STUDIES ON SULFUR BASED TERNARY COMPOSITE CATHODE MATERIAL FOR LITHIUM SULFUR BATTERIES

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Abstract - Unique sulfur (S) anchoring materials and the corresponding tools for subduing capacity are now required to advance the performance of Li-S batteries. In this work, carbon coated Sulfur / polymer composite was prepared by solvent less reaction. The physical characterizations of the prepared composite was investigated using XRD, RAMAN and SEM. Raman analysis specifies that D and G bands were well matched with the sulfur based ternary composite. The functional group vibration of the ternary composite was studied using FTIR. The XRD pattern reveals that the diffraction peaks of sublimed sulfur was clearly observed in the ternary composite, which is due to the limited pore volume of the carbon matrix. The prevailing study indicates that sulfur based ternary composite is a promising candidate for the cathode material mainly in Lithium Sulfur Battery.

Key Words: ternary composite, lithium sulfur battery, sulfur/polymer composite, solvent less reaction, carbon matrix

1. INTRODUCTION

Elemental sulfur has expected a great deal of consideration recently as a promising cathode material for lithium/sulfur (Li/S) batteries, due to its high theoretical specific capacity of 1672 mAh g⁻¹ [1-3]. In addition, sulfur also has advantages of low cost, abundance in nature and eco friendliness [4]. However, in spite of these advantages, the commercialization of lithium sulfur batteries has a number of difficult problems to overcome. Firstly, sulfur is electrical insulating. Secondly, polysulfides, which are formed during the discharge process of the Li/S battery, are generally soluble in liquid electrolyte [5]. Tremendous efforts have been made in recent years to overcome these problems, such as forming sulfur/carbon or sulfur/conductive polymer composites [6-10]. Among them, the sulfur/ polymer composites with core-shell structure in which sulfur is the core and polymers are the shell, exhibited enhanced cyclability and rate capability [11-12]. Polyvinylidene fluoride (PVDF) is valued for its toughness, stability, low weight, low thermal conductivity, high chemical corrosion resistance, and heat resistance. PVDF is the standard binder material used in the production of composite electrodes for lithium-ion batteries. Additionally, PVDF is used because it is chemically inert over the potential range used, and does not react with the electrolyte or lithium.

In this work, sulfur/PVdF/Acetylene Black composite cathode material was prepared by a low temperature heat-treatment, which provided a homogeneous distribution of sulfur, PVdF and AB in the system. This technique is a simple and energy beneficial preparation method due to its processing in the non-aqueous media. The composition, structure and morphology of the prepared composite were investigated. The preparation of the obtained composite cathode material may be an effective strategy to improve the sulfur utilization and restrain the solubility of lithium polysulfides.

2. EXPERIMENTAL

Sublimed sulfur and PVdF was mixed with the weight ratio of 4:1. After that high porous nature of carbon source (Acetylene black) mixed with S/PVdF composite in the ratio of 7:3. The resulting mixture was heated at 155°C for 20h. Then the material was cooled to room temperature and SPA composite was obtained. Figure.1 shows the schematic diagram of SPA composite preparation.
3. RESULTS AND DISCUSSION

3.1 XRD Analysis

Figure 2 shows the XRD patterns of sublimed sulfur, pristine PVdF, AB and SPA composite. XRD pattern of the commercialized Sulfur indicates high crystallinity and phase purity. All of the identified peaks can be perfectly indexed to orthorhombic phase of sulfur (JCPDS card no: 08-0247). The XRD pattern for PVdF exhibits the semi-crystalline nature of the polymer. The broad diffraction humps indicates that the carbon source is an amorphous nature. In contrast the diffraction peaks of sublimed sulfur were clearly observed in the SPA composite which is due to the limited pore volume of the carbon matrix.

3.2 Raman Analysis

Raman spectroscopy is an effective technique for describing the structure and quality of carbon materials. Fig.3 illustrates the Raman spectra for Pristine Sulfur, PVdF, AB and SPA composite. The characteristic peak of high purity carbon source exhibits at a ~1337 cm\(^{-1}\) (D band) and at ~1588 cm\(^{-1}\) (G band), the former is assigned to disordered carbon and the latter represents the graphitic carbon [13]. The pure sulfur exhibits a characteristic peak below 500 cm\(^{-1}\) that is originated from the A1 symmetry mode of the S-S bond [14]. Importantly, the sulfur in the SPA composite does not show noticeable characteristic sulfur peaks, implying that the sulfur was well wrapped by the carbon matrix. The relative intensity ratio of I\(_D\)/I\(_G\) is proportional to the defect degree of carbon materials [15]. The intensity ratio of D band and G band (I\(_D\)/I\(_G\)) for SPA is 0.85, indicating a higher electronic conductivity [16].
3.3 Functional group analysis

Fig.4 shows that the FTIR spectra for pristine sulfur, PVdF, AB and SPA composite in the wave number range of 4000–400 cm\(^{-1}\). The peak around 3500 cm\(^{-1}\) indicates the presence of OH functional groups, due to the presence of moisture in the surface samples [17]. The band located at 3023 cm\(^{-1}\) and 2924 cm\(^{-1}\) corresponds to the CH\(_2\) asymmetric and symmetric vibration of PVdF. The absorption peak appeared at 1408 cm\(^{-1}\) was attributed to CH\(_2\) wagging vibration. The C–C band of PVdF was observed at 1190 cm\(^{-1}\) [18]. The peaks at 884 and 882 cm\(^{-1}\) were related to C–C–C asymmetrical stretching vibration and CF stretching vibration of PVdF [19]. In addition to that, the peak around 1600 cm\(^{-1}\) in the samples correspond to C=H stretching vibration. The positions of the absorption peak around 2300 cm\(^{-1}\) in the samples indicate C–H stretching vibration. The peak below 500 cm\(^{-1}\) represents the presence of elemental sulfur in the SPA composite [14]. Therefore, it could be concluded that the PVdF structure is successfully obtained via solvent less reaction.

3.4 SEM Analysis

Fig.5 shows SEM images of SPA composite. From Fig, it can be seen that no large bulk sulfur particles exist, suggesting the sulfur is very well distributed in the SPA composite. Carbon matrix cannot be identified in the SEM images, owing to the low content of the carbon host material in the SPA composite. This result is very well agreed with XRD results.

4. CONCLUSIONS

Sulfur/ Poly (vinylidene) Fluoride composite was prepared by a solvent less reaction and carbon host matrix (Acetylene Black) was introduced as conductive additives for SPA ternary composite cathode. From a series of measurements, it showed that sulfur/ PVdF composite was coated by carbon source and the sublimed sulfur particles were uniformly dispersed. Raman analysis specifies that D and G band was well matched with the sulfur based ternary composite. The XRD data reveals that the diffraction peaks of sublimed sulfur was clearly observed in the ternary composite which is due to the limited pore volume of the carbon matrix. From FTIR spectra, characteristic peaks of PVdF are also observed in the SPA composite, although with reduced intensity due to the lower content of PVdF. In
morphological study, no large bulk sulfur particles can be easily observed on the surface of the SPA composite implying the sulfur particles were also good dispersion in the obtained sample which statement is very well agree with XRD analysis. In summary, it could be observed a simple approach to improve the composite with suitable properties and superior performing Li-S cells can be estimated for the application of high energy density batteries.

REFERENCES


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BIographies

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