Improvement of Electrochemical Property of VS₄ Electrode Material by Amorphization via Mechanical Milling Process

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Improvement of electrochemical property of VS$_4$ electrode material by amorphization via mechanical milling process

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Abstract

Amorphous VS₄ (a-VS₄) electrode material was synthesized by mechanical milling of crystalline VS₄ (c-VS₄). The columbic efficiency of the a-VS₄ cell was significantly improved (ca. 86%) at the first cycle as compared with the c-VS₄ cell (ca. 77%), resulting in the improved capacity retention for prolonged cycling. Pair distribution function (PDF) analysis obtained from X-ray total scattering data, revealed that the radial atomic distribution of a-VS₄ at initial stage was similar to that of the low-crystalline VS₄ appeared after the first cycle of c-VS₄. This is suggestive that the amorphization via mechanical milling process gave rise to the preparation of “first cycled VS₄” which would contribute to the improved columbic efficiency at the first cycle and the resulting improved capacity retention for prolonged cycling. The structure of a-VS₄ could be visualized by first-principles molecular dynamic calculation of “first-cycled VS₄”.

Keywords: amorphous VS₄, mechanical milling, high capacity, columbic efficiency
1. Introduction

Rechargeable lithium/sulfur (Li/S) batteries have been attracting much attention as next generation high-energy battery. In conventional Li/S systems, sulfur or lithium sulfide is used as an active material in positive electrode with ether-based liquid electrolyte. Owing to their poor electronic conductivity and dissolution of lithium polysulfide (Li$_2$S$_n$) into the electrolyte, a large amount of carbon material is necessary to improve the conductivity, as well as to suppress the migration of Li$_2$S$_n$ (by trapping on the porous surface of carbon material), and it limits the energy density of the battery.

Utilization of transition metal polysulfides (Li$_x$MS$_y$) have several advantages to substitute for sulfur or lithium sulfide in Li/S systems. Electronic conductivity and specific gravity of Li$_x$MS$_y$ is higher than those of sulfur or lithium sulfide, which lead to higher energy density of Li/S batteries. Furthermore, utilization of Li$_x$MS$_y$ has an advantage to suppress significantly the dissolution of lithium polysulfide into organic electrolytes, as compared with elemental sulfur or lithium sulfide, because of the formation of chemical bonding between transition metal and sulfur, resulting in suppressing the dissociation to be solved as Li$_2$S$_n$ in electrolytes; indeed, the UV-vis absorption spectra of the electrolyte for the TiS$_4$ cell showed significantly reduced absorption intensity around 250 – 300 nm, where polysulfides show strong absorption peaks, as compared to the TiS$_2$ + S blended cell.³

VS$_4$ (Patronite) is one of the promising positive electrode materials in Li/Li$_x$MS$_y$ batteries due to its high theoretical capacity (ca. 1195 mAh g$^{-1}$). Cho and Shin’s group employed a hydrothermal reaction to prepare VS$_4$/reduced graphene oxide (rGO) nanocomposite material for anode in Li batteries and studied the
discharge/charge mechanism across a wide voltage range (3.0 - 0.01 V). They proposed that the electrochemical reaction \((\text{VS}_4 + 8\text{Li} \rightarrow \text{V} + 4\text{Li}_2\text{S})\) occurs at the initial discharge, and the following reaction \((\text{Li}_2\text{S} \rightleftharpoons \text{S} + 2\text{Li}^+ + 2e^-)\), similar to conventional Li/S systems, proceeds after the first cycle, while metallic vanadium remains inert.\(^9,10\) More recently, the discharge/charge mechanism of \(\text{VS}_4/\text{rGO}\) was studied in detail by Britto et al.;\(^11\) they reported that lithiation of \(\text{VS}_4\) resulted in the formation of \(\text{Li}_3\text{VS}_4\), followed by \(\text{Li}_{3+x}\text{VS}_4\) \((0.5 < x < 1)\), and eventually \(\text{Li}_2\text{S}\) plus elemental V, and a phase similar to \(\text{VS}_4\) was partially re-formed during charging process, which was indicated by short-range characterization using \(^{51}\text{V}\) nuclear magnetic resonance spectroscopy (NMR), S K-edge X-ray absorption near edge spectroscopy (XANES), and pair distribution function (PDF) analysis of X-ray data.

Although \(\text{VS}_4/\text{carbon composites}\) exhibited superior electrochemical properties and the analyses of the composites have been well studied, simple \(\text{VS}_4\) itself could be a promising cathode material and the analysis of its discharge/charge mechanism would be still useful for designing \(\text{VS}_4\) as practical cathode material in Li/S batteries. Recently, we have studied discharge/charge mechanism using X-ray absorption and total scattering measurements and suggested that a low crystalline phase similar to \(\text{VS}_4\) was formed at first cycle and discharge/charge reactions would proceed reversibly after the second cycle.\(^12\) This observation was consistent with the first-principles calculations carried out for demonstrating electrochemical performances of \(\text{VS}_4\); Lian et al.\(^13\) demonstrated the multiple phase transformations during \(\text{Li}^+\) insertion, starting with the transformation from \(\text{VS}_4\) to \(\text{Li}_3\text{VS}_4\) and followed by gradual decomposition to result in an amorphous phase, accompanying with the long-range migration of \(\text{Li}_2\text{S}\) molecules. Based on these results, we thought that the synthesis of \(\text{VS}_4\) with similar local structure to the first-cycled \(\text{VS}_4\)
(an amorphous phase) would be an effective way for further improvement of electrochemical performance of VS$_4$. Herein, we employed mechanical milling process to prepare amorphous VS$_4$ and evaluated its electrochemical property. Also, for comprehensive understanding and visualization of the discharge/charge mechanism, we carried out density functional theory-based molecular dynamics (DFT-MD) calculation of VS$_4$ sample for Li insertion/extraction reactions.

2. Experimental

2.1 Sample preparation

We synthesized amorphous VS$_4$ (a-VS$_4$) using crystalline VS$_4$ (c-VS$_4$) as starting material via mechanical milling process at room temperature. c-VS$_4$ was prepared as reported previously;$^{12}$ powders of V$_2$S$_3$ (99%, Koujundo chemicals, Japan) and sulfur (99.9%, Wako, Japan) were weighed out at 1 : 6 molar ratio, and the mixture was sealed in a glass tube under vacuum, followed by heated at 400°C for 12 h. The heated sample was then crushed with mortar, and again sealed in a glass tube and reheated under the same condition. After cooling to room temperature, excessive sulfur was removed by annealing at 200°C under vacuum. 2.0 g of c-VS$_4$ and 500 zirconia balls (4 mm diameter) were put into 45 ml zirconia pot under Ar atmosphere and was set in planetary ball mill apparatus (Fritsch pulversitite 7), which was treated at a rotation speed of 270 rpm for 40 h (with 15 min rest time for each 1 h milling, and interval scratching of the pot-inside after each 10 h milling) to obtain a-VS$_4$. 

2.2 Sample characterization

The crystalline phases were examined by powder X-ray diffraction (XRD) using D8 ADVANCE (BrukerAXS) with a Cu-Kα radiation source within a 2θ range of 10 - 80 degrees. A TITAN3 G2 60-300 electron microscope (FEI, Co, Ltd) was used for the transmission electron microscopy (TEM) measurements. The α-VS₄ powder was directly dispersed on a Cu-mesh-supported carbon film for TEM measurements. Scanning electron microscopy (SEM) imaging (JSM-6510, JEOL) was used for microstructural observation. The electronic conductivities of the samples were measured with two electrode cell at 25°C using a frequency response analyzer (SI 1260, Solartron Analytical), covering a frequency range from 0.1 Hz to 1 MHz with an applied voltage of 10 mV, after the sample powder was cold-pressed into a pellet with 10 mm diameter and 0.5 mm thickness under the pressure of 360 MPa in Ar atmosphere.

The electrochemical cells were assembled in an Ar-filled glove box. The working electrode consisted of 10.0 mg of VS₄, 5.0 mg Ketjen Black, and 2.0 mg polytetrafluoroethylene (PTFE) powder with an Al-mesh current collector. The counter-electrode was a Li foil of thickness 0.2 mm. A solution of 1 M (M = mol dm⁻³) LiPF₆ in 50 : 50 ethylene carbonate (EC) and dimethyl carbonate (DMC) by volume (Tomiyama Pure Chemical Industries, Ltd.) was used as the electrolyte. The electrochemical measurements were carried out at 30°C at current density of 59.8 mA g⁻¹ (0.05C) using a TOSCAT-3100 battery-testing system (Toyo System). For ex situ PDF analysis, the electrode materials were removed from the Al-mesh current collector and washed with DMC, and the pellets (3 mm diameter) were prepared and sealed with kapton film in Ar atmosphere. X-ray total scattering data were collected using a BL28XU
at SPring-8. The photon energy of the incident energy X-rays was 38.0 keV. The data were corrected and Fourier transformed to obtain $g(r)$ using BL04B2 software\textsuperscript{14,15} with Q-range of 0.7 – 16 Å.

2.3 DFT-MD calculations

The first-principles DFT-MD calculations were carried out using OpenMX.\textsuperscript{16} The model clusters for Li$_x$VS$_4$ ($x = 0, 1, 3, 5$) contained $1 \times 1 \times 2$ unit cells, and first they were structurally optimized with the lattice parameters unrestricted. Then the MD simulations were carried out for 500 MD steps (500 fs; 1 MD step corresponds to 1 fs). The atomic models were exhibited using VESTA software.\textsuperscript{17}

3. Results and discussion

Figure 1 shows the XRD patterns of the samples depending on the mechanically milling (MM) time, including $c$-VS$_4$ (MM-0h) and $a$-VS$_4$ (MM-40h). The $a$-VS$_4$ sample showed clear intensity reduction and broadening of the diffraction peaks ascribed to $c$-VS$_4$, indicating that crystallinity of VS$_4$ is lowered with mechanical milling process. Some small peaks in $a$-VS$_4$, such as $2\theta = 24, 33,$ and $54^\circ$, are assigned as V$_2$O$_3$, which was contaminated in the initial V$_2$S$_3$ reagent, and are also observed in $c$-VS$_4$ with enlarged intensity scale.

Lowered crystallinity was also confirmed by TEM observations. As shown in Figs. 2 (a)-(c), any distinct lattice fringes originated from the long-range ordering of the constituent atoms were not observed even in the most enlarged scale in the $a$-VS$_4$
sample. Also, the electron diffraction pattern showed no distinct spots, indicating that the sample was in an amorphous state. The morphologies of c-VS$_4$ and a-VS$_4$ are shown in Figs. 2 (e) and (f), respectively. The particle changes from needle-like to sphere-like shape via mechanical milling, and the averaged particle size, represented as $D_{50}$, changes from 8.0 $\mu$m (c-VS$_4$) to 2.7 $\mu$m (a-VS$_4$). The measured electronic conductivities of the samples are shown in Fig. 3. The conductivity increases shortly with the milling time and attains nearly constant after several tens hours. The higher conductivity value of a-VS$_4$ ($3.3 \times 10^{-5}$ S cm$^{-1}$ at 25$^\circ$C), as compared to that of c-VS$_4$ ($6.7 \times 10^{-7}$ S cm$^{-1}$), would be due to its smaller particles and is comparable to other amorphous metal polysulfides (e.g., $10^{-5} - 10^{-6}$ S cm$^{-1}$ for a-TiS$_4$)$^{18}$.

The electrochemical property of these materials was examined with carbonate-based electrolyte and Li metal anode at 59.8 mA g$^{-1}$ (0.05C) in the voltage range of 1.0 – 3.0 V (Fig. 4). The cell with a-VS$_4$ sample shows a high discharge capacity of ca. 950 mAh g$^{-1}$, which is similar to that of the c-VS$_4$. The voltage plateau in the first discharge of the a-VS$_4$ rises up to 2.0 V, as compared to that of the c-VS$_4$ (1.9 V), which is consistent with the above-mentioned improved electronic conductivity via mechanical milling process. Also, the reduced resistivity of the electrochemical reactions due to the increased reaction sites via amorphization would be responsible for such changes in voltage plateau. The coulombic efficiency at the first cycle is 86%, which is significantly improved as compared with the c-VS$_4$ cell (77%), resulting in the improved cycle capability for prolonged cycling; the capacity retention after 20 cycles is ca. 43% and 27% for a-VS$_4$ and c-VS$_4$ cells, respectively (Fig. 4(b)). The degree of the improved coulombic efficiency might be related quantitatively with the “degree of amorphization” of c-VS$_4$, which is observable qualitatively in the XRD profiles depending on the MM
time (Fig. 1).

For examining the improved mechanism of reversibility in the first cycle, we carried out the PDF analyses for the $\alpha$-VS$_4$ cathode to clarify the local structure during Li insertion/extraction reactions. Figure 5 shows the $g(r)$ of $\alpha$-VS$_4$ and those after the first discharge (Li$_5$VS$_4$) and charge (LiVS$_4$). Data for $c$-VS$_4$ and the histogram of partial correlation calculated on the basis of the crystallographic data for VS$_4$ (JCPDS No.072-1294) are also shown for comparison. By comparing with the calculated histogram, the short-range profile of $c$-VS$_4$ is assigned as follows; 2.0 Å as $S_2^{2-}$ dimers ((S – S)$_2^{2-}$), 2.4 Å as S – V interatomic distance, and 3 – 5 Å as several S – S and S – V interatomic distances, respectively. The $g(r)$ of $\alpha$-VS$_4$ shows very similar but slightly deviated profile to that of $c$-VS$_4$; both show similar peaks at 2.4 and 3.2 Å but with different broadness, and the profiles around 3 – 5 Å are rather different. This is indicative that the local structure (atomic position) of $\alpha$-VS$_4$ is slightly deviated from that of $c$-VS$_4$.

After the initial lithiation (Li$_5$VS$_4$), the correlations of (S – S)$_2^{2-}$ dimers at 2 Å disappeared, while they are recovered after the following de-lithiation (LiVS$_4$). V – S bond at 2.4 Å is shifted to shorter value and rather broadened after lithiation, suggesting that the coordination number around V atoms are lowered via increasing Li atoms coordinated to S atoms. A notable point is that the $g(r)$ after the first cycle (LiVS$_4$) is very similar to that of the initial one ($\alpha$-VS$_4$). This is indicative that the $\alpha$-VS$_4$ showed reversible structural changes for the Li insertion/extraction reactions. This makes a clear contrast to the case of $c$-VS$_4$, where the $g(r)$ of the cycled $c$-VS$_4$ shows rather different profile to the initial one. Such local structural reversibility would be responsible for the improved coulomb efficiency, Fig. 4, and the improved capacity retention for prolonged cycling. Although some other factors, such as higher conductivity of $\alpha$-VS$_4$, might contribute to the
improved coulombic efficiency and cycle capability, these factors would affect little to
the present improvement, because similar improved electrochemical performances were
observed under lower current density (0.01C).

For further analyses and visualization of the discharge/charge mechanism of
\(a\)-VS\(_4\), we carried out the DFT-MD calculations for the model cluster Li\(_x\)VS\(_4\) (\(x = 0, 1, 3, 5\)). c-VS\(_4\) (JCPDS No.072-1294) was used as the starting material for the simulations.
First, c-VS\(_4\) was lithiated stepwise to the composition of Li\(_x\)VS\(_4\) (\(x = 1, 3, 5\)), and then
Li\(_3\)VS\(_4\) was de-lithiated stepwise to Li\(_x\)VS\(_4\) (\(x = 3, 1, 0\)). Each radial distribution function
(RDF) was calculated and compared with the corresponding \(g(r)\) shown in Fig. 5. Figure
6(a) shows the RDF of the lithiated (Li\(_5\)VS\(_4\)) and de-lithiated (Li\(_0\)VS\(_4\)) clusters. Although
there observed some inconsistency between \(g(r)\) and calculated RDF profiles, some
characteristic features in \(g(r)\) were consistently observed in the calculated RDF; the (S –
S)\(^2\) dimers at 2.0 Å disappeared after lithiation (Li\(_5\)VS\(_4\)) and recovered after de-lithiation
(Li\(_0\)VS\(_4\)), and V – S bond at 2.4Å was rather broadened after lithiation (Li\(_5\)VS\(_4\)).
Therefore, the present DFT-MD simulations provide one of the plausible local structure
models of lithiated/de-lithiated VS\(_4\). One notable point is that the RDF of de-lithiated
cluster (Li\(_0\)VS\(_4\)) showed similar profile to \(g(r)\) of the initial \(a\)-VS\(_4\), Fig. 5. This is
suggestive that the \(a\)-VS\(_4\) could be visualized using the cluster model of Li\(_0\)VS\(_4\). Actually,
the calculated structural models of Li\(_x\)VS\(_4\) are shown in Fig. 7. The local structure of
Li\(_0\)VS\(_4\) was similar to that of c-VS\(_4\) but distorted slightly from the pristine state, though
such local structure could be one of the plausible models of \(a\)-VS\(_4\). This Li\(_0\)VS\(_4\) also
showed very similar local structure to that of LiVS\(_4\) (after de-lithiation), suggesting a
superior structural reversibility of \(a\)-VS\(_4\) for Li insertion/extraction reactions, which
would result in the improved coulomb efficiency in the initial cycle. Of course, further
investigation is needed for discussing more detailed discharge/charge mechanism (such as the change of valence state of V and S), we are now carrying out the spectroscopic measurements of the discharged/charged \(a\)-VS\(_4\) using, for example, XAFS technique, and the results will be reported in the near future.

4. Conclusion

We have prepared amorphous VS\(_4\) (\(a\)-VS\(_4\)) electrode material by mechanically milling the \(c\)-VS\(_4\) for an attempt to apply in Li/Li\(_x\)MS\(_y\) battery. The columbic efficiency of the \(a\)-VS\(_4\) cell was significantly improved (\(ca.\) 86\%) at the first cycle as compared with the \(c\)-VS\(_4\) cell (\(ca.\) 77\%), resulting in the improved capacity retention for prolonged cycling. PDF analysis revealed that the \(g(r)\) of \(a\)-VS\(_4\) at initial stage was similar to that of the low-crystalline VS\(_4\) appeared after the first cycle. This is suggestive that the amorphization via mechanical milling process gave rise to the preparation of “first cycled VS\(_4\)” which would contribute to the improved columbic efficiency, as well as the improved cycle capability.

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Figure captions

Figure 1  XRD patterns of the VS₄ samples depending on the mechanically milling (MM) time, including c-VS₄ (MM-0h) and a-VS₄ (MM-40h). Data for VS₄ (JCPDS No. 072-1294) are also shown for comparison.

Figure 2  (a)-(c) TEM images and (d) electron diffraction pattern of a-VS₄. SEM images of (e) c-VS₄ and (f) a-VS₄ are also shown.

Figure 3  Measured electronic conductivity of the VS₄ samples depending on the mechanically milling time.

Figure 4  (a) Discharge/charge curves of Li | 1M LiPF₆/(EC+DMC) | VS₄ cell at 59.8 mA • g⁻¹ (0.05C). Solid and dashed lines donate the curves with a- and c-VS₄ cathode cells, respectively. (b) Cycle capability of a- and c-VS₄ cells. (c) The points for ex-situ PDF analysis.

Figure 5  PDF patterns of a-VS₄ and those after the first discharge (Li₃VS₄) and charge (LiVS₄). Data for c-VS₄ and histogram of partial correlation, based on JCPDS No. 072-1294, are also shown for comparison. The red, blue and green frequencies show S – S, S – V, and V – V bonds, respectively.

Figure 6  Radial distribution function for c-VS₄, Li₃VS₄, LiVS₄, and Li₀VS₄,
simulated by DFT-MD calculations.

Figure 7  Structural models of Li$_x$VS$_4$ for lithium insertion and extraction using DFT-MD simulations.
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Figure 2  K. Koganei et al.
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Figure 4(a)  K. Koganei et al.
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Figure 5  K. Koganei et al.
Figure 6    K. Koganei et al.

Radial distribution function (a.u.)

Li$_0$VS$_4$

LiVS$_4$

Li$_5$VS$_4$

c-VS$_4$

$\text{total}$

$\text{S-S}$

$\text{S-V}$

$\text{V-V}$

$r / \text{Å}$
Figure 7  K. Koganei et al.