Novel 3.9 V Layered Na$_3$V$_3$(PO$_4$)$_4$ Cathode Material for Sodium Ion Batteries

Rui Liu,† Haodong Liu,‡ Tian Sheng,§ Shiyaó Zheng,∥ Guiming Zhong,⊥ Guorui Zheng,† Ziteng Liang,† Gregorio F. Ortiz,⊥ Weimin Zhao,‡ Jinxiao Mi,* V and Yong Yang†,*,#

†Collaborative Innovation Center of Chemistry for Energy Materials, State Key Laboratory for Physical Chemistry of Solid Surface, Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, P. R. China
‡Department of NanoEngineering, University of California San Diego, 9500 Gilman Drive, La Jolla, California 92093, United States
§College of Chemistry and Materials Science, Anhui Normal University, 189 South Jiuhua Road, Wuhu, Anhui 241000, P. R. China
∥Xiamen Institute of Rare Earth Materials, Haixi Institutes, Chinese Academy of Sciences, Xiamen 361021, P. R. China
⊥Departamento de Química Inorgánica e Ingeniería Química, Instituto Universitario de Química Fina y Nanoquímica, Edificio Marie Curie, Campus de Rabanales, Universidad de Córdoba, 14071 Córdoba, Spain
‡School of Energy Research, Xiamen University, Xiamen 361005, P. R. China
#Department of Material Science and Engineering, Xiamen University, Xiamen 361005, P. R. China

Supporting Information

ABSTRACT: A new compound Na$_3$V$_3$(PO$_4$)$_4$ is successfully synthesized for sodium ion batteries using a sol–gel method. Composition analysis through ICP-OES confirms the stoichiometry of Na$_3$V$_3$(PO$_4$)$_4$. Structural analysis based on XRD reveals that the new material crystallizes in a monoclinic system with a C2/c space group. The new compound exhibits a layered structure containing 3D Na$^+$ ion channels allowing excellent cycling and rate performance. Even at a high current rate of 3C (1C = 45 mA/g), it still delivers 82% of the theoretical capacity. Meanwhile, 92% of its capacity is retained after 100 electrochemical cycles. The voltage profiles of Na$_3$V$_3$(PO$_4$)$_4$ show that it can reversibly uptake nearly one Na$^+$ ion with a 3.9 V voltage plateau, which is the highest value among Na-containing V-based orthophosphates ever reported.

KEYWORDS: XRD, BVS, polyanion, sodium ion batteries, vanadium, cathode

Lithium ion batteries (LIBs) play a critical role in portable devices and electrical vehicles. However, due to the low abundance and high cost of lithium resources, they may not fulfill the requirements of large-scale storage systems for renewable energy sources like wind and solar. Consequently, sodium ion batteries (SIBs) have experienced a renaissance thanks to a similar working mechanism as LIBs and a high abundance of sodium resources. In this context, considerable efforts have been made to explore potential cathode materials for SIBs. Polyanion-based compounds have attracted extensive interest due to their cycling stability, safety, and adjustable operating voltage.

It is well-known that V-based phosphates show extreme structural versatility because of the multiple coordinations and oxidation states (from +2 to +5) of vanadium ions.\cite{1,2,3} In recent years, various cathodes in the Na$_2$O–V$_2$O$_5$–P$_2$O$_5$ ternary system (Figure 1, inset) have been explored with highly attractive electrochemical features, as summarized by Masquelier et al.\cite{10} For instance, Na$_3$V$_2$(PO$_4$)$_3$ features an open NASICON frame and is well-known as one of the most competitive candidates as a practical cathode material for SIBs due to its excellent electrochemical performance.\cite{11,12,13} Another compound, Na$_3$V(PO$_4$)$_2$, shows a layered structure in which the 2D Na$^+$ diffusion channels make it a promising high power cathode material.\cite{9} Additionally, the V$^{3+}$/V$^{4+}$ redox couple in mixed orthophosphate–pyrophosphates such as Na$_3$V$_4$–(P$_2$O$_7$)$_2$PO$_4$ and Na$_3$V$_3$(P$_2$O$_7$)$_2$ exhibits voltages as high as 4.0 V (vs Na$^+$/Na) because of the strong interaction between the VO$_6$ octahedra and P$_2$O$_5$ group.\cite{14,15}

For the first time, we successfully synthesized new compound Na$_3$V$_3$(PO$_4$)$_4$ with a unique 3D Na diffusion net and 3.9 V voltage plateau by carefully screening the Na$_2$O–V$_2$O$_5$–P$_2$O$_5$ ternary system.\cite{10} XRD reveals that the as-prepared light green powder (Figure 1, inset) adopts a monoclinic structure with space group C2/c, which is isostructural with previously known Na$_3$Fe$_3$(PO$_4$)$_4$ (ICSD

Received: June 2, 2018
Accepted: July 17, 2018
Published: July 17, 2018
No. 95532). The XRD Rietveld refinement of the product is carried out using the parameters of the monoclinic crystal structure of Na3Fe3(PO4)4 as the starting model (Figure 1). Small Rwp and Rs demonstrate that the structure of Na3V3(PO4)4 can be well-indexed to the C2/c space group, with unit cell parameters of a = 19.6724(4) Å, b = 6.40406(10) Å, c = 10.58904(19) Å, β = 91.9666(17)°, and V = 1333.3 Å³. There is a trace amount of Na3V2(PO4)3 impurity (~2 wt%: ICSD No. 248140) in the product identified from Rietveld refinement. The comparison of the calculated patterns of Na3V3(PO4)4 and Na3V2(PO4)3 is shown in Figure S1. The detailed structure information is summarized in Tables S3 and S4.

Figure 2 shows that Na3V3(PO4)4 adopts a layered structure built from VO6 octahedra and PO4 tetrahedra via corner sharing or edge sharing. More specifically, P(1)O4 tetrahedra and V(2)O6 octahedra interconnect via a common O(2)−O(4) edge and O(1) and O(3) corners to form infinite chains along the b axis, as shown in Figure 2a,c. The chains are connected by [V(1)O6−2P(2)O4] clusters (Figure 2a,d) sharing common O(2), O(4), O(5), and O(6) corners to form infinite V3(PO4)4 slabs in the bc plane (⟨001⟩) (Figure 2e and Figure S2a). However, one oxygen atom (O(7)) in the PO4 tetrahedra is terminal, which does not link to the VO6 octahedra (Figure S2b). The successive two-dimensional layers further stack along the a direction to form a three-dimensional layered crystal structure. There are two different oxygen interstitial sites in the layered structure; Na(1) is located at 4e with 6-fold coordination while Na(2) sites are at 8f with 7-fold coordination. Interestingly, both Na(1) and Na(2) ions are located between the successive V3(PO4)4 layers, Na layers and V2(PO4)3 layers alternatively stack along the a direction to form the layered structure (Figure 2a,b). This layering enables 3D Na+ diffusion pathways due to large holes in the V3(PO4)4 slabs, as shown in Figure 2e. The BVS maps shown in Figure 2e,f further demonstrate interlayer Na(1)−Na(1) and Na(1)−Na(2) paths and intralayer Na(2)−Na(2) paths. The 3D channel should facilitate migration of Na+ ions.

The SEM image in Figure S3a shows that the morphologies of the secondary particles are irregular with the particle size from several to tens of micrometers. A closer view in Figure S3b shows the plate-like morphology of the primary particles with a diameter 500–1000 nm and thickness of around 200 nm. ICP results further determine that the atomic ratios of Na/V/P are 2.92(8)/3.00(8)/4, being fit well with their theoretical values. From the charge balance and the structural similarity with Na3Fe3(PO4)4, we can deduce the charge valence of vanadium ions is +3 in Na3V3(PO4)4.

The electrochemical performance of Na3V3(PO4)4 as a novel Na insertion host was evaluated by cyclic voltammetry (CV) at a scan rate of 0.05 mV/s and galvanostatic charge/discharge at various C rates, as shown in Figure 3. It should be clarified that a pair of small peaks or plateaus at ~3.4 V indicated by dashed circles are caused by the slight amount of Na3V2(PO4)3 impurity, and the abnormal voltage steps highlighted by the asterisks could be attributed to the unstable potential of the Na counter electrode. One anodic peak at 4.0 V and cathodic peak at 3.8 V can be seen in the CV curve (Figure 3a, inset), which originates from the V5+/V4+ redox reaction in Na3V2(PO4)3. We want to emphasize that the high voltage is worth an in-depth investigation because, as far as we know, it is the highest V5+/V4+ couple (3.9 V) among Na-containing vanadium-based orthophosphates (e.g., Na4VO(PO4)2, Na4VOPO4, Na3V(PO4)2, and Na3V2(PO4)3) etc.). From the view of thermodynamics, density functional theory (DFT) calculations have also confirmed that the removal of the first Na atom from the original unit cell could occur at a theoretical potential of 4.03 V (Figure 3a). Indeed, this new compound
exhibits a discharge capacity of 34 mAh/g with a relatively flat voltage plateau at 3.9 V in cell 811 (indicating the weight ratio of the active material, acetylene black, and PVDF is 8/1/1), which fits well with the CV and theoretical results, as shown in Figure 3a. However, the capacity of cell 811 drops to 21 mAh/g at 3C. Since the color of Na3V3(PO4)4 powder is green, this indicates a large band gap. Considering the fact that 3D Na+ channels exist in the structure, the rate performance of Na3V3(PO4)4 might be hindered by electronic conductivity instead of ionic diffusivity. This hypothesis was verified by preparing cell 721 and cell 631 with higher content of acetylene black. Figure 3a clearly shows a progressive improvement of the rate performances of the cells as a result of increasing the content of acetylene black. More specifically, cell 811, cell 721, and cell 631 show 47%, 60%, and 82% of the theoretical capacity at 3C, respectively. We believe surface coating with a conductive material or doping with alien ions could further improve the electronic conductivity and thus enhance the rate performance of Na3V3(PO4)4.

Benefiting from the polyanionic framework, Na3V3(PO4)4 also shows outstanding structural stability upon long-term cycling. As shown in Figure 3b, the XRD pattern of the Na3V3(PO4)4 electrode from cell 811 after 5 cycles shows a negligible change compared to the pristine one. Consequently, the new material delivers superior cycling performances, as can be seen from the inset of Figure 3b. For instance, cell 631 still maintains 92% of its initial capacity after 100 cycles at 3C.

In summary, Na3V3(PO4)4 is successfully synthesized for the first time using a simple sol–gel method. The composition of the as-synthesized material can be readily controlled as a new layered polyanionic vanadium-based cathode material with 3D diffusion paths for Na ions, which is distinguishable from other V-based phosphates and enables robust cycling stability and rate performance. This new material can uptake nearly one Na+ ion with voltage plateaus at 3.9 V, which is the highest reported voltage among V-based orthophosphates. These findings support and expand upon the development of novel vanadium-based cathode materials for SIBs.

**ASSOCIATED CONTENT**

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsaem.8b00889.

Detailed experimental procedures, calculating method, XRD refinement results, scheme of structure, and SEM figures (PDF)

**AUTHOR INFORMATION**

Corresponding Authors
*E-mail: jxmi@xmu.edu.cn. (J.M.)
*E-mail: yyang@xmu.edu.cn. (Y.Y.)

**ORCID**
Rui Liu: 0000-0001-6985-9129
Tian Sheng: 0000-0001-5711-3012
Shiyao Zheng: 0000-0001-5002-5204
Guiming Zhong: 0000-0003-2313-4741
Gregorio F. Ortiz: 0000-0003-3104-8018
Jinxiao Mi: 0000-0002-4316-457X

**Author Contributions**
The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

**Notes**
The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work is financially supported by the National Key Research and Development Program of China (Grants 2018YFB0905400, 2016YFB0901500) and National Natural Science Foundation of China (Grants 21233004, 21428303, 21621091). The authors are also grateful to Ministerio de Economía y Competitividad and FEDER funds (MINECO (MAT2017-84002-C2-1-R)).

**REFERENCES**


