



## Analysis of the discharge/charge mechanism in VS<sub>4</sub> positive electrode material



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### ABSTRACT

Among transition metal sulfides, VS<sub>4</sub> is a promising candidate material for the positive electrode in rechargeable Li/metal-sulfide batteries, due to its long, flat plateau at about 2.0 V and its high theoretical capacity (1195 mAh g<sup>-1</sup>). In this study, we prepared VS<sub>4</sub> positive electrode material by heating in a sealed tube, and studied local structural changes during charge/discharge cycles via X-ray absorption and scattering spectroscopies, focusing on the reversibility of VS<sub>4</sub>. The findings reveal that a VS<sub>4</sub>-like local structure was formed in the first cycle, and that subsequent cycles showed reversible changes.

### 1. Introduction

Recently, rechargeable lithium/sulfur (Li/S) batteries have attracted attention because of their high theoretical energy density. Li/S battery systems are regarded as a candidate replacement for present state-of-the-art Li-ion batteries (LIBs) for electric vehicles. However, several major technical challenges remain, such as dissolution of lithium polysulfide (Li<sub>2</sub>S<sub>n</sub>,  $n > 2$ ) into organic electrolytes [1] and electronic insulation of elemental sulfur, which cause low cycle life and low energy efficiency.

To address these problems, researchers have examined transition-metal sulfides [2–8]. Utilizing these materials as substitutes for sulfur improves electronic conductivity and overcomes the dissolution of lithium polysulfide into organic electrolytes because of low solubility in electrolytes. Specifically, nanostructured transition metal sulfides and carbonaceous material nanocomposites have been proposed as anode materials for LIBs due to their high specific energy, lower volumetric expansion, and high cycle stability. The research trends for material designs and their electrochemical properties were summarized well in a recent review [6].

For the positive electrode material of Li/metal-sulfide batteries, VS<sub>4</sub> (Patronite) is the most promising of several candidate materials, due to its discharging voltage plateau at about 2.0 V and its high sulfur content, which conveys high specific capacity (ca. 1195 mAh g<sup>-1</sup>). It also

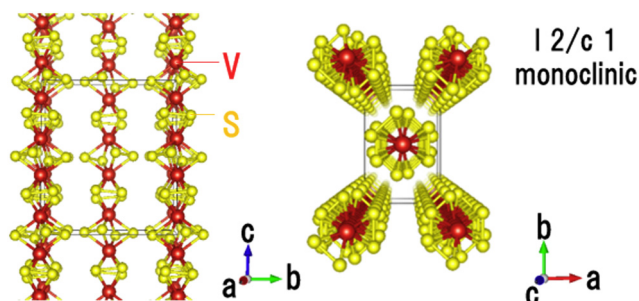
has potential as a negative electrode material in combination with high-voltage positive electrode materials [7,8]. VS<sub>4</sub> was discovered in 1906 [9] and its crystal structure was analyzed in 1964 [10]. VS<sub>4</sub> has a linear chain structure, composed of V<sup>4+</sup> ions and S<sub>2</sub><sup>2-</sup> dimer, and stacks with weak van der Waals force [10] (Fig. 1). The structural models were described using VESTA software [11]. The interchain distance is 5.83 Å. In previous works, Cho and Shin's group employed a hydrothermal reaction to prepare VS<sub>4</sub>/reduced graphene oxide (rGO) nanocomposite materials [7,8], and studied the discharge/charge mechanism across a wide voltage range (3–0.01 V). They proposed that the electrochemical reaction (VS<sub>4</sub> + 8Li → V + 4Li<sub>2</sub>S) occurs at the initial discharge, and that (Li<sub>2</sub>S ↔ S + 2Li<sup>+</sup> + 2e<sup>-</sup>) reaction follows after the first cycle, while metallic vanadium remains inert [7]. However, more recently, the discharge/charge mechanism of VS<sub>4</sub>/rGO material was studied to characterize short-range structure using <sup>51</sup>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 [12]. It was proposed that a phase similar to VS<sub>4</sub> was formed in the charging process. Although VS<sub>4</sub>/rGO has been well studied so far for negative electrode material, VS<sub>4</sub> itself could be a promising cathode material and the analysis of its discharge/charge mechanism would be useful for designing VS<sub>4</sub> as practical cathode material in Li/metal-sulfide batteries.

In this study, we prepared VS<sub>4</sub> as a positive electrode material in the

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**Fig. 1.** The structure of  $VS_4$ . (a) Side view of monoclinic  $VS_4$ . (b) View along the c-axis, showing V atoms (red) and S atoms (yellow) [10]. The structural models were described using VESTA software [11]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

absence of carbonaceous material by thermal treatment under vacuum in a sealed glass tube, and studied its discharge/charge mechanism using *ex situ* pair distribution function (PDF) analysis and *ex situ* V and S K-edge X-ray absorption fine structure (XAFS) spectral analysis to elucidate the intrinsic electrochemical properties of  $VS_4$  itself, particularly in the absence of a graphitic layer. Through these structural analyses, we evaluate the applicability of  $VS_4$  as a positive electrode material for use in Li/meta-sulfide battery technology.

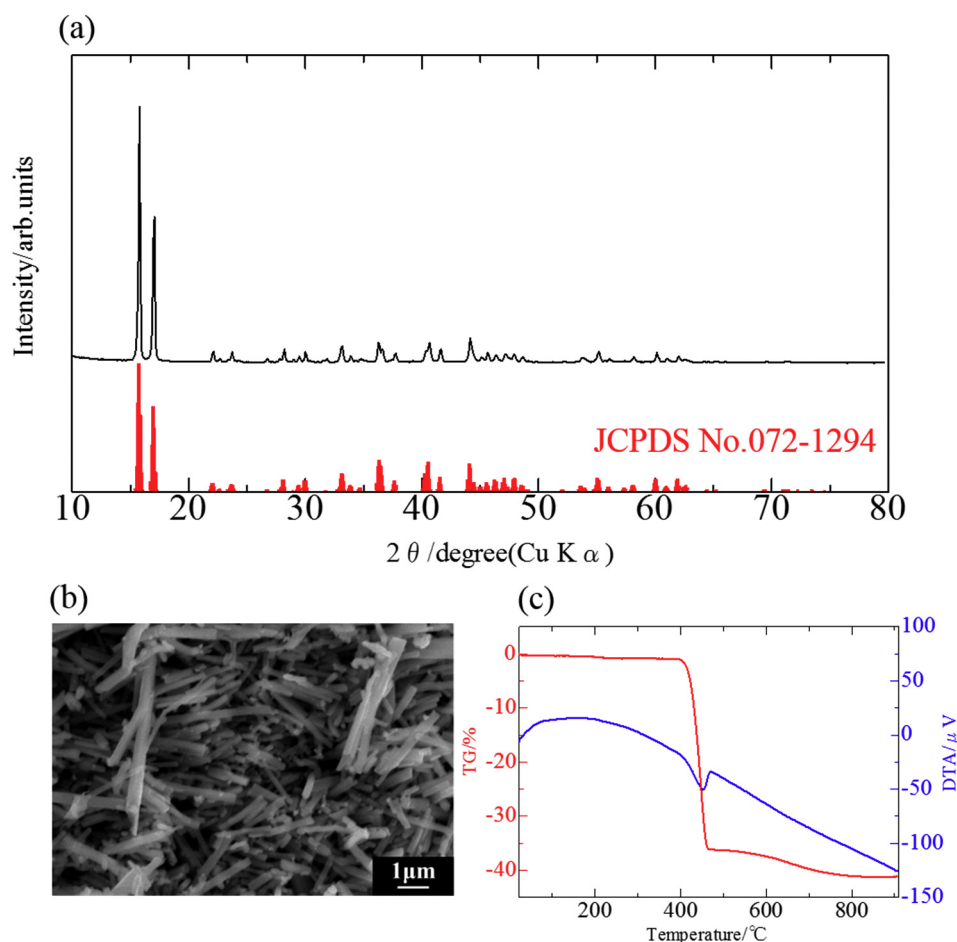
## 2. Experimental

Powders of  $V_2S_3$  (99%, Koujundo Chemicals, Japan) and sulfur (99.9%, Wako, Japan) were weighed out at 1:6 mol ratio. The mixture was sealed in a glass tube under vacuum and heated at 400 °C for 12 h. The heated sample was then crushed with a mortar, and again sealed in a glass tube and reheated under the same conditions. After cooling to room temperature, excessive sulfur was removed by annealing at 200 °C under vacuum.

The crystalline phases were evaluated by powder X-ray diffraction (XRD) using D8 ADVANCE (Burker AXS) with a  $Cu-K\alpha$  radiation source within a  $2\theta$  range of 10–80°. Scanning electron microscopy (SEM) imaging (JSM-6510; JEOL) was used for microstructural observations. Thermogravimetric (TG) and differential thermal analysis (DTA) data were obtained between 23 and 900 °C at heating rate of 10 °C/min in Ar atmosphere.

The electrochemical cells were assembled in an Ar-filled glove box. The working electrode consisted of 10.0 mg  $VS_4$ , 5.0 mg Ketjen Black, and 2.0 mg polytetrafluoroethylene (PTFE) powder with an Al-meshed current collector. The counter-electrode was a Li foil of thickness 0.2 mm. A solution of 1 M  $LiPF_6$  in 50:50 ethylene carbonate (EC) and dimethyl carbonate (DMC) by volume (Tomiya Pure Chemical Industries, Ltd.) was used as the electrolyte. The electrochemical measurements were carried out at 30 °C at a current density of  $59.8 \text{ mA g}^{-1}$  (0.05C) using a TOSCAT-3100 battery-testing system (Toyo System).

For *ex situ* PDF analysis, the electrode materials were stripped from the Al-meshed current collector and washed with DMC. Pellets (3 mm



**Fig. 2.** (a) XRD patterns of  $VS_4$  prepared by heating elemental sulfur and  $V_2S_3$  under vacuum. Data for  $VS_4$  (JCPDS No. 072-1294) are also shown for comparison. (b) SEM image of  $VS_4$  powder. (c) TG/DTA curve of  $VS_4$  in Ar atmosphere.

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