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Exfoliated V_5S_8/graphite nanosheet with excellent electrochemical performance for enhanced lithium storage

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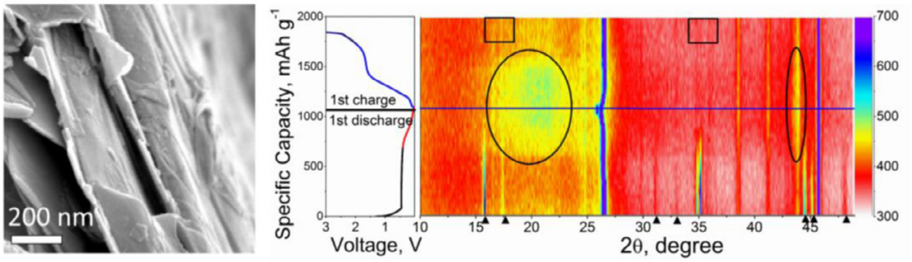
HIGHLIGHTS

- V_5S_8/graphite has been synthesized by a method of sulfuration and exfoliation.
- *In situ* XRD analysis reveals the reaction mechanism of V_5S_8/graphite.
- Exfoliated V_5S_8/graphite facilitates the Li^+ ion insertion and extraction.
- V_5S_8/graphite shows superior electrochemical property for lithium ion batteries.

GRAPHICAL ABSTRACT



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ABSTRACT

Nanostructured V_5S_8/graphite hybrid (V_5S_8/C) has been synthesized by a facile method combined solid state sulfuration with liquid exfoliation. The SEM and TEM results reveal that the V_5S_8/C hybrid is consisted of ultrathin V_5S_8 nanosheet and graphite flake. Due to efficient exfoliation of V_5S_8 sheet and effective incorporation of graphite flake, excellent electrochemical property of V_5S_8/C hybrid is demonstrated for lithium ion batteries. Surprisingly, V_5S_8/C hybrid delivers a high specific capacity of 1112 mAh g^{-1} at 0.1 A g^{-1}; even up to 1.0 A g^{-1}, a high capacity of 846 mAh g^{-1} is achieved after 700 cycles. Moreover, *in situ* XRD analysis indicates that the high capacity of V_5S_8/C is derived from the combined Li^+ intercalation and conversion reactions. While the excellent cycle performance and superior rate capability are attributed to the reduced stacking of the V_5S_8 layers and overcoating of conductive graphite material, which can relax the strain and lower the barrier for Li^+ insertion and extraction.

1. Introduction

The rapid developmental lithium-ion batteries (LIBs) have been extensively employed in small consumer electronics and portable devices because of their remarkable merits, such as high safety, environmental friendliness and admirably electrochemical performance [1,2]. The ever-increasing demand for large-scale electric vehicles has attracted growing attentions and interests. Currently, the intensively used anode material for LIBs commerce is graphite, owing to relatively low potential plateaus and stable structure. Whereas, the insufficient capacity of graphite (372 mAh g^{-1}) is hardly satisfied the enormous requirements for high performance LIBs [3,4]. Therefore, it is starve to search alternatives with excellent properties to store large amounts of energy

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in the limited space, which can be achieved by exploring novel electrode materials with rational design [5].

In order to achieve the goal of good performance LIBs, extensively and intensively attempts have been made to investigate possible anode materials with high electrochemical property, such as alloying materials (Si, Sn, Sb and Ge) [6–9], metal oxides(Co_3O_4, TiO_2) [10,11] and transition metal dichalcogenides (TMDs) [12,13]. Although alloy materials could yield an amazing specific capacity via (de)alloying mechanisms, poor cycle performance caused by large volume expansion and severe structural degradation still need to be further resolved [14,15]. While metal oxides have received particular attentions due to their high capacity and safe working voltage, yet it is necessary to improve the weaknesses of low electronic conductivity and poor cyclicity [16]. However, TMDs are of great interests owing to their unique covalently bond, forming two-dimension (2D) layers and stacking together through weak Van der Waals interactions [17]. The 2D structure facilitates the migration of Li^+ ion, demonstrating as potential alternatives to conventional anode materials for LIBs [18].

Among them, the nanostructured MoS_2 [19] and WS_2 [20] have been widely researched for energy storage because of their superior electrochemical performance. In addition, Layered vanadium sulfide materials are also presented many advantages in the field of supercapacitor [21] and moisture responsiveness [22], magnetic materials [23], even for storage batteries [24–26]. Fang et al. [25] showed the VS_2/graphene for LIBs anode with a considerable reversible capacity of 525 mAh g^{-1} after 100 cycles. Rout et al. [26] demonstrated that VS_4 nanosheet with various templates delivered an excellent capacity of 1105 mAh g^{-1} and long-term cyclicality with 95% capacity retention over 100 cycles. Although latest studies are focused on the synthesis of vanadium sulfide by hydrothermal method with nanostructure, it is required further investigation on adopting other facile approach while persevering the excellent electrochemical performance.

In this study, the construction of V_5S_8/graphite (V_5S_8/C) hybrid nanosheet is fabricated, which results in a high capacity and excellent cyclicity as superior anode for lithium storage. Unlike common approaches, the synthesis of V_5S_8/C hybrid can be in a large quantity by an available method, which is combination of solid-state reaction and liquid exfoliation with sonication. It is noted that the liquid exfoliation is a highly effective way to exfoliate bulk material into individual layers, which exhibits unique properties when blending with suspensions of other nano-materials [27–29]. Indeed, the enhanced rate capability and cycle stability have benefited from the synergistic effect between V_5S_8 and graphite. Specifically, the novel structure of V_5S_8 nanosheet and the effective incorporation of conductive graphite are expected to shorten transport length for Li^+ ions and electrons, as well as accommodate the strain and buffer the volume changes during continuous cycling.

2. Experimental

2.1. Material synthesis

The bulk material V_5S_8 was prepared by solid-state reaction. Specifically, 5 g sulfur and 1 g V_2O_5 powders were hold in two individual corundum boats, then placed in the upstream and middle side of tubular furnace, respectively. Under the mixture of 8% H_2 and 92% Ar atmosphere, the boats were annealed at 180 °C for 1 h initially and then at 750 °C for 2 h. Finally, black V_5S_8 powders were collected after the system was cooled to room temperature.

The thin V_5S_8 nanosheets were synthesized by a facile liquid exfoliation method. Specifically, 1 g as-synthesized V_5S_8 powder and 5 mg NaOH were added into 50 mL flasks, and 25 mL dispersion solvent N-methyl-2-pyrrolidone (NMP) was poured to mingle the mixture. The sealed flask was ultrasonicated for 4 h in ice-bath condition, subsequently the dispersion materials were centrifuged at 5000 rpm for 10 min. The unexfoliated sediments with thick V_5S_8 flakes were removed. Eventually, the remained supernatants without NaOH were filtered and washed by deionized water to obtain finally products.

The V_5S_8/C hybrid was prepared by the similar approach as mentioned above, yet with graphite flakes adding into the precursors. The mass ratio of graphite in V_5S_8/C hybrid is about 15 wt% after heat-treatment.

2.2. Material characterizations

The structure was confirmed by X-ray diffraction (XRD) (Bruker D8 Advance, Cu Kα radiation). For *in situ* XRD experiment, the *in situ* cell configuration and specifically testing conditions were as similar as previously literature [30]. Raman spectra were obtained at 514 nm laser excitation (Horiba Jobin Yvon, ARAMIS). The microstructure was observed by transmission electron microscopy (TEM, Tecnai G2 F20 S-TWIN, Japan) and scanning electron microscopy (SEM, Philips, FEI Quanta 200 FEG) equipped with the energy-dispersive X-ray spectroscopy (EDS). X-ray photoelectron spectrometer (XPS) was conducted with an energy of 35.75 eV (PHI, PHI5300 system).

2.3. Electrochemical measurement

The V_5S_8/C active material was mixed with carbon black and polyvinylidene difluoride (PVDF) in NMP solvent with a weight ratio of 7:2:1, then cast into aluminum foils to frabricate the electrode. The diameter of electrode roundel is 12 mm and the loading content is about 1.0–1.5 mg cm^{-2}. 2032-type coin cell was made by using 1 M $LiPF_6$ in a mixture of ethylene carbonate/dimethyl carbonate/ethylmethyl carbonate (EC/DMC/EMC) solution (1:1:1 by volume), lithium tablet and polyethylene membrane (Celguard2400) as the electrolyte, counter electrode and separator, respectively. The galvanostatically discharge-charge test was performed by a LAND battery system (LAND CT2001A) at room temperature (25 °C). Capacities and currents were calculated on basis of total mass of the V_5S_8/C composite. Cyclic voltammetry (CV) with a scan rate of 0.1 mV s^{-1} between 0.01 and 3.0 V and electrochemical impedance spectra (EIS) between 100 kHz and 0.01 Hz were acquired and investigated by an electrochemical workstation (CHI660E).

3. Results and discussion

The XRD patterns of bulk and exfoliated V_5S_8 and V_5S_8/C are shown in Fig. 1A. In all cases, the diffraction peaks are high crystallinity and consistent with the hexagonal structure V_5S_8 (JCPDS: 81-1596). The superstructure of V_5S_8 is consisted of ordered V vacancies in a NiAs-type structure in accordance with previous researches [31,32]. Moreover, a small peak at 26.3° in the sample of bulk and exfoliated V_5S_8/C, purely refers to the (002) plane of carbon, which confirms the presence of graphite in V_5S_8/C sample. Commonly, the peak at 14.2° is ascribed to the primary (002) diffraction peak in the bulk V_5S_8/C, indicating that the layered V_5S_8 sheets grow well along the c axis during annealing. However, it is clearly observed that exfoliated V_5S_8/C basically maintain the position of diffraction peaks and the layered crystallinity, yet the peak density of (002) is considerably reduced in comparison with bulk V_5S_8/C sample, well suggesting the successful exfoliation of V_5S_8/C sheet [33,34]. Furthermore, to know the unique structural information of V_5S_8/C, Fig. 1B shows the Raman spectra of