Improvement of Cycle Capability of VS₄ by Addition of Phosphorus Element

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ABSTRACT

Vanadium tetrasulfide (VS₄) have been attracting attention as the promising positive electrode material for next generation batteries because of its high theoretical capacity (1196 mAh g⁻¹). In this study, a typical element (i.e., Phosphorus) was introduced into VS₄ for an attempt to improve the electrochemical cycle performance of VS₄. The prepared PₓVS₄ showed significant increase in cycle capability; e.g., ca. 70% after 50 cycles for P₀.₄VS₅.₀ sample cell, being much higher than that of pristine VS₄ cell (ca. 10%). The PDF (pair distribution function) analyses indicated that the structural reversibility of VS₄ for Li insertion/extraction reactions was improved by the phosphorus addition.

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1. Introduction

Recently, with the diversification of lithium-ion batteries advancing, research and development of new active materials that can be rechargeable with high energy density are desired. Lithium-sulfur batteries are expected as next-generation batteries because of their high theoretical energy density. However, problems remain such as the dissolution of lithium polysulfide formed during discharge/charge in the electrolyte and the low conductivity of sulfur materials. Therefore, a composite electrode with a carbonaceous material was developed to enhance the electron conductivity of S, and the excellent electrochemical properties of the carbon-sulfur composite electrode were reported.

Also, as an alternative approach to improve the conductivity of sulfur, transition metal polysulfide materials that incorporate transition metals into the materials themselves are attracting attention. So far, we have reported some metal polysulfide materials (TiS₄, Li₂TiS₄, VS₄, Li₄FeS₄, etc.) exhibited higher electronic conductivity and lower solubility in electrolytes than those using elemental sulfur. Among them, vanadium tetrasulfide (VS₄) showed very high discharge capacity (950 mAh g⁻¹) and sulfur powder (99.9%, Wako, Japan) with a molar ratio of 1 : 6 were sealed in a glass tube under vacuum and heated at 400 °C for 5 h. After cooled down to room temperature, excessive sulfur was removed by annealing at 200 °C in vacuum, resulting in c-VS₄ powder.

PₓVS₄ was synthesized by mechanochemical treatment of the mixed powder of the above c-VS₄ and PₓSₐ (99%, Sigma-Aldrich, Japan) using a planetary ball-milling apparatus at a rotation speed of 270 rpm for 40 h.

2. Material characterization

The crystalline phases were evaluated by powder X-ray diffraction (XRD) using D8 ADVANCE (Buerker AXS) with a Cu-Kα radiation source in a 2θ range of 10–80°.

The conductivity of the synthesized material was measured by the two-terminal method.

XAFS measurement was performed to examine the valence state and local structure around sulfur and phosphorus atoms. S K-edge and P K-edge XAFS measurements were performed at BL-10 at Synchrotron Radiation Center (Ritsumeikan University). The sample was then transferred using an Ar-filled vessel and was set inside the apparatus of the beamline under vacuum. S K-edge and P K-edge XAFS spectra were obtained by Total Electron Yield (TEY) and Partial Fluorescence Yield (P FY).

X-ray total scattering measurements were also conducted to investigate the degradation mechanism of the PₓVS₄ cathode. The measurement was carried out in BL28XU at SPring-8. After the sample cell was disassembled, the electrode material was collected, washed with DMC, pressed into pellet, and then sealed in a Kapton film. The photon energy of the incident X-ray was 38.0 keV.

2.3 Electrochemical measurement

The electrochemical cells were constructed in an Ar-filled glove box. The working electrode consisted of 10.0 mg active material, 5.0 mg Ketchen Black and 2.0 mg polytetrafluoroethylene (PTFE) powder with an Al-mesh current collector. For the counter electrode, a Li foil having a thickness of 0.2 mm was used. The electrolyte was composed of 1.0 M Li₄SBO₂, 1.0 M LiBOB, and 0.05 M LiClO₄ in DMC. The electrochemical cell was fabricated in Ar-filled glove box. The cyclic voltammetry, charge-discharge tests, and X-ray powder diffraction measurements were performed in an Ar-filled glove box.
used was a 50:50 by volume solution of 1 M LiPF₆ in ethylene carbonate (EC) and dimethyl carbonate (DMC) (Toyama Pure Chemical Industries, Ltd.). TOSCAT-3100 (Toyo System) was used for the electrochemical measurement. The electrochemical discharge/charge tests were carried out at a current density of 119.6 mA g⁻¹ (corresponding to 0.1 C) between 2.6 and 1.5 V.

3. Results and Discussions

The XRD patterns of PₓVSᵧ, as well as MM-VS₄ (prepared by the mechanochemical treatment of c-VS₄) and P₂S₅, are shown in Fig. 1. As reported previously,¹⁹,²⁰ the MM-VS₄ sample showed a broad peak at 15°, indicating an amorphous phase formed by the mechanical treatment, and several small peaks assigned to V₂O₃, which was contaminated in the initial V₂S₃ powder and was not removed completely by heating in sulfur-rich atmosphere. In PₓVSᵧ samples, the peak around 15° shifted to lower angle with the incorporation of phosphorus ion. This is indicative of the change of short-range order by phosphorus addition. The details of structural analysis will be discussed later in the analysis of total X-ray scattering and XANES.

Figure 2 shows the conductivity of the combined MM-VS₄ and PₓVSᵧ. As the amount of phosphorus addition into the material increases, a decrease in conductivity is confirmed.

Figure 3 shows the electrochemical performance of the sample cells. The shape of the initial discharge/charge curve changed by phosphorus addition. Also, the initial discharge capacity decreased and irreversible capacity increased with the amount of phosphorus addition (x in PₓVSᵧ). (Fig. S1) Phosphorus doping roughly decrease the conductivity of VS₄, though small amount of doping slightly increased it. Such observation could be originated from the decrease in conductivity with P doping (x-value) shown in Fig. 2, though they are not directly associated with it.

However, the phosphorus addition was effective for improving the cycle capability of the cells; the capacity retention after 50 cycles was significantly improved with x-value.

Figure 4 shows discharge/charge curves with electrochemical cycling. The curve shape of MM-VS₄ is significantly different after the initial discharged/charged, and the polarization tends to increase.

Figure 1. (a) XRD patterns of PₓVSᵧ, MM-VS₄ and P₂S₅, and (b) the enlarged view at 2θ = 10–20°.

Figure 2. Conductivity of MM-VS₄ and PₓVSᵧ.

Figure 3. (a) Initial discharge/charge curves of Li||1 M LiPF₆/(EC+DMC)/active materials cell at 0.1 C. (b) Capacity retention (vs. 2nd Discharge) and Coulomb efficiency of MM-VS₄ and PₓVSᵧ.
with the cycle. On the other hand, curves shape of P₀.₄VS₅.₀ is not changed significantly even after the initial discharge/charge, and the polarization increasing with the cycle tends to be small. This result suggests that phosphorus addition is suppressed the structural change of VS₄ for Li insertion/extraction reactions, resulting in the improvement of the structural reversibility.

To investigate the discharge/charge mechanism of PₓVS₄, we performed total X-ray scattering measurements for a given discharged/charged electrodes, and performed PDF analysis of the acquired data (Fig. 5). The result of PDF analysis for MM-VS₄ sample indicated that a peak derived from Li₂S was observed at the first discharge end (1.5 V) and disappeared at the subsequent charge
indicating a reversible electrochemical reaction in the initial cycling. After 10 cycles, a peak derived from Li$_2$S was observed even at the charge end (2.6 V). These results suggest that electrochemically inactive Li$_2$S, which might be formed, for example, by breaking the conductive path during prolonged cycling, accumulated in the MM-VS$_4$ electrode and it causes an electrochemically irreversible reaction. On the other hand, in P$_x$VS$_y$, the peak derived from Li$_2$S was not observed at the initial discharge end (1.5 V), but was observed at the discharge end after 10th cycle. But, the peak derived from Li$_2$S was not observed at the charge end (2.6 V), up to the 20th cycle. The above results suggest that the addition of phosphorus improved the reversibility of the discharge/charge reaction, thereby improving the electrochemical cycling.

To investigate the valence state and local structure around S and P atoms through the electrochemical reaction in P$_x$VS$_y$, we performed S K-edge and P K-edge XAFS measurements. Figure 6 shows the S and P K-edge X-ray absorption near-edge structure (XANES) spectra. The S K-edge XANES spectra showed similar profile to that of Li$_3$PS$_4$ after the 1st discharge, and it returned to the initial one after the subsequent charge. And these profiles repeated reversibly after discharge and charge up to the 20th cycle. This is indicative of the reversible change of the valence state and local structure around S atoms in the P$_x$VS$_y$ sample for Li insertion/extraction reactions. Such changes were observed both on the bulk (PFY) and surface (TEY). Also, characteristic features originated from Li$_2$S was not obviously observed, due probably to the overlaps of similar spectra of other sulfur compounds (P$_2$S$_5$ or Li$_3$PS$_4$), though Li$_2$S component was observed in PDF spectra (Figs. 5 and 6). All the P K-edge XANES spectra showed similar profiles to Li$_3$PS$_4$. Slight differences were observed in the initial discharge/charge.

Figure 6. XANES spectra of (a) S K-edge (PFY), (b) S K-edge (TEY), (c) P K-edge (PFY) and (d) P K-edge (TEY) of as-prepared P$_{0.4}$VS$_{5.0}$ and from the initial discharge/charge to 20th discharge/charge. (Solid-line; after discharge, Dot-line; after charge)
charge, which would be due to slight deformation of the local structure around P atoms for Li insertion/extraction reactions, and such slight deformation disappeared to result in the formation of stable local structure based on PS$_4$ octahedra. However, as the cycle proceeded, the peak intensity around 2148 eV reduced, and new energy peaks around 2152 eV and 2158 eV appeared, particularly in TEY mode. The newly appeared peaks could be assigned to be originated from PO$_4^{3-}$ and PF$_6^-$, respectively, which would be formed considerably on the surface of P$_x$VS$_y$. These results suggest that some decomposition products derived from the electrolyte (LiPF$_6$/(EC + DMC)) accumulate on the electrode surface as the electrochemical cycling proceeds, and such high-resistive surface by-products would be responsible for the degradation of cycle capability.

Figure 7 shows the Fourier transforms of $k^3$-weighted extended X-ray absorption fine structure (EXAFS) of P K-edge spectra. As in the XANES spectra (Fig. 6), all the EXAFS spectra of P$_x$VS$_y$ showed similar profile to Li$_2$PS$_4$. Similarly, in the initial discharge/charge, a slight profile change due to a slight deformation of the local structure around the P atom in the Li insertion/extraction reaction was observed. Such observations were also confirmed by the radial distribution shown also in Fig. 7, where the nearest neighbor distribution changed reversibly for several cycles and showed almost no changes after 10 cycles. This suggests that the local structure around P atoms in P$_x$VS$_y$ was rearranged by Li insertion/extraction reactions and gradually optimized during electrochemical cycling. Such structural change (formation of PS$_4$ tetrahedra in the V - S - P network) could contribute to the improvement of reversibility for Li insertion/extraction. Also, assuming that introduced P atoms all contributed to form PS$_4$, the present sample P$_x$VS$_{4+2.5y}$ is nominally described as VS$_{4+1.5y}$x(PS$_4$), which suggests that the amounts of electrochemically active S atoms decrease with P content, being roughly consistent with the results shown in Table S1.

Of course, future investigation is needed for discussing more detailed phosphorus addition mechanism. Currently, we are carrying out the spectroscopic measurements of P$_x$VS$_y$ using Raman spectroscopy, and investigating structural changes associated with discharging/charging. The results will be reported in the near future.

4. Conclusions

We prepared P$_x$VS$_y$ positive electrode material by mechanochemical treatment of c-VS$_4$ and P$_2$S$_5$. From the change in the shape of the initial discharge curve, phosphorus addition into VS$_4$ changed the discharge/charge mechanism. The profiles of PDF analysis after discharge/charge showed electrically inactive material (Li$_2$S) formation/accumulation in VS$_4$ with the electrochemical cycling. On the other hand, in P$_x$VS$_y$, Li$_2$S was formed at the discharge end, but it was disappeared after charge end, suggesting a reversible electrochemical cycling. The profile of XAFS showed the reversible change of the local structure around sulfur atoms for Li insertion/extraction reactions, and the formation of phosphorus compounds on the active material surface. From the above results, the addition of phosphorus to VS$_4$ showed the effect of reversible change the structure of S, resulting in the improvement of cycle performance, and the primary cause of capacity degradation of electrochemical cycling is the formation of highly-resistive by-products on the active material surface.

Supporting Information

The Supporting Information is available on the website at DOI: https://doi.org/10.5796/electrochemistry.21-00026.

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