)_{0.5} precipitates. Therefore, the solution pH value for the preparation of pure-phase NaV₂O₅

should be controlled below 8.6. As the solution pH value increase as the reaction progresses, the range of the reaction solution pH values needs to be controlled by the initial solution pH value.



Figure 4. The effect of the initial solution pH value on final solution pH value.

To save the consumption of sulfuric acid during the process of adjusting pH value, the optimal initial solution pH value for the synthesis of the pure-phase NaV_2O_5 with a high recovery was proposed to be 4.0.

3.2. Effect of Reaction Temperature

To investigate the effects of reaction temperature during NaV_2O_5 preparation, several experiments with different reaction temperatures were conducted. The initial solution pH value, H₂ gas partial pressure, and reaction time were fixed at 4.0, 4 MPa, and 2 h, respectively.

Figure 5 shows that the V precipitation percentage increased from 86% to 99% by raising the reaction temperature from 150 to 200 °C. However, by further raising the reaction temperature, the V precipitation percentage was no longer increased. This result indicates that the increase of the reaction temperature is beneficial to the HHR reaction, because the increase of the temperature can enhance the reaction activity of hydrogen [29,30].

As shown in Figure 6, only a few diffraction peaks of the product obtained at 150 °C were attributed to the desired product of NaV₂O₅, most of which were indexed to a mixture of V(V) vanadates of Na₂V₆O₁₆·3H₂O and Na₂V₆O₁₆. This result revealed that the reaction activity of H₂ at 150 °C was too low to reduce all the V(V) to NaV₂O₅. After increasing the reaction temperature to 175 °C, the characteristic peaks ascribed to Na₂V₆O₁₆·3H₂O and Na₂V₆O₁₆ disappeared, and were replaced by the diffraction peaks ascribed to a mixture of NaV_{0.64}O₅ and NaV₂O₅ (Figure 6b). After increasing the reaction temperature to 200 °C, the product could be identified as the pure-phase NaV₂O₅ (Figure 6c). Moreover, the intensity of the diffraction peaks of NaV₂O₅ obtained at 200 °C was much stronger than that obtained at 180 °C. The diffraction peaks of the product obtained at 225 °C had no obvious change (Figure 6d,e). Combined with the results obtained from Figure 5, it was revealed that almost all the V(V) (99%) can be reduced to the pure-phase NaV₂O₅ by H₂ gas with a facile reaction temperature of 200 °C.

To save the consumption of energy in heating the autoclave, the optimal reaction temperature for the synthesis of pure-phase NaV_2O_5 with a high recovery was proposed to be 200 °C.



Figure 5. The effect of reaction temperature on vanadium precipitation percentage.



Figure 6. The phase compositions of the products obtained at (**a**) 150 °C, (**b**) 175 °C, (**c**) 200 °C, (**d**) 225 °C, and (**e**) 250 °C under an initial solution pH value of 4, a H₂ gas partial pressure of 4 MPa, and a reaction time of 2 h.

3.3. Effect of H₂ Gas Partial Pressure

To explore the effects of H_2 gas partial pressure during NaV_2O_5 preparation, the initial solution pH value, reaction temperature, and reaction time were fixed at 4.0, 200 °C, and 2 h, respectively.

As shown in Figure 7, V precipitation percentage improved from 82% to 99% when the H_2 gas partial pressure was improved from 1 MPa to 4 MPa. V precipitation percentage had no obvious change when the H_2 gas partial pressure was increased above 4 MPa. This result indicates that the increase of the H_2 gas partial pressure can facilitate the hydrothermal hydrogen reduction reaction, because the increase of the H_2 gas partial pressure can enhance the thermodynamic driving force of the hydrothermal hydrogen reduction and increase the solubility of hydrogen in the solution [29,30].



Figure 7. The effect of H₂ gas partial pressure on vanadium precipitation percentage.

As shown in Figure 8a, when the H₂ gas partial pressure was only 1 MPa, the as-prepared product was a mixture of some pentavalent vanadates of Na₂V₆O₁₆·3H₂O, Na₆V₁₀O₂₈·18H₂O, and Na₂V₆O₁₆ and the reduced powers of Na_{0.287}V₂O₅ and NaV₂O₅. As the H₂ gas partial pressure was increased to 2 MPa, some diffraction peaks indexed to those pentavalent vanadates disappeared, and were replaced by the diffraction peaks ascribed to the desired product of NaV₂O₅ (Figure 8b). When the H₂ gas partial pressure was increased to 3 MPa, the amount of the diffraction peaks attributed to NaV₂O₅ increased further (Figure 8c). After increasing the H₂ gas partial pressure to 4 MPa, the prepared product was identified as pure-phase NaV₂O₅ without any other phases (Figure 8d). The diffraction peaks had no obvious change as the H₂ gas partial pressure was increased to 5 MPa (Figure 8e).

To reduce the consumption of the H_2 gas, the optimal H_2 gas partial pressure for the synthesis of pure-phase NaV₂O₅ with a high recovery was proposed to be 4 MPa.



Figure 8. The phase compositions of the products obtained at (**a**) 1 MPa, (**b**) 2 MPa, (**c**) 3 MPa, (**d**) 4 MPa, and (**e**) 5 MPa under an initial solution pH value of 4, a reaction temperature of 200 °C, and a reaction time of 2 h.

3.4. Effect of Reaction Time

To investigate the effects of the reaction time during NaV₂O₅ preparation, the initial solution pH value, reaction temperature, and H₂ gas partial pressure were fixed at 4.0, 200 °C, and 4 MPa, respectively.

As shown in Figure 9, the V precipitation percentage rose greatly, from 87.88% to 99.58%, as the reaction time was prolonged from 0.5 to 2 h. However, further prolonging the reaction time did not cause the V precipitation percentage to increase.



Figure 9. The effect of reaction time on vanadium precipitation percentage.

As can be seen from Figure 10a, some pentavalent vanadates of $Na_2V_6O_{16}\cdot 3H_2O$, $Na_6V_{10}O_{28}\cdot 18H_2O$, and $Na_2V_6O_{16}$ could be precipitated from the solution before the reduction reaction. As the reaction lasted for 0.5 h, the pentavalent vanadates of $Na_2V_6O_{16}\cdot 3H_2O$ and $Na_2V_6O_{16}$ mostly disappeared, and the reduction intermediate powers of $Na_{0.287}V_2O_5$ and the desired product of NaV_2O_5 could be observed (Figure 10b). When the reaction time was prolonged to 1 h, the intensity of the diffraction peaks ascribed to $Na_2V_6O_{16}\cdot 3H_2O$, $Na_6V_{10}O_{28}\cdot 18H_2O$, and $Na_2V_6O_{16}$ became weak; on the contrary, the intensity of the diffraction peaks of NaV_2O_5 became strong (Figure 10c). Additionally, the diffraction peaks ascribed to $Na_{0.287}V_2O_5$ could not be observed, and a new peak ascribed to $Na_{0.64}V_2O_5$ was observable. When the reaction lasted for 1.5 h, most of the diffraction peaks attributed to $Na_2V_6O_{16}\cdot 3H_2O$, and $Na_2V_6O_{16}\cdot 3H_2O$, and $Na_2V_6O_{16}$ ould not be detected, and the intensity of the diffraction peaks ascribed to $Na_{0.287}V_2O_5$ became strong (Figure 10d). When the reaction proceeded for 2 h, the product was identified as pure-phase NaV_2O_5 without any other phases (Figure 10e). By extending the reaction time to 4 h, no obvious change was detected in the diffraction peaks of the product (Figure 10f). Therefore, it only takes 2 h to prepare the pure-phase NaV_2O_5 .



Figure 10. The phase compositions of the products obtained at (**a**) 0 h, (**b**) 0.5 h, (**c**) 1.0 h, (**d**) 1.5 h, (**e**) 2 h, and (**f**) 4 h under an initial solution pH value of 4, a reaction temperature of 200 °C, and a H_2 gas partial pressure of 4 MPa.

To make the process less time-consuming, the optimal reaction time was proposed to be 2 h to synthesize the pure-phase NaV_2O_5 with a high recovery.

Based on the above, the optimal conditions of initial solution pH value, reaction temperature, H_2 gas partial pressure, and reaction time for the preparation of pure-phase NaV₂O₅ were ascertained as 4.0, 200 °C, 4 MPa, and 2 h, respectively. Excitingly, the formation time was greatly shortened, by nine times, compared with the most time-saving (18 h) hydrothermal process at present [16]. Moreover, the synthesis process can be considered as low-cost due to the low-cost raw material of ASPVS. Therefore, this novel fast process for NaV₂O₅ synthesis may have great application prospects.

3.5. Structural Characterization

To further verify the structure of the as-prepared product, the single XRD pattern of the powder obtained at the optimal conditions was measured, as shown in Figure 11.

Figure 11 shows that all the diffraction peaks of the as-prepared powders agree with the orthorhombic NaV₂O₅ with lattice constants a = 1.132 nm, b = 0.361 nm, and c = 0.480 nm according to the values reported in the literature (JCPDS No. 70-0870). No peaks of impurities or any other phases could be detected, indicating that the product is of high purity. Moreover, the diffraction peaks are very sharp and strong, indicating the high crystallization of the product. According to the ISCD collection data, a model of the orthorhombic NaV_2O_5 can be drawn out (inset in Figure 11). It can be seen that NaV_2O_5 demonstrates a typical layer structure. The vanadium atom in NaV_2O_5 is bonded with five oxygen atoms to form an individual structure unit of VO₅, which looks like a pyramid. Two VO₅ units with the same underlying orientation bond with each other along the *a* axis by sharing one oxygen atom to form a bridge unit. Two bridge units with the opposite underlying orientation bond together by sharing three corner oxygen atoms to form a ladder-like unit with double chains. The ladder-like unit with double chains arranges in a zigzag pattern along the *a* axis and arranges in parallel along the b axis forming the ab plane of the crystal. Sodium ions are located in the layers, which are stacked along the *c* axis, acting as scaffolds in the layer structure. The layered structure provides a fast passage for the de-intercalation of sodium ions; thus, NaV_2O_5 may be used as an electrode material. These results agree well with those of previous research works [5,6,16,18,24].



Figure 11. X-ray diffraction (XRD) pattern of the as-obtained NaV₂O₅.

Based on the results shown in Table 2, the molar ratio of Na to V_2O_5 was close to 1, indicating the as-obtained product was NaV_2O_5 . The sum of the content of sodium and vanadium reached up to 99.98%, indicating the purity of the as-obtained NaV_2O_5 reached up to 99.98%. The contents of other elements appeared in trace accounts, indicating impurity elements hardly co-precipitated with NaV_2O_5 during the reaction.

Table 2. Chemical composition of the as-obtained NaV₂O₅.

Items	V_2O_5	Na	Р	Al	Fe	Si	Mg
Content (wt. %)	88.74	11.24	0.003	0.001	0.002	0.001	0.001

3.6. Electrochemical Performance

The NaV₂O₅ powders obtained under the optimal conditions were assembled as sodium ion batteries to conduct corresponding electrochemical performance tests, as shown in Figure 12. It was clear that the initial discharge capacity was 196.4 mAh/g, and the sodium ion battery still had a specific discharge capacity of 120 mAh/ g after 50 cycles. The Coulombic efficiency at different currents was no less than 97% from the second cycle to the 40th. These results indicate that the as-prepared NaV₂O₅ powders have a potential application in sodium ion batteries.



Figure 12. Cycling performance at the current density of 100 mA/g in 0.01-3 V.

3.7. Synthesis Mechanism

The synthesis of NaV₂O₅ in the hydrothermal hydrogen reduction is a complex process which not only involves a series of reduction reactions with the phase transformation from V(V) ions to NaV₂O₅ but also involves a crystal growth process. Herein, the synthesis mechanism of NaV₂O₅ was divided into a phase transformation mechanism and a crystal growth mechanism in order to better understand the synthesis mechanism of NaV₂O₅.

3.7.1. Phase Transformation Mechanism

The phase transformation mechanism can be determined by further investigating the results shown in Figure 10. It can be seen that several kinds of vanadates, including $Na_2V_6O_{16}$ · $3H_2O$, $Na_6V_{10}O_{28}$ · $18H_2O$, $Na_2V_6O_{16}$, $Na_{0.287}V_2O_5$, $Na_{0.64}V_2O_5$, and NaV_2O_5 , were obtained during the whole synthesis process. The models of those vanadates are shown in Figure 13. Based on the phase transformation in the synthesis process, the phase transformation mechanism can be proposed as follows.

On the one hand, before the reduction reaction, V(V)ions can bond with the free sodium ions in a certain proportion to precipitate from the solution in the form of $Na_2V_6O_{16}$ · $3H_2O$, $Na_6V_{10}O_{28}$ · $18H_2O$, and $Na_2V_6O_{16}$ (Figures 10a and 13a), because the high temperature and high pressure can cause a low solubility for those vanadates. The relevant chemical reaction of this pentavalent vanadate pre-sedimentation process is expressed as Equations (2) to (4). In the initial period of the reduction, the V(V)ions can be reduced by H_2 , so the polarity of V(V) ions will be reduced, resulting in a decrease in the binding force between V ions and water molecules (H_2O), as well as between V and oxygen atoms [18]. As a result, the water molecules in the interlayer of $Na_2V_6O_{16}$ · $3H_2O$ and $Na_6V_{10}O_{28}$ ·18H₂O

are gradually removed, and the vanadate of Na_{0.287}V₂O₅ is formed in the reduction process (Figure 10b). The relevant chemical reaction of this process of hydrogen reduction with dehydration is expressed as Equations (5) to (7). As the reduction proceeds, the V ions valence state can be further lowered and sodium ions will be inserted into the structure of Na_{0.287}V₂O₅ in order to balance the charge [18], leading to the transformation of Na_{0.287}V₂O₅ to Na_{0.64}V₂O₅ and then to the desired product of NaV₂O₅ (Figure 10c–e, Figure 13b). The relevant chemical reaction of this sodium ion insertion process is expressed as Equations (8) and (9). On the other hand, in the initial period of the reduction reaction, some V ions that have been reduced to a lower valence state can also bond to the non-reduced V(V) ions and free sodium ions in a certain proportion to precipitate from the solution as Na_{0.287}V₂O₅ [18]. The relevant chemical reaction of this process is expressed as Equations (10) and (11). With a prolonged time, the valence state of V ions in the Na_{0.287}V₂O₅ to maintain the charge in balance [18], which also leads to the formation of NaV₂O₅. Both of the above two aspects simultaneously lead to the formation of pure-phase NaV₂O₅.



Figure 13. Schematic of the synthesis mechanism for rod-like NaV_2O_5 mesocrystals. (a) The phase transition in the process of the formation of $Na_2V_6O_{16}$ · $3H_2O$, $Na_6V_{10}O_{28}$ · $18H_2O$, and $Na_2V_6O_{16}$ before the introduction of H_2 gas to the autoclave; (b) the phase transition mechanism in the formation of NaV_2O_5 during the hydrothermal hydrogen reduction; (c) the crystal growth of rod-like NaV_2O_5 mesocrystals follows a self-assembly oriented attachment mechanism.

$$V_{10}O_{28}^{6-} + 6Na^{+} + 18H_2O = Na_6V_{10}O_{28} \cdot 18H_2O$$
 (2)

$$V_6O_{16}^{2-} + 2Na^+ + 3H_2O = Na_2V_6O_{16} \cdot 3H_2O$$
(3)

$$V_6 O_{16}^{2-} + 2Na^+ = Na_2 V_6 O_{16}$$
(4)

$$400 \text{Na}_6 \text{V}_{10} \text{O}_{28} \cdot 18 \text{H}_2 \text{O} + 287 \text{H}_2 + 1826 \text{H}^+ = 2000 \text{Na}_{0.287} \text{V}_2 \text{O}_5 + 1826 \text{Na}^+ + 8400 \text{H}_2 \text{O}$$
(5)

$$2000Na_2V_6O_{16} \cdot 3H_2O + 861H_2 + 2278H^+ = 6000Na_{0.287}V_2O_5 + 2278Na^+ + 8000H_2O$$
(6)

$$2000Na_2V_6O_{16} + 861H_2 + 2278H^+ = 6000Na_{0.287}V_2O_5 + 2278Na^+ + 2000H_2O$$
(7)

$$2000Na_{0.287}V_2O_5 + 706Na^+ + 353H_2 = 2000Na_{0.64}V_2O_5 + 706H^+$$
(8)

$$100Na_{0.64}V_2O_5 + 36Na^+ + 18H_2 = 100NaV_2O_5 + 36H^+$$
(9)

$$2400\text{Na}^{+} + 400\text{V}_{10}\text{O}_{28}^{6-} + 287\text{H}_2 + 1826\text{H}^{+} = 2000\text{Na}_{0.287}\text{V}_2\text{O}_5 + 1826\text{ Na}^{+} + 1200\text{H}_2\text{O}$$
(10)

$$4000\text{Na}^{+} + 2000\text{V}_{6}\text{O}_{16}^{2-} + 861\text{H}_{2} + 2278\text{H}^{+} = 6000\text{Na}_{0.287}\text{V}_{2}\text{O}_{5} + 2278\text{ Na}^{+} + 2000\text{H}_{2}\text{O}$$
(11)

3.7.2. Crystal Growth Mechanism

To investigate the crystal growth mechanism, the products prepared at different reaction times were analyzed by SEM.

Figure 14a shows that the resultant products were composed of a disorderly accumulation of small rods when the reaction lasted for 0.5 h. These small rods were identified as a mixture of un-reduced and reduced sodium vanadates, according to the XRD results (Figure 10b). As the reaction time was increased to 1 h, the small rods became much longer compared with those obtained at 0.5 h. In addition, evidence could be found that a few rods assembled with each other and demonstrated a "slender belts" morphology (Figure 14b). After increasing the reaction time to 1.5 h, more evidence could be found that the long rods further assembled together to form some rod-like mesocrystals (Figure 14c). When the reaction lasted for 2 h, the as-prepared product was demonstrated to consist of typical rod-like mesocrystals (Figure 14d). The corresponding EDS element mapping analysis revealed that the rod-like mesocrystals only consist of the elements Na, V, and O (Figure 14f). Moreover, the relevance of Na, V, and O was quite good. Combining with the XRD results drawn from Figure 10e, the rod-like mesocrystals could be confirmed as NaV_2O_5 . From the partial magnified image of the rod-like NaV_2O_5 mesocrystals, it can be seen that the individual NaV_2O_5 rods in the bunch were aligned in the same direction and assembled together (Figure 14e). The fact that the crystals stack preferentially in a certain direction indicates that the growth of NaV₂O₅ crystals in the HHR process may follow a self-assembly oriented attachment mechanism [16–18].



Figure 14. Scanning electron microscopy (SEM) image of the products obtained at different reaction times of (**a**) 0.5 h, (**b**) 1 h, (**c**) 1.5 h, and (**d**) 2 h under an initial solution pH value of 4, a reaction temperature of 200 °C, and a H₂ gas partial pressure of 4 MPa. (**e**) The partial magnified image; (**f**) energy-dispersive spectrometry (EDS) element mapping analysis of the product obtained at 2 h.

Figure 15a,b reveal that the NaV₂O₅ mesocrystals obtained had a rod-like morphology, which appeared similar to that in the images obtained from the SEM analysis. From the magnified image of the end of the individual NaV₂O₅ mesocrystal (Figure 15c), it can be clearly observed that the mesocrystal was composed of many nanorods with the same preferred orientation. Moreover, some cleavages between the nanorods at the ends of the crystal supply more evidence for the self-assembled oriented attachment mechanism for rod-like NaV₂O₅ formation (Figure 15c). The lattice fringes of 0.473 nm associated with the (001) plane [16,18] can be measured from the high-resolution transmission electron microscope (HRTEM) image of NaV₂O₅ (Figure 15d). The lattice fringes in the direction of the length measured as 0.375 nm correspond to the (010) plane [16], revealing that the crystal's preferential growth direction is (010) (Figure 10d). These agree with the XRD results. From the analysis of the selected area electron diffraction (SAED) pattern, diffraction spots of (010), (001), and (011) can be clearly identified, which is in good agreement with the orthorhombic NaV₂O₅. From the above information, it can be concluded that NaV₂O₅ nanorods with the same preferential crystal growth direction assemble together in the (001) direction to form rod-like NaV₂O₅ mesocrystals with a preferential crystal growth direction of (010).



Figure 15. Transmission electron microscopy (TEM) characterization of NaV₂O₅ mesocrystals synthesized under the optimal conditions. (**a**,**b**) TEM images of NaV₂O₅mesocrystals; (**c**) partial magnified image of the NaV₂O₅ mesocrystals; (**d**) high-resolution transmission electron microscope (HRTEM) image of NaV₂O₅ (inset is the corresponding selected area electron diffraction (SAED) pattern).

Based on the above, a crystal growth mechanism can be proposed (Figure 13c). First of all, many small rod nuclei are obtained through nucleation. As the surface energy can be drastically reduced when the interface is eliminated, the generated small NaV_2O_5 rods will then spontaneously combine with each other along the same crystal orientation (010) to maintain the system at the lowest systematic energy. Ultimately, rod-like NaV_2O_5 mesocrystals with a (010) preferential crystal growth orientation, consisting of many nanorods stacking with each other along the (001) direction, are obtained.

4. Conclusions

In summary, we reported a novel fast process for synthesizing NaV₂O₅ mesocrystals from an alkaline-stripped pentavalent vanadium solution by introducing the technology of hydrothermal hydrogen reduction. The optimal conditions for NaV₂O₅ synthesis were ascertained to be an initial solution pH value of 4.0, a reaction temperature of 200 °C, a H₂ gas partial pressure of 4 MPa, and a reaction time of 2 h. The synthesis time (only 2 h) was greatly shortened, by nine times, compared with the most time-saving (18 h) hydrothermal process at present. XRD analysis revealed that the as-prepared powders demonstrate a typical layered orthorhombic structure of NaV₂O₅. The purity of the as-prepared NaV₂O₅ reached up to 99.98%. Electrochemical tests showed that the as-prepared powder had a potential application in sodium ion batteries. Electron microscopy analysis revealed that the rod-like NaV₂O₅ mesocrystals demonstrated a preferential growth direction of (010), and were formed by a large number of nanorods assembled in the (001) direction. Furthermore, the synthesis mechanism of NaV₂O₅ was proposed as follows: pentavalent vanadate pre-sedimentation, hydrogen reduction with dehydration, sodium ion insertion, and finally self-assembly oriented attachment. The synthesis process can be considered to be time-saving and low-cost, thus offering promising application prospects for NaV₂O₅ synthesis.

Author Contributions: G.Z. and Y.Z. provided the original ideas and designed the experiments; G.Z. and L.Z. performed the experiments; G.Z. analyzed the data; S.B. contributed reagents/materials/analysis tools; and G.Z. wrote the paper.

Funding: This work was financially supported by the National Key Science-Technology Support Programs of China (NO. 2015BAB03B05), the National Natural Science Foundation of China (NO. 51874222 and NO. 51804226).

Conflicts of Interest: The authors declare no conflict of interest.

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