



Synthesis and characterization of sulfur–carbon–vanadium pentoxide composites for improved electrochemical properties of lithium–sulfur batteries



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ABSTRACT

Sulfur (S)–carbon (C)–vanadium pentoxide (V_2O_5) composites were prepared by wet ball milling, and their physical and electrochemical properties were evaluated. Firstly, the effect of the carbon content of S–C composite electrodes on their physical and electrochemical properties was investigated. The S–C composite electrode with 60 wt.% S delivers a first discharge capacity of 1077 mAh g^{-1} . However, its capacity markedly decreases to 606 mAh g^{-1} after 10 cycles, which corresponds to a capacity fading rate of 47 mAh g^{-1} per cycle. To improve the electrochemical performance of the S–C composite electrode, carbon was partially replaced by V_2O_5 . The S–C– V_2O_5 composite electrode with a composition of 60 wt.%–S, 30 wt.%– V_2O_5 and 10 wt.%–C exhibits a lower capacity fading rate of 23 mAh g^{-1} per cycle in the first 10 cycles and better capacity retention than the S–C composite electrode over 50 cycles.

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1. Introduction

The increase in the demand for clean and sustainable energy has prompted intense effort toward the realization of high-performance energy storage technologies. Among the many available energy storage technologies, lithium(Li)-ion batteries with Li-intercalation compounds as positive electrodes have achieved great success for use in portable electronic devices [1,2]. A typical rechargeable Li-ion battery requires heavy host compounds (e.g., CoO_2) to accommodate guest atoms (e.g., Li), which greatly limits its energy density to less than 210 Wh kg^{-1} . As a result, Li-ion batteries cannot provide a sufficiently long driving range for electric vehicles (EVs) [3]. On the other hand, a Li–sulfur (S) battery as a typical integration reaction battery system [4] may open a new horizon for EVs. As the sulfur cathode has a theoretical specific capacity of 1672 mAh g^{-1} , a Li–S battery can achieve an energy density of 2654 Wh kg^{-1} when combined with a lithium metal anode, which is 3–5-fold higher than those of current Li-ion batteries [5]. In addition, sulfur is a highly abundant element source on earth and is not geographically isolated [6], which may reduce the cost of cathode materials. However, Li–S batteries have

serious problems [7–9], including low utilization of the active material and a poor cycle life because of the insulating property of sulfur and the high solubility of lithium polysulfides in organic electrolytes.

To overcome the above-mentioned problems, much effort has been devoted to designing S-based cathodes, thus far. Various polymer [10] and modified separators [11] have been studied to enhance the electronic conductivities of sulfur or trap polysulfides within a carbon framework. Zhang et al. [12] reported a nanostructured S/polyacrylonitrile (PAN) composite with an original network-like structure via in situ polymerization of acrylonitrile in the presence of nanosized S particles followed by a low temperature heat treatment, which delivered a specific capacity of 1510 mAh g^{-1} at first cycle, and a very high reversible capacity of 1177 mAh g^{-1} was achieved at the following cycle. The embedding of elemental sulfur in microporous carbon was first proposed by Ji et al. [13]. They used a conductive microporous carbon framework to precisely constrain a sulfur nanofiller within its channels, and then modified the polymer to facilitate Li^+ ingress/egress and reduce the solubility of the polysulfides. Therefore, a discharge capacity of 1320 mAh g^{-1} was obtained and remained at 1100 mAh g^{-1} in the following 10 cycles without significant capacity fading. Other carbon materials, including micro/mesoporous carbon spheres [14–17], hollow carbon [18], graphene [19] and graphene oxide [20] have been employed to

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improve the performance of sulfur-based cathodes. However, carbon is an electrochemically inactive material in the integration reaction of Li–S batteries, and therefore, its quantity in the electrode should be reduced as much as possible. A recent advanced approach involving the adoption of metal oxides, such as silica [21] and alumina [22], also presented an alternative way to further confine polysulfides. In particular, the S cathode performance by incorporating S in TiO_2 as a yolk–shell structure exhibited a marked increase in the capacity retention of Li–S cathodes, showing an initial specific capacity of 1030 mAh g^{-1} at 0.5C and capacity fading of 0.033% per cycle within 1000 cycles [23].

Vanadium pentoxide (V_2O_5) is one of the most common cathode materials in the field of Li batteries [24,25] and has a few advantages when used as an additive in sulfur cathodes. It is an electrochemically active material in the cut-off voltage range from 1.5 to 4V [25,26], which closely matches that for sulfur cathodes (from 1.5 to 3V), and it also positively contributes to the capacity of sulfur cathodes. In our previous studies, several composite electrodes, such as LiFePO_4/C [27], LiMnPO_4/C [28], $\text{Li}_2\text{FeSiO}_4/\text{C}$ [29] and SiO_2/C [30], were synthesized by wet ball milling (WBM). In this study, we prepared sulfur (S)–carbon (C)– V_2O_5 composite electrodes by WBM and then investigated their physical and electrochemical properties.

2. Experimental

2.1. Synthesis of S–C– V_2O_5 and S–C composites

Commercial sulfur (98% purity), carbon (acetylene black) and V_2O_5 (98% purity) with targeted weight ratios were mixed by WBM with ethanol as a medium. The rotation speed was fixed at 800 rpm and the ball-milling time was 4 h. After the WBM, the obtained slurry was dried at 60°C in an oven.

2.2. Physical characterization

X-ray diffraction (XRD) analysis was performed using a Rigaku Ultima IV diffractometer with a D/teX Ultra X-ray detector using $\text{Cu-K}\alpha$ radiation. Fourier transform infrared (FT-IR) absorption spectra were recorded between 600 and 4000 cm^{-1} using a Shimadzu IRAffinity-1 Miracle-10 FT-IR spectrophotometer. The morphology of samples was examined by scanning electron microscopy (SEM; KEYENCE, VE-9800). The sulfur content was measured by using an element analyzer (CHNS Corder MT-6, YANACO).

2.3. Electrochemical characterization

The electrochemical performance of composite samples was investigated using a CR2032 coin-type cell. The cell comprised a lithium metal negative electrode and a S–C– V_2O_5 or S–C positive electrode, which were separated by a microporous polypropylene film. A 1.0 mol dm^{-3} lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) in dimethoxyethane (DME) and 1,3-dioxolane (DOL) with a 1:1 volume ratio (Tomiya Pure Chemical Co., Ltd.) was used as the electrolyte. The positive electrode consisted of 80 wt.% S–C– V_2O_5 or S–C composite, 10 wt.% polyvinylidene fluoride (PVdF) as a binder and 10 wt.% acetylene black. A slurry prepared by dispersing these materials in 1-methyl-2-pyrrolidinone (NMP) was spread uniformly onto an aluminum foil using the doctor blade technique. After drying the slurry-coated foil in a vacuum oven for 4 h at 60°C , it was punched into circular discs, which were then scraped to standardize their area to 1 cm^2 . The loading of the composites was approximately 1.2 mg cm^{-2} . All cells were assembled inside a high-purity argon-filled glove box (99.9995% gas purity). The cells were

galvanostatically cycled between 1.5 and 3V for the S–C composite at 0.1C ($1\text{C} = 1675 \text{ mA g}^{-1}$) and between 1.5 and 4V for the S–C– V_2O_5 composite at 100 mA g^{-1} on multichannel battery testers (Hokuto Denko, HJ1010mSM8A). The current density and specific capacity were calculated from the mass of sulfur in the electrode.

Cyclic voltammetry (CV) measurements were performed in the potential window of 1.5 to 4.0V (vs. Li/Li^+) at a scanning rate of 0.1 mV s^{-1} . Electrochemical impedance spectroscopy (EIS) measurements were carried out using a Solartron 1255B frequency response analyzer connected to a Solartron SI 1287 electrochemical interface. The amplitude of the ac signal was 10 mV in the frequency range from 100 kHz to 0.1 Hz. The measurements were performed at room temperature.

3. Results and discussion

3.1. Physical and electrochemical properties of S–C composites

Fig. 1 presents the XRD patterns of the S–C composites prepared with carbon contents from 10 to 70 wt.%. The XRD patterns of sulfur and acetylene black are also shown in the figure as references. The sharp diffraction peaks of pristine sulfur indicate an orthorhombic structure with the space group P_{nmm} . The S–C composites have characteristic peaks corresponding to orthorhombic sulfur. This may indicate that the WBM does not significantly change the structure of the sulfur. However, the peak intensity of sulfur gradually decreases with increasing carbon content owing to the amorphous state of carbon.

The first charge and discharge curves of the S–C composite electrodes with different sulfur contents are given in Fig. 2. All the discharge curves of the S–C composite electrodes with various sulfur contents have two voltage plateau regions, corresponding to the multistep reduction reaction of sulfur during the discharge process. The upper plateau at approximately 2.3V is caused by the transformation of sulfur to higher-order lithium polysulfides (Li_2S_n , $3 < n < 8$), while the lower plateau at approximately 2.1V corresponds to the transformation of the higher-order lithium polysulfides to lower-order lithium polysulfides (Li_2S_n , $n \leq 2$), which can precipitate the solid products of Li_2S_2 and Li_2S owing to their low solubility in the electrolyte [31]. The S–C composite electrode with 70 wt.% carbon exhibits a first discharge capacity of

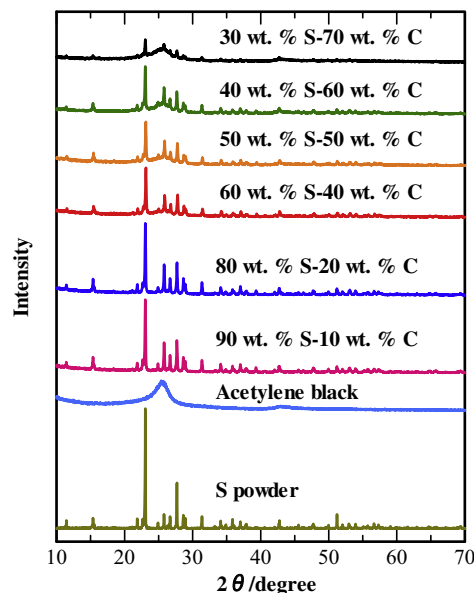


Fig. 1. XRD patterns of S–C composites prepared with different carbon contents.

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