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### Optimization of Synthesis method to Higher Performance NVP –Independent Study Report

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# Optimization of Synthesis method to Higher Performance

## NVP –Independent Study Report

He Zhou, Peng Bai

### Abstract

Anode-free alkali metal batteries, favored by the small volume and high energy density, are plagued by the poor interfacial stability of the deposited metals. The successful stabilization of sodium (Na) in the glyme-based electrolytes has made the anode-free Na metal battery a promising candidate in place of the commercial lithium-ion batteries.  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  (NVP), a cathode material with high stability, will be studied in this independent study to improve the performance of the anode-free Na metal battery. High quality NVP will be synthesized through hydrothermal assisted sol-gel method and applied in anode-free SIBs. Control experiments will be performed to explore the best synthesis condition such as annealing temperature annealing time, and material adding order, which guarantees the performance and stable output. The amount of carbon coating which improves the active material conductivity but decreases the overall capacity will be optimized.

### Introduction

Due to the emerging market of electrical equipment and stationary energy storage, the demand of batteries is projected to increment incredibly <sup>[1]</sup>. Lithium-ion batteries (LIBs) has had one of the most wide-range application in energy storage field since its commercialization <sup>[2]</sup>. However, there is still much concern about the limitation of lithium-ion batteries, such as its reducing reserves and restriction of energy density <sup>[3,4]</sup>. Sodium-ion batteries (SIBs) gradually become promising option to future energy storage since its plentiful storage in this planet, low toxicity, and similar chemical properties to lithium <sup>[5,6]</sup>. Nevertheless, because of some potential drawbacks, including poor intercalation/deintercalation kinetics and higher redox potential contrasted with lithium, the ideal electrode material should have robust and flexible crystal structure to accommodate  $\text{Na}^+$  ion <sup>[5,7]</sup>.

Among many sorts of cathode,  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  (NVP), a typical sodium super ionic conductor (NASICON) compound, has extraordinary properties on high  $\text{Na}^+$  conductivity and structure stability.<sup>[8]</sup> However, the major disadvantage of NVP is its relative low electron conductivity, which hinders the widespread application.<sup>[9]</sup> Plenty

of studies aim to increase the electron conductivity of NVP, and carbon coating is a typical procedure. In Jun Chen's research, they creatively develop a hydrothermal assisted sol-gel method to synthesize NVP@C core shell structure nanocomposite [6]. Based on their work, we will set groups of control experiments to explore the best synthesis condition and apply materials to anode-free alkali metal batteries. The condition of experiment includes reaction time, annealing temperature, and order of adding materials. Our result will provide valuable information of NVP synthesis.

## **Method and Experiment**

### **Synthesis**

The nanocomposite NVP@C is obtained by hydrothermal assisted sol-gel method. In this method, 4mmol  $V_2O_5$ , 12mmol  $NH_4H_2PO_4$ , and 6mmol  $Na_2CO_3$  separately added to 70mL deionized water and stir magnetically at room temperature in beaker. 6mmol ascorbic acid and 6mL polyethylene glycol 400 (PEG-400) would be added subsequently. Stirring for 30 min, the formed suspension was transferred to 100mL Teflon-lined autoclave and then sealed it in  $180^\circ C$  for 40h. Afterward, autoclave is normally cooled to room temperature. The obtained brown mixture was treated by ultrasonic for 90min to disperse evenly, and then heated by water bath at  $95^\circ C$  to evaporate water, or centrifuged to separate water. The resulting material was dried at  $120^\circ C$  overnight. This precursor was fully grounded and preheated at  $350^\circ C$  for 4h. The preheated material also completely grounded and annealed at  $750^\circ C$  to  $850^\circ C$  for 6-8 hours. Both preheating and annealing process were carried out in tube furnace and argon atmosphere.

### **Material Characterization**

X-ray diffraction (XRD) measurements were conducted to acquire basic crystal information of materials. Morphologies features were investigated by scanning electron microscope (SEM).

### **Electrochemical evaluation**

The electrochemical measurements were realized by coin cells. The coin cells were assembled in glovebox filled with argon. The working electrode was an 8mm-diameter aluminum foil covered by slurry which contains active material, binder (PVDF) and conductive agent ( $C_8$ ) with mass ration 8:1:1. The counter electrode was 10mm copper foil to make anode-free cells. The electrolyte is 1mol/L  $NaPF_6$  in

diglyme. The cyclic voltammograms (CV) was obtained on work station.

## Result and discussion

### 1 The initial experiment

In initial experiment, we added solid state powder of  $V_2O_5$ ,  $NH_4H_2PO_4$ ,  $Na_2CO_3$  in beaker at the same time according to the molar amount as shown above, and then add 70mL deionized water, ascorbic acid, and PEG-400 in order. The preheating and annealing process were not completed in strict Argon atmosphere. Other operations followed the method mentioned above.

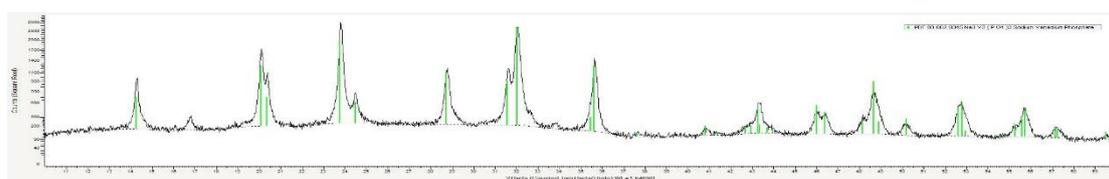


Figure 1 XRD pattern of this batch

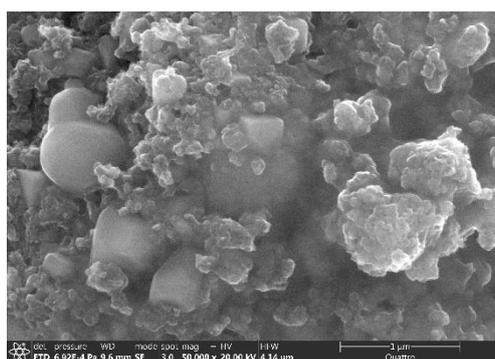


Figure 2 SEM pattern of this batch

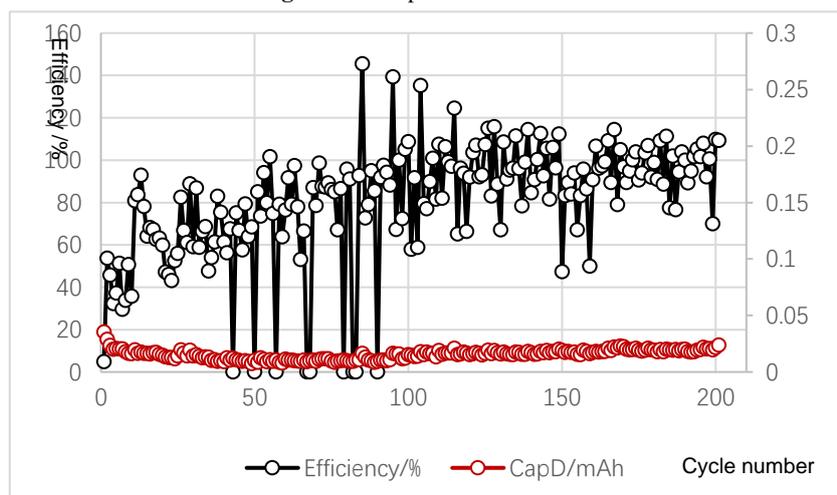


Figure 3 Cycle-Efficiency & Capacity plot of initial NVP

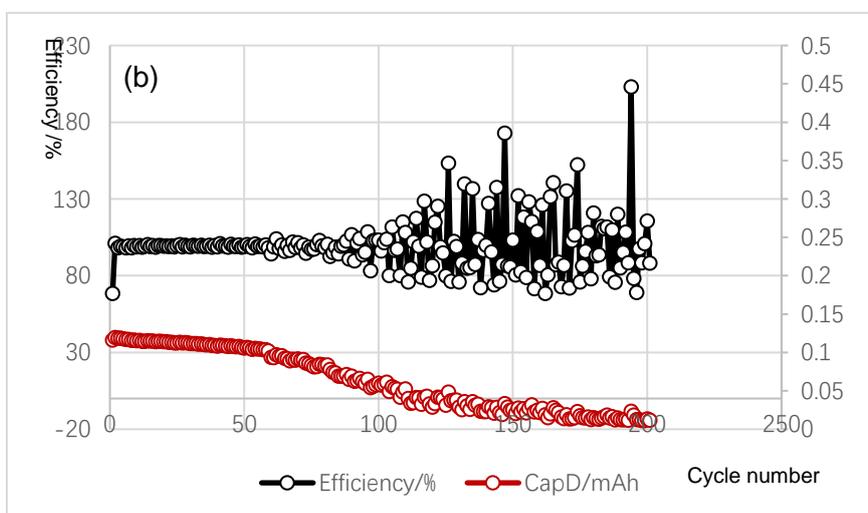
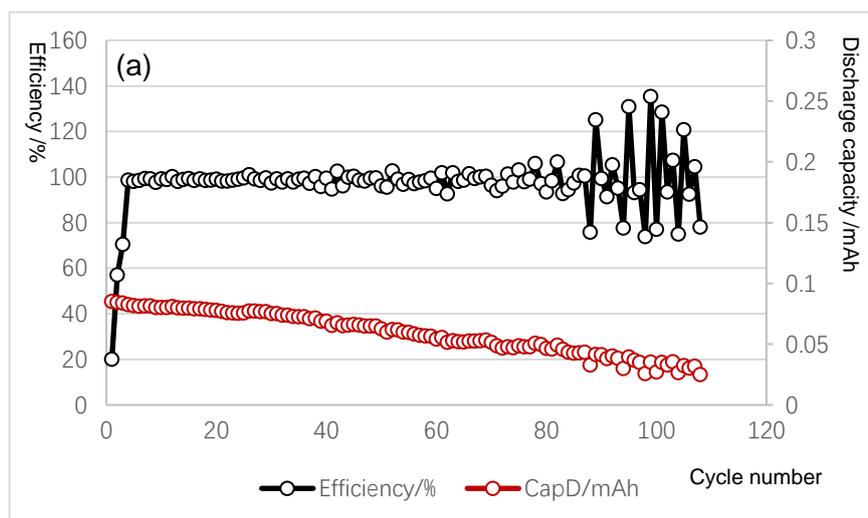
The XRD plot of first batch (Figure 1) shows that NVP was successfully synthesized, yet the intensity is not high and there are impurity peaks exist, which demonstrate that

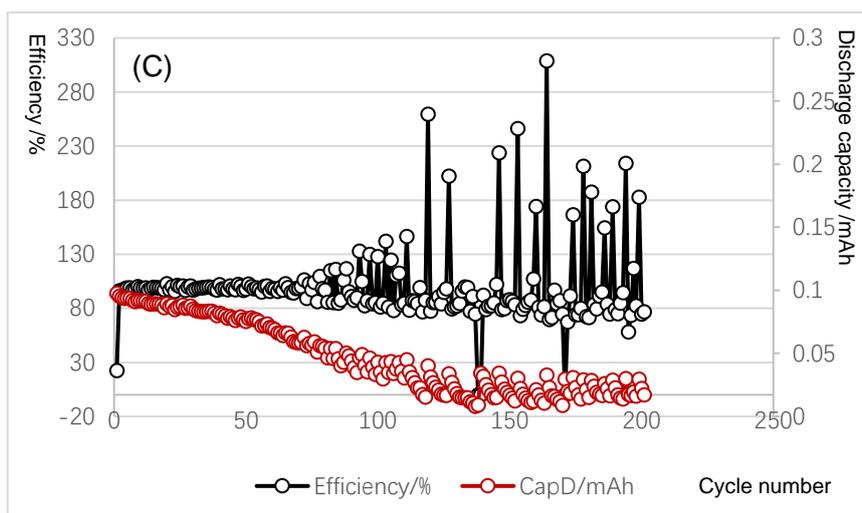
the yield is not high. The SEM pattern in Figure 2 shows that the resulting materials fused together but not generate an even nanosized morphology. In addition, Cycle-Efficiency & Capacity plot (Figure 3) displays the fluctuation of efficiency. This time batteries maximum capacity is 38.80mAh/g, which is far lower than NVP's theoretical capacity 118mAh/g. According to these conclusions, we assumed that since preheating and annealing process were not carried out in strict argon ambient, the reactive molecules in the air might react with the material at high temperature, resulting in impurities. Besides, how to obtain a uniform nano particle of material is another problem need to be solved.

## 2 Annealing conditions

### 2.1 Pressure

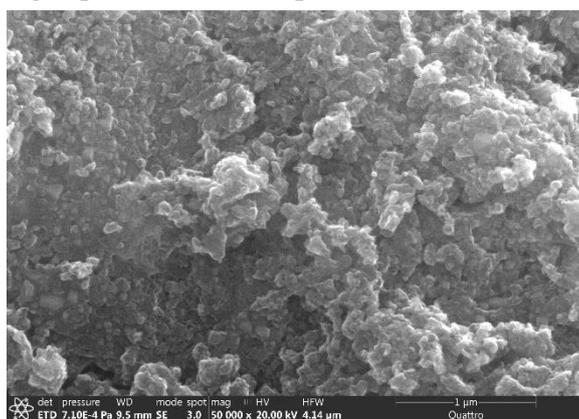
Annealing pressure was the only variable in this group of experiment. We set three different situations: positive pressure, regular pressure, and negative pressure. We used vacuum pump to vacuumize the tube furnace and refilled argon to create a strict argon ambient. The resulting material denoted as NVP@C-AP. Different pressure will be determined by the volume of filled argon and the performance of each synthesized NVP under each condition are shown in Figure 4 below.





**Figure 4** Cycle-Efficiency & Capacity plot of NVP@C-AP: a is the diagram for the batch which annealed in negative pressure; b is the diagram for the batch which annealed in positive pressure. c is the diagram for the batch which annealed in regular pressure.

In the three groups of controlled experiments, the maximum capacity obtained under positive pressure, negative pressure and regular pressure was 81.15 mAh/g, 80.27 mAh/g and 80.49 mAh/g, respectively. Other data of these batches will be detailed in Table S1. The capacities gained in different conditions are have little difference, and the retention rate of these materials are relatively lower, which means the material is still not stable. However, contrasted to the initial experiment, the capacity in these batches becomes higher. Therefore, we infer that the annealing pressure may not influence the material's performance in coin cell, but the strict argon atmosphere could be the main cause of capacity enhancement. In the subsequent experiments, we adopted the method of vacuumizing and then charging argon gas to regular pressure to ensure a stricter argon gas protection atmosphere.

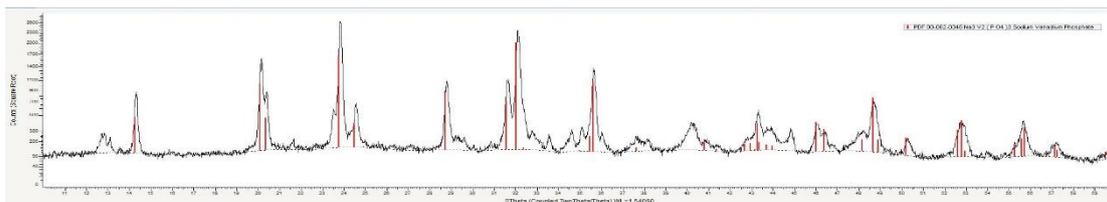


**Figure 5** SEM diagram of material synthesized in positive pressure

In Figure 5, the picture displays the morphology of material. In positive pressure, the dispersed and uniform nanoparticles were still formed. Therefore, pressure cannot impact the morphology of material.

## 2.2 Temperature & times

Annealing temperature and time are significant factor to impact the crystallinity of materials. We show the XRD diagram before annealing process in Figure S1. No peaks exhibit in diagram indicate that annealing is the only process to generate crystallinity of material. In Zhou's research [10], 800°C 8h annealing process made their materials reach the best performance. Therefore, this batch of material, we increase the temperature and time of annealing process to 800°C, 8h.



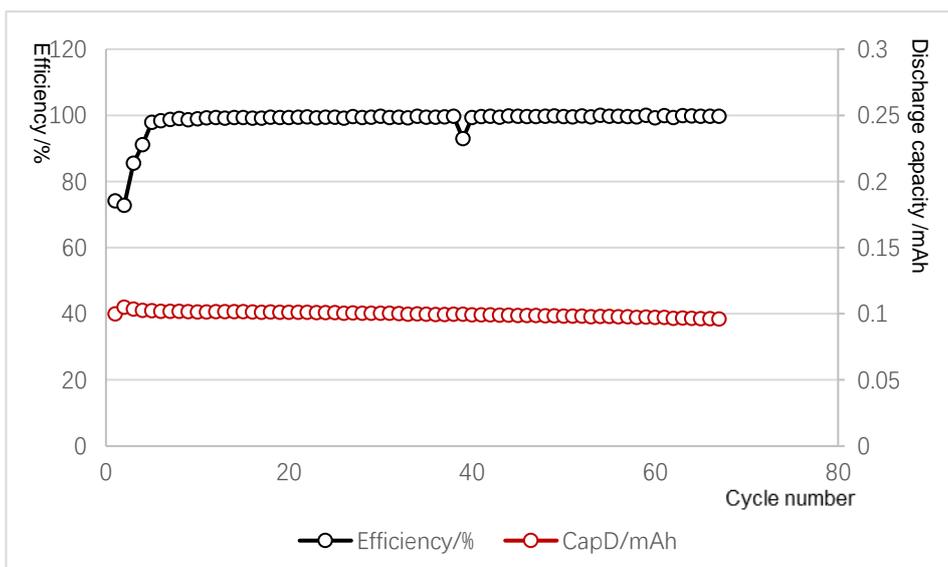
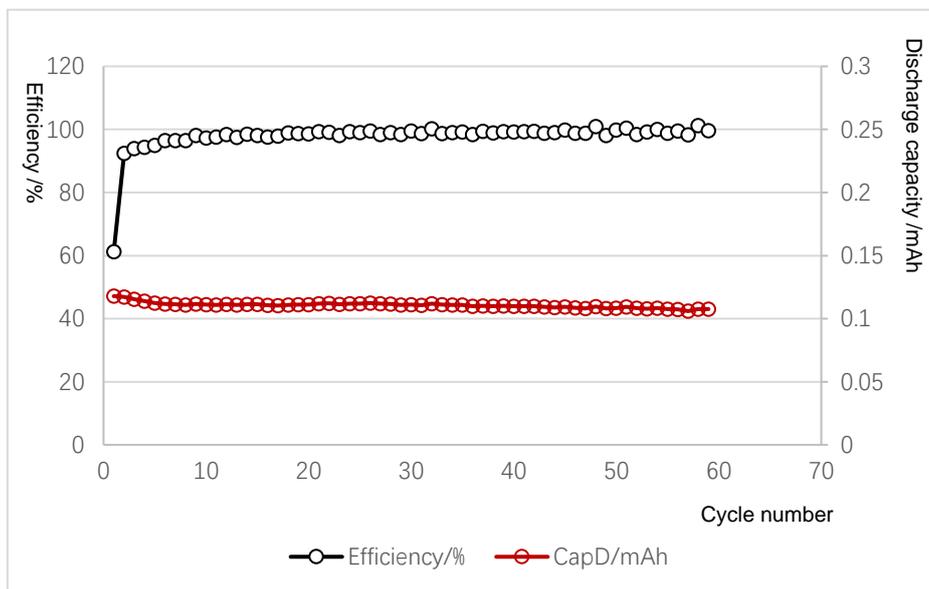
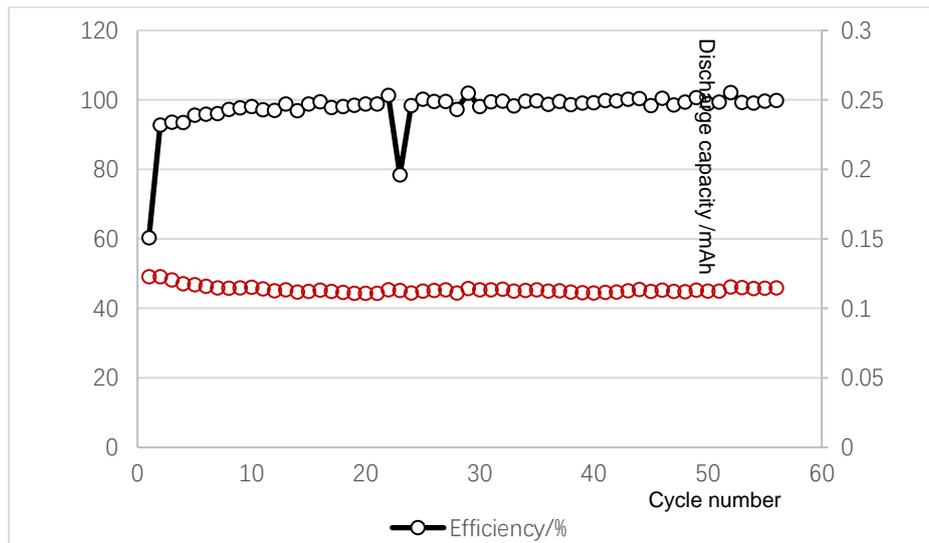
**Figure 6** XRD diagram of material annealing in 850°C for 8h

As shown in Figure 6, after 800°C, 8h annealing process, more impurities appear in material. Meanwhile, there were some crystals generate on crucibles after annealing, which didn't take place after 750°C annealing process. The maximum capacity of the battery made by this material was only 52.64mAh/g. All these phenomena demonstrate that excessive annealing temperature and time not only cause material loss, but also degrade the performance of cells. Therefore, in the rest of experiments, we kept 750°C, 6h as annealing temperature and time.

## 3 Material addition orders and pretreatments

In pervious synthesis, small and uniform NVP@C particle still wasn't formed, which could be the main reason that rendered bad performance of batteries. According to Chen's research [5], under the combined action of ascorbic acid and PEG-400, the content of large size and amorphous NVP@C will be greatly reduced in the reaction process. The role of ascorbic acid is not only to reduce V(V) to V(III), but also to carbonize and coating NVP in advance, limiting its size growth.

In order to get uniform and fully reacted product, V<sub>2</sub>O<sub>5</sub> was added to 17.5mL deionized water and then ultrasonic treat for 30min. After weighing NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> and Na<sub>2</sub>CO<sub>3</sub>, add 17.5mL distill water to make the solution. Drop these two solutions individually to V<sub>2</sub>O<sub>5</sub> suspension under ultrasonic condition to get rid of the generated CO<sub>2</sub>. After another 20min, transfer the container to hot plate, and stir it magnetically. Add ascorbic acid solution and PEG-400, and then stir for 30min. Other process followed the method mentioned above. Annealing temperature and time is 750°C, 6h. The resulting NVP denoted as NVP@C-ao



**Figure 6.** Cycle-Efficiency & Capacity plot of NVP@C-ao

In this experiment, we obtained the highest capacity so far, which reached to

90.6mAh/g, and retention rate reaches to 94.9% from 5<sup>th</sup> cycle to 65<sup>th</sup> cycle.

#### 4 Other treatments and reactions

Regularly, after ultrasonication process, we evaporate water to condense the mixture, but this method usually takes longer time. We try to use centrifuge to separate water and solid, but final XRD (Figure S2) shows that materials were washed away during centrifuge process. Thus, we kept evaporate water to condense the mixture.

We also tried a new method to synthesis nanosized NVP@C, detailed synthesis method is shown in supplementary information. XRD results and cycle-efficiency plot of materials synthesized by this method are shown in the figure7 & 8 below.

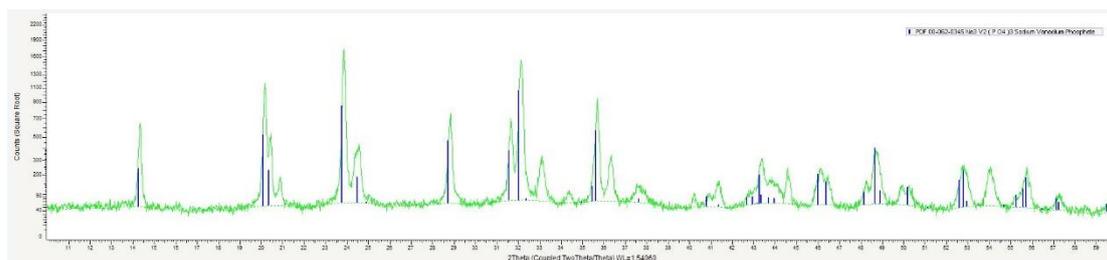


Figure 7 XRD diagram of NVP synthesized by new method

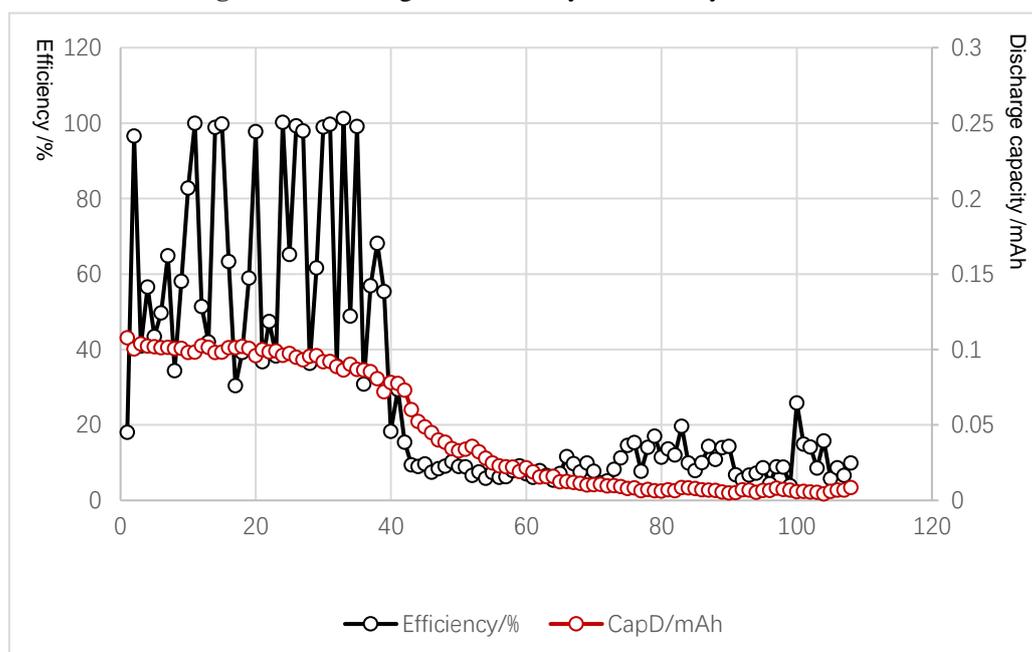


Figure8 Cycle-efficiency diagram of NVP synthesized by new method

From the figures, the material synthesized by this method has high impurity content and poor battery performance. This method will not be discussed detailly in this report, but it will be optimized in the future.

### Summary and Future work

In this independent study, we synthesized materials by hydrothermal sol-gel assisted method, and explored the effects of annealing temperature, time, annealing pressure, and material addition sequence on NVP synthesis, and achieved initial results. The

maximum capacity of the synthesized materials can reach 90.6mAh /g at present. For that batch of NVP, we will apply XRD and SEM to identify the crystallinity and morphology.

The capacity is still not high enough compared to the theoretical capacity; therefore, the experiment will be optimized in future. Particle size has a great influence on battery performance. The subsequent experiments will mainly focus on how to reduce the particle size of materials. pH is another important factor which could influence reducibility of ascorbic acid and its binding ability to vanadium, so pH will be another condition for optimization.

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## Supplementary Information

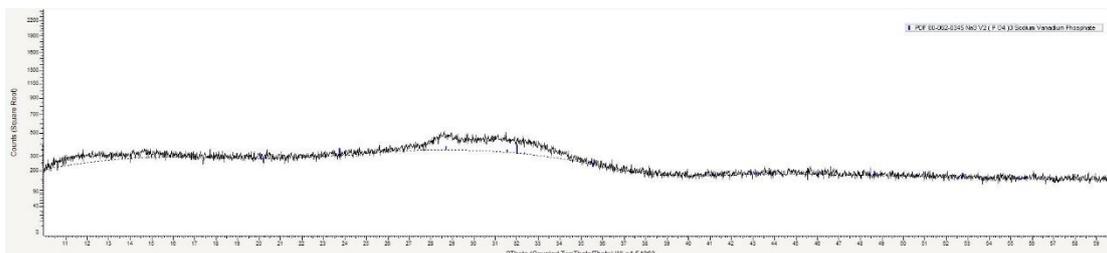


Figure S1 XRD diagram of materials before annealing process

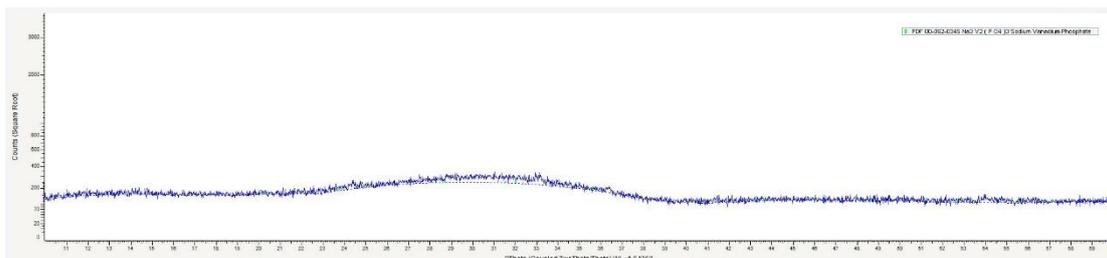


Figure S2 XRD diagram of material using centrifuge to split water

Table S1 the capacity and retention rate of materials in different annealing pressure

Condition	Capacity/ $\text{mAh}\cdot\text{g}^{-1}$	Retention rate (5 <sup>th</sup> to 105 <sup>th</sup> )
Negative pressure	77.99	13.11%
Negative pressure	73.97	63.22%
Negative pressure	81.15	39.85%
Positive pressure	51.24	12.20%
Positive pressure	80.27	46.86%
Positive pressure	69.06	24.72%
Regular pressure	80.49	12.44%

### New method to synthesize NVP@C nano particle

A  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  (NVP)-based carbon composite (NVP)@C was fabricated by a sol-gel approach. First, 80 mL of a  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  precursor solution containing  $\text{C}_6\text{H}_8\text{O}_7\cdot\text{H}_2\text{O}$  (2 mmol),  $\text{NH}_4\text{VO}_3$  (2 mmol),  $\text{NH}_4\text{H}_2\text{PO}_4$  (3 mmol), and NaOH (3 mmol) was stirred intensely at 80 °C for 8 h. Next, the sol was dried at 60 °C to form a gel precursor, which was ground into a powder and preheated at 350 °C for 4 h. Finally, the obtained sample was annealed at 800 °C for 8 h in an argon atmosphere to obtain the target product.