Electrochemical and Thermal Properties of NASICON Structured Na$_3$V$_2$(PO$_4$)$_3$ as a Sodium Rechargeable Battery Cathode: A Combined Experimental and Theoretical Study

Soo Yeon Lim, Heejin Kim, R. A. Shakoor, Yousung Jung and Jang Wook Choi

Electrochemical and Thermal Properties of NASICON Structured $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ as a Sodium Rechargeable Battery Cathode: A Combined Experimental and Theoretical Study

Soo Yeon Lim, a Heejin Kim, a R. A. Shakoor, a,b Yousung Jung, a,c,z and Jang Wook Choi a,c, ∗

aGraduated School of EESW (WCU), bDepartment of Materials Science and Engineering, and cKAIST Institute NanoCentury, Korea Advanced Institute of Science and Technology, Yuseong-gu, Daejeon 305-701, Korea

A combined experimental and computational study on Na$_3$V$_2$(PO$_4$)$_3$ has been carried out to investigate its structural, electrochemical, and thermal properties as a sodium battery cathode. The synthesized material by a sol-gel process was well-indexed to the R-3m space group in the framework of a rhombohedral NASICON structure. Galvanostatic measurements indicate that at 3.4 V vs. Na/Na$^+$, 1.4 Na reversibly reacts with each Na$_3$V$_2$(PO$_4$)$_3$, which corresponds to a specific capacity of 84.8 mAhg$^{-1}$. Moreover, this material shows excellent rate capabilities and good cycling performance. Ex-situ XRD analyzes indicate that this material reacts with Na ions based on a reversible two-phase reaction. Thermal analyzes employing TGA/DSC and In-situ XRD at various temperatures show that this material maintains good thermal stability up to 450 °C even in the desodiated state. The promising electrochemical and thermal properties suggest that this material with the well-defined NASICON structure is a promising cathode for large-scale sodium rechargeable batteries.

© 2012 The Electrochemical Society. [DOI: 10.1149/2.015209jes] All rights reserved.

Manuscript submitted March 16, 2012; revised manuscript received May 29, 2012. Published August 14, 2012.

Renewable energy resources such as solar and wind power are promising due to their abundance and possibility of mitigating strong dependence on fossil fuels. However, those resources suffer from apparent drawbacks due to their transient natures and fluctuations. An effective approach to handle this limitation is to use electrical energy storage systems (ESSs) that can efficiently store excessive energy and release it when needed. Among various ESS technologies, rechargeable batteries are capable of reversibly storing and releasing electrical energy without involving “Carnot” cycles, thus potentially allowing for high efficiencies.

Lithium ion batteries (LIBs) have dominated over other rechargeable batteries for mobile electronics primarily due to their superior performance in power and energy densities. Nonetheless, sodium ion batteries (SIBs) could be more suitable for large-scale utility grid applications dealing with the energy storage of renewable resources. The primary reason is that device scalability is very critical for grid applications, and various advantages of SIBs including abundant resources, low material cost, and easy accessibility of new reserves could be crucial for the scalability. Beside the scalability, high power performance is another critical standard for batteries targeting grid applications because they are expected to fulfill high rate operations such as frequency regulation and load balancing maintenance. The standards in various aspects for ESS applications were recently suggested. For reference, the traditional ESSs for utility grids use pumped hydropower facilities. However, they are location-dependent and suffer from low efficiencies and inevitable large capital investment.

Considering that these two aspects - scalability and power performance - are very critical for utility grid applications, in this study, we investigate a vanadium-based NASICON (Sodium Super Ionic Conductor) material, namely Na$_3$V$_2$(PO$_4$)$_3$, as a SIB cathode material. Our electrochemical studies show that the intrinsically well-defined NASICON channel structure that facilitates excellent ionic conductivity results in decent performance in specific capacity, rate capability, and cycle life. Also, theoretical calculations provide correlations between the crystal structure and electrochemical properties. Moreover, various analyzes at different temperatures show that Na$_3$V$_2$(PO$_4$)$_3$ holds good thermal stability, thus suggesting the safe nature of this material, which is also critical for large-scale utility grid applications.

Experimental

Synthesis.— The NASICON structured Na$_3$V$_2$(PO$_4$)$_3$ was synthesized by a sol-gel method. The compound was prepared by first sequentially adding 0.305 g of ammonium metavanadate (NH$_4$VO$_3$, Sigma-Aldrich, 99.9%), 0.119 g of sodium hydroxide (NaOH, Sigma-Aldrich, ≥97.0%, pellet), 0.205 mL of phosphoric acid (H$_3$PO$_4$, Sigma-Aldrich, 85 wt% in H$_2$O) to 100 mL of 0.02 M aqueous citric acid solution (HOC(COOH)(CH$_2$COOH)$_2$, Sigma-Aldrich, ≥99.5%) while the solution was continuously stirred. Next, ammonium hydroxide (NH$_4$OH, Aldrich, 28.0 ~ 30.0% NH$_3$ basis) was slowly added to the solution to adjust its pH to 9 at which metal ions can be chelated by citric acid. Then, water was evaporated at 80 °C to transform the solution from sol to gel. After the transformation, the gel was dried in an oven at 70 °C for 1 day. Once the gel became completely dry, the gel was heat-treated at 350 °C for 5 h under nitrogen atmosphere to remove CO$_2$, H$_2$O, and NH$_3$. After this step, the compound was ground once again in a mortar to ensure uniform mixing between precursors. Finally, the powder was annealed at 700 °C under nitrogen atmosphere for 12 h to produce the final compound.

Characterization of Physical Properties.— In order to obtain the crystal structure of the compound, X-ray diffraction (XRD) analyzes were performed using a conventional X-ray diffractometer (D/MAX RB, 12 kW) with Cu Ka radiation in the 2θ range of 10˚ ~ 60˚ with a scan rate of 1˚/min. A multi-purpose attachment X-ray diffractometer (RIGAKU, D/MAX-2500) and a high/low temperature X-ray diffractometer (RIGAKU, D/MAX-ra5000) with Cu Ka radiation were used for Ex-situ electrochemical and In-situ thermal XRD analyzes, respectively. The morphology of the compound was investigated using scanning electron microscopy (FE-SEM, Philips, XL30 FEG). The thermal stability of the compound was tested by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements under nitrogen atmosphere at a heating rate of 10˚C/min. The infrared (IR) spectra was obtained using an FT-IR Spectrometer (Jasco, FT/IR-4100, Japan) under a transmission mode based on the KBr pellet method in the range of 550 ~ 2000 cm$^{-1}$.

Electrochemical Tests.— In order to evaluate the electrochemical properties of Na$_3$V$_2$(PO$_4$)$_3$, 2032 coin-type half-cells with thin sodium disks used as both the reference and counter electrodes were prepared. For this, a slurry was prepared by mixing 75 wt% of the active material, 15 wt% of super P, and 10 wt% poly(vinylidene fluoride) (PVDF) in N-methyl-2-pyrrolidone (NMP). The slurry was cast onto aluminum foil using the doctor blade technique. The cast samples were dried in a vacuum oven at 70 °C for 12 h. The mass loading of the active material was typically ~ 1.5 mg cm$^{-2}$. The final cells were assembled by sandwiching polyethylene separators (Celgard 2400) between both electrodes in an argon-filled glove box. 1 M sodium perchlorate (NaClO$_4$) in propylene carbonate (PC) was used as electrolyte.
Electrochemical properties were tested by galvanostatic measurements in the voltage range of 2.5 ~ 3.8 V (vs. Na/Na⁺) using a battery cycler (WBCS 3000, Wonatech Co.). The voltages described hereafter are with respect to Na/Na⁺.

Density Functional Theory for Voltage calculations.— In order to obtain insight into the operational potentials and formation energy in conjunction with the crystal structure, spin-polarized density functional theory (DFT) calculations were performed using the Vienna Ab initio Simulation Package (VASP) with the projector-augmented wave (PAW) pseudopotentials. The Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional was used with the Hubbard U-corrections in the rotationally invariant form introduced by Dudarev. The effective single U-J parameter of 4.2 eV was used for vanadium atom. In previous calculations for vanadium phosphates including (Li,V)(PO₄)₃,5 Li₂V₂(PO₄)₃,11 and Li₂V₃(P₂O₇)(PO₄)₂,12 a smaller value of U parameter (3.1 eV) was used for vanadium following the Wang et al.’s approach13,14 and results in the underestimated redox potentials compared to those observed in the experiments. The underestimated potentials probably originate from the improper value of the U parameter since Wang et al. estimated the U value from the experimental formation enthalpies of vanadium oxides that typically have smaller inductive effects compared to those of vanadium phosphates that locate polyanions next to vanadium. In order to reflect the stronger inductive effect in Na₉V₃(P₂O₇)(PO₄)₂, in this study, we used a higher U parameter of 4.2 eV. Indeed, Kuang et al. reported that a larger value of U parameter (4.0 eV) gives more consistent results with experiments for Li₅V(P₂O₇)(PO₄)₂.15 A plane-wave basis with an energy cutoff of 520 eV was used, and a 2 × 2 × 1 k-points mesh was sampled for well converged energy values. All calculations were performed in a ferromagnetic ordering. The calculated crystal structures were visualized using the VESTA program. We assumed a ferromagnetic ordering for all of calculations since the magnetic structure of rhombohedral Na₉V₃(P₂O₇)(PO₄)₂ has not been reported. In fact, the calculated energy difference between ferromagnetic (FM) and antiferromagnetic (AFM) ordering turned out to be less than 3 meV per formula unit, thus implying that the magnetic structure is insignificant for the energy calculation of Na₉V₃(P₂O₇)(PO₄)₂. 

Results and Discussion

Fig. 1a shows an XRD spectrum of the as-synthesized Na₉V₃(PO₄)₂. The XRD pattern was well-indexed to the R-3m space group under the rhombohedral NASICON structure with a = b = 8.7306 Å and c = 21.7863 Å. Rhombohedral Na₉V₃(PO₄)₂ has a three-dimensional framework in which alkali metal ions can easily diffuse through well-defined ion channels. As illustrated in Fig. 1b and 1c, octahedral VO₆ corner-shares with tetrahedral PO₄, which builds up [V₂(PO₄)₃]₃⁺ units in the c-axis direction and each [V₂(PO₄)₃]₃⁺ unit is interconnected through PO₄ to the same neighboring units. Na ions selectively occupy Na1 and Na2 sites. While Na1 is located between [V₂(PO₄)₃]₃⁺ units along the c-axis, Na2 is located at the same z value as the phosphorous atoms. If Na ions occupy all of the Na1 and Na2 sites, total four Na ions can be contained within each formula unit of Na₉V₃(PO₄)₂, one for Na1 site and three for Na2 sites. However, Na₉V₃(PO₄)₂ is more favorable to be synthesized due to the stable oxidation state of V³⁺ compared to the relatively unstable state of V⁵⁺ in Na₉V₃(PO₄)₂. In the crystal structure of Na₉V₃(PO₄)₂, one Na ion occupies Na1 site (1.0 occupancy) and two Na ions occupy Na2 site (0.67 occupancy). This will be described more in detail when the DFT results are discussed.

An SEM image of the as-synthesized Na₉V₃(PO₄)₂ (Fig. 1a inset) shows that the particle size is randomly distributed within the range of 1 ~ 5 μm. The formation of the designated material was also confirmed by an FT-IR analysis and the result is shown in Fig. 2. The vibration from V³⁺:O²⁻ bonds in VO₆ octahedra was detected at 629 cm⁻¹ and 979 cm⁻¹. The presence of P-O bonds of PO₄ tetrahedra was detected at 575 cm⁻¹ and 1048 cm⁻¹. The infrared bands in the range of 1150 ~ 1250 cm⁻¹ can be attributed to the stretching vibration of PO₄ units. The XRD and FT-IR analyzes indicate that the as-synthesized compound by the sol-gel method was properly synthesized. In order to evaluate this material as a SIB cathode, the electrochemical measurements were carried out, and their data are presented in Fig. 3. In the first cycle, the galvanostatic characterization (Fig. 3a) measured at a C/5 rate (1C: each charge or discharge sweep takes 1 h) shows clear plateaus around 3.4 V with charging and discharging capacities of 117.4 and 84.8 mAh/g, respectively. From the observed specific capacities, it is found that 2.0 and 1.4 Na ions per each formula unit of Na₉V₃(PO₄)₂ participate in the charging and discharging processes in the first cycle. For reference, the theoretical capacity of Na₉V₃(PO₄)₂ is 117.6 mAh/g when two Na atoms

Figure 1. (a) An XRD diffraction pattern of Na₉V₃(PO₄)₂ synthesized by a sol-gel method, (inset) an SEM image of the synthesized Na₉V₃(PO₄)₂ and (b), (c) the crystal structure of Na₉V₃(PO₄)₂ at different orientations.

Figure 2. An FT-IR spectrum of Na₉V₃(PO₄)₂ recorded in the range of 550 ~ 2000 wavenumbers.
as summarized in Fig.3d, capacities were measured at various C-rates and (d) the summarized rate performance during the discharging processes.

Figure 3. (a) Charging/Discharging profiles of Na3V2(PO4)3 at a C/5 rate in the voltage range of 2.5 ∼ 4.0 V vs. Na/Na+. (b) Cycling performance at 1C. (c) Discharging voltage profiles at different C-rates and (d) the summarized rate performance during the discharging processes.

are presumed to be involved in the reaction for each Na4V2(PO4)3. We anticipate that the relatively smaller discharge capacity compared to that of the charge in the same cycle is due to the increased kinetic barriers probably resulted from the structural changes during the Na extraction. The increased kinetic barrier was suggested for the isostructural Na3Ti2(PO4)3 case.22 The Na ion locations involved in charging-discharging within the given crystal structure will be described later when DFT data are discussed. It is also noteworthy that the hysteresis gap between charging and discharging curves is only 0.05 V at a C/5 rate, which implies that this material allows for good electronic and ionic conduction. The observed operation potential and specific capacities render this material promising as a SIB cathode. A variety of SIB cathodes have been studied and following materials are most representative: NaVPO4F23 and Na2FePO4F24 exhibited specific capacities of 73 and 115 mAh/g with redox potentials around 4.0 and 3.0 V at C/7 and C/15, respectively. Despite the decent specific capacities, however, these SIB cathode materials suffer from inferior rate capabilities perhaps due to impaired electric conductivities originating from the fluorine addition. As a layered structure, Nax[Fe1/2Mn1/2]O2 exhibited a high capacity of 190 mAh/g around 2.75 V at C/15, but showed limited cycle life (78% retention after 30 cycles).25 It is also anticipated that the layered structures suffer from relatively inferior safety. Manganese-based materials have also been investigated, and Na3Mn2O8 exhibited 128 mAh/g between 2.0 and 4.0 V at C/10. But, the operation potential was not exclusively defined.26 As a vanadium-based material, Na4V2O12 exhibited a high specific capacity of 142 mAh/g in the range of 1.5 ∼ 4.0 V at C/7 but suffered from poor cycle life (20% retention after 30 cycles).27

As shown in Fig. 3b, this material exhibits decent cycling performance. When cycled at a 1C rate, a reversible capacity of 66.5 mAh/g was retained throughout 50 cycles: After 50 cycles, only 2.7% of the initial capacity was lost, indicating that Na insertion/extraction within this material is highly repeatable. During these cycles, the columbic efficiency increases from 94.4% at the first cycle to 97.5% after 50 cycles. The efficient Na insertion/extraction based on the well-defined channels also results in good rate capability. As shown in Fig. 3c and summarized in Fig. 3d, capacities were measured at various C-rates. Even at 1C and 10C rates, specific capacities of 61.9 and 31.7 mAh/g are retained. This indicates that even when the current density increases by 10 and 100 times with respect to 0.1C, 75 and 38% of the original capacity are preserved, respectively. When the C-rate returns to 0.2C after the high rate tests, the original capacity is recovered, again suggesting that Na insertion/extraction with this material is robust. The decent cycling and rate performance are attributed to the well-developed three-dimensional channel structure, as we initially expected from its NASICON structure. It is noteworthy that by utilizing the efficient Na ionic transport, this material exhibits the good rate performance even with micrometer-scale particles in the absence of carbon-coating. The rate performance is superior to that of most of other SIB cathodes23,28 and is even comparable to that of most Li battery cathodes. We expect that the performance could be improved further by reduction of particle sizes.

The correlation between the potential profile and crystal structure was investigated further using the DFT calculations. For this, we first simulated the stable structures for various desodiated states (x = 0 ~ 4, Na4V2(PO4)3). As discussed in Fig. 1, this compound contains two kinds of Na sites, Na1 and Na2. Within these two kinds of sites, total four sites are available for Na assignment such that one Na site is assigned to Na1 and three Na sites are assigned to Na2. First, our calculation indicates that the most stable sodium ordering of the Na4V2(PO4)3 turns out to be identical to that of Na3Ti2(PO4)3, where among three Na atoms, one occupies the Na1 site and the other two occupy two of the three Na2 sites.29 As for the partially deintercalated states, Na4−xV2(PO4)3 with 1 ≤ x ≤ 3, the detailed occupancies of the sodium sites have never been reported. Thus, the most stable sodium ordering and occupancy of each sodium site were first identified by ab initio geometry optimization. For this optimization, the Ewald summation technique30 was used as an input. For reference, as for the fully occupied state, Na4V2(PO4)3, it is likely to be very difficult to directly synthesize the phase due to its mixed valence states of V3+ and unstable V2+.31 However, this state can be achieved by electrochemical reduction below 2 V vs. Na/Na+.23,24

The voltage profile was calculated by obtaining energy differences between the stable structures of different desodiated states (Fig. 4a and 4b).32 According to the calculation, Na ions are extracted in the sequence from three Na ions at the Na2 sites to one Na ion at the Na1 site, as schematically illustrated in Fig. 4a. This sequence is associated with the relative energy difference between the Na1 and Na2 sites that was evaluated from the energy of a single vacancy at each site. The Na occupancy energy for the Na1 site is 130 and 75 meV/f.u. lower compared to those of the Na2 site with x = 3 and 1, respectively.

Figure 4. Voltage profiles estimated from first principle calculations. (a) Voltage profiles estimated from DFT calculations. (inset) The stable sodium orderings calculated for different desodiated states (b) Formation energies calculated for different desodiated states.
indicating that the Na2 sites are mainly active in the composition region of $1 \leq x \leq 3$. This trend of site occupancy is consistent with the previous report for isostructured Na$_3$Ti$_2$(PO$_4$)$_3$ in that the Na1 site is fully occupied but Na2 site is empty at the desodiated compound, Na$_3$Ti$_2$(PO$_4$)$_3$.\textsuperscript{35}

Obviously, for the case of the as-synthesized Na$_3$V$_2$(PO$_4$)$_3$, only two Na ions are extracted from the Na2 sites because only two out of the three available Na2 sites are initially occupied by Na ions. Based on these structural characters, the calculation gives three plateaus for Na$_3$V$_2$(PO$_4$)$_3$, 1.84 V ($3 \leq x \leq 4$), 3.08 V ($1 \leq x \leq 3$), and 4.34 V ($0 \leq x \leq 1$), and the second plateau ($1 \leq x \leq 3$) matches with the plateau observed in the experiment, which corresponds to the two-phase reaction between Na$_3$V$_2$(PO$_4$)$_3$ and Na$_1$V$_2$(PO$_4$)$_3$. The two-phase reaction was supported by the formation energies of intermediate structures with respect to those of the initial and final phases (Fig. 4b). The convex hull for the lowest formation energy at each desodiated state in the entire $x$ range of $1 \leq x \leq 3$ indicates that the formation of the two end phases is most energetically favorable, and the two-phase reaction between Na$_3$V$_2$(PO$_4$)$_3$ and Na$_1$V$_2$(PO$_4$)$_3$ is therefore preferred. For the calculation of the minimum energy structure at each composition, total energy was calculated for an unit cell containing 6 formula units of Na$_3$V$_2$(PO$_4$)$_3$. For this, 20 lowest electrostatic energy configurations determined by the Ewald summation were used as an input for geometry optimization.\textsuperscript{30} Indeed, the preference of two-phase reactions between those two phases was verified by Ex-situ electrochemical XRD data, which will be discussed in the next paragraph. It is noteworthy that the calculated voltages are lower than the experimental ones by ~0.3 V. These underestimated voltages are in similar tendency to those of the recent reports for Na$_3$V$_2$(PO$_4$)$_3$ (0.4 V)\textsuperscript{11} and Li$_3$V$_2$(PO$_4$)$_3$ (0.65 V)\textsuperscript{22} that used the same U-parameter for vanadium. This tendency is attributed to the strong inductive effect of six PO$_4$ groups that surround each vanadium octahedron in the NASICON structure.

The crystal structure was monitored in a more stepwise manner by obtaining XRD spectra at different potentials during charging and discharging in the first cycle (Fig. 5). A couple of points are noteworthy from these Ex-situ XRD data: First, as indicated from a single flat plateau in the galvanostatic measurements, this material undergoes two-phase reactions in the process of charging and discharging. During the charging process, the peaks corresponding to Na$_3$V$_2$(PO$_4$)$_3$ (black dotted lines) gradually decrease and those corresponding to Na$_1$V$_2$(PO$_4$)$_3$ (gray dotted lines) continuously grow. During the discharging process, these peak intensity changes take place reversibly, verifying that the two-phase reaction is reversible. Second, from the peak analyzes for the end phases, it was found that as the material undergoes the phase transformation, the lattice parameters are changed from $a = b = 8.7306$ Å, $c = 21.7863$ Å (pristine) to $a = b = 8.4272$, $c = 21.4871$ (desodiated). The unit cell volume also decreases from 1438.16 Å$^3$ to 1321.5 Å$^3$ after desodiation, indicating the lattice contraction upon the extraction of Na ions.

Thermal stability of this material was also thoroughly investigated because safety has become increasingly critical for large-scale battery applications. To this end, TGA and DSC were performed for the as-synthesized and desodiated phases. As shown in Fig. 6a and 6b, TGA data indicate that only 1.6 and 1.27% of the initial mass were
lost for the as-synthesized and desodiated phases, respectively, during the temperature increase up to 450 °C. Also, DSC data for both phases confirm that this material does not encounter any phase transformations in the same temperature range as it does not show any endothermic/exothermic peaks.

The excellent thermal stability of Na₃V₂(PO₄)₃ was verified further by In-situ thermal XRD analyzes. XRD data were obtained at various temperatures in the temperature range of 25 ~ 450 °C for the as-synthesized (Fig. 7a) and desodiated (Fig. 7b) states. All of the XRD data measured in this temperature range exhibit the same peak locations, indicating that no secondary phases are formed. Both pristine and desodiated of main peaks are well-indexed as in Fig. 1a. However, it was observed that lattice parameters corresponding to various crystal orientations increase, as the XRD peaks shift to lower 2θ values. The increase in the lattice parameters originates from more significant lattice vibrations upon heating. Overall, the decent thermal stability of this material is ascribed to the stable P-O bonding.36,37 Although basic electrochemical data with this structure were reported,32 comprehensive electrochemical and thermal investigation in conjunction with theoretical calculations have never been reported.

Conclusion

We report NASICON structured Na₃V₂(PO₄)₃ as a SIB cathode. It was observed that after the initial period that shows the discrepancy between charging and discharging capacities, ∼1.4 Na per each Na₃V₂(PO₄)₃, reversibly participate in the charging and discharging processes, which corresponds to a capacity of 84.8 mAh/g. The intrinsically well-defined channel structure endows this material with decent cycling and rate performance. Moreover, owing to the stable P-O bonding, this material shows decent thermal stability up to 450 °C, thus suggesting the safe character during cell operations. Overall, this material holds various advantages attractive for large-scale ESSs.

Acknowledgments

We acknowledge the financial support by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MEST) ((NRF-2010-C1AAA001-0029031 and NRF-2012-R1A2A1A01011970) and the World Class University Program (R-31-2008-000-10055-0).

References