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A SIMPLE APPROACH TO PREPARE SULFUR/PVDF COMPOSITE FOR LITHIUM/SULFUR BATTERIES

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ABSTRACT- In recent years, rechargeable Li–S batteries have gained great attraction, because of their high theoretical energy density (2600 Whkg^{-1}) and high theoretical specific capacity (1675 mAhg^{-1}).Sulfur is naturally abundant, inexpensive and nontoxic. Despite this, the practical development of the Li–S batteries is a formidable challenge, because of few critical issues including the highly insulating nature of sulfur, high solubility of lithium polysulfides in the electrolyte and volume expansion of the active material. To effectively restrain the dissolution and diffusion of polysulfides and strengthen the electronic conductivity of sulfur composite, coating sulfur with polymers were developed. In this work, a facile preparation for S/PVDF composite via solid state reaction has been carried out. The structure and morphology of the obtained sample was characterized by XRD, FTIR, RAMAN and HR-SEM and the results are discussed.

Keywords- Li-S batteries, energy density, specific capacity

1. INTRODUCTION

Lithium-sulfur (Li-S) battery is a promising energy system with a high theoretical energy density (2600 Wh kg^{-1}), which is approximately seven times larger than those of the current LIBs. However, lithium-sulfur (Li-S) batteries have some disadvantages, including the dissolution of lithium polysulfides from sulfur-based cathodes [1], the shuttle mechanism at slow charge/discharge rates [2], and the insulating nature of sulfur [3]. Polymers used for sulfur electrode requires not only strong adhesion for electrode powders against volumetric expansion of sulfur but also powerful capability to block polysulfide transport against PSS [polysulfide shuttle]. Using some new binders, which have high adhesion ability for bonding the electrode materials to the current collector, good ionic conductivity, as well as low solubility in the organic electrolytes result in a decrease in the cell resistance. Development of functional binders such as polyvinylidene fluoride (PVDF)[4], polyethylene oxide [5], gelatin [6], polyvinylpyrrolidone (PVP) [7] and Naalginate [8] has become a new trend in the Li-S battery technology. Recently, polymers have received plenty of attention because they can play different roles in improving the performance of cathode [9-11] as a result of their good electrochemical stabilities and their favorable morphologies. Especially, PVDF has also acquired immense importance in scientific and technological research because of its excellent mechanical, pyroelectric, ferroelectric, and piezoelectric properties. PVDF is a semi crystalline polymer in which each monomer unit (CH_2-CF_2) has a spacing of 2.6Å with two dipole moments, one due to $CF_2$and the other due to CH_2[12,13]. In this work, a facile method to prepare a sulfur/PVDF composite via a simple manual mixing of the sulfur and polyvinylidene fluoride followed by heat treatment and investigation of its physical properties as a cathode for lithium secondary batteries.

2. EXPERIMENTAL

Raw materials for fabrication of sulfur cathode were kept in a vacuum oven (60°C) to remove residual water. S-PVDF composite was prepared via a solid state reaction. Sulfur and PVDF were mixed in 4:1 weight ratio by mild manual mixing for half an hour. The mixture was heated in muffle furnace at 200 °C for 3 h.

3. MATERIALS CHARACTERIZATION

The chemical transformation of the composite during the preparation process was investigated by Fourier Transform Infrared Spectroscopy (Thermo Nicolet 380, 0.5cm^{-1}) and micro Raman (SEKI focal). The crystalline phases of the sample were determined by X- ray diffraction (PANalytical X'pert PRO powder X-ray diffractometer) equipped with Cu Kα radiation. The surface morphology of the composite was examined by high resolution scanning electron microscopy (HRSEM) with energy dispersive X-ray (EDX) (FEG, Quanta250).

4. RESULTS AND DISCUSSION

The X,Pert PRO PANalytical X-ray diffractometer was used to do the structural analysis of the composites at room temperature. The crystal structures of the obtained materials are investigated by XRD. Fig.[1] shows the XRD patterns of pure PVDF, sulfur, before heat treatment of S/PVDF composite and after heat treatment of the composite. The diffraction peaks at 2θ = 19.9˚, 18.3˚ and 26.7˚demonstrate crystalline nature of PVDF [Fig 1(a)]. The peaks at 2θ = 23-29˚of the sublimed sulfur are consistent with F_{ddd} orthorhombic [Fig 1(b)]. From the XRD pattern of the before heat treatment of S and PVDF[Fig1(c)]., it is clearly observed the diffraction peaks of sulfur become very weak, which may be due to the high loading of sulfur. In contrast, after heat treatment of S/ PVDF composite [Fig 1(d)], the weak diffraction peaks of PVDF indicates good dispersion of sulfur with in the polymer matrix.

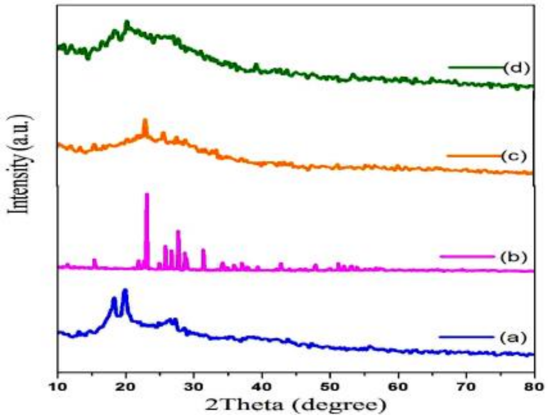


Figure.1. XRD patterns of (a) pure PVDF, (b) pristine sulfur,(c) before heat treatment of S/PVDF composite and(d) after heat treatment of S and PVDF

Fourier Transform Infrared Spectroscopy (FTIR) offers quantitative and qualitative analysis for organic and inorganic samples. FTIR identifies chemical bonds in a molecule by producing an infrared absorption spectrum. FTIR is an effective analytical instrument for detecting functional groups and characterizing covalent bonding information.The FTIR spectrum of prepared pure PVDF and S/PVDF composite is shown in Figure (2). The constant absorption region in the FTIR spectra of PVDF from 1440 cm^{-1}to1000cm^{-1}corresponds to fluorocarbon absorption. The constant absorption band in the range 1440 cm^{-1}to 1000 cm^{-1}is important because it shows the changes produced by the irradiation corresponding to transformation from α-phase to β and γ-phases. The characteristic absorption bands of the as prepared composite (SFA) at 1190cm^{-1} and 1405cm^{-1} were due to the absorption peaks of CF_2 stretching and CH_2 stretching modes respectively. The peak at around 2900cm^{-1} corresponding to the symmetric stretching vibrations of CH_2 group in the pristine PVDF. The absorption band at 760cm^{-1} is related to rocking vibration [14]. The band at 608cm^{-1} is assigned to a mixed mode of CF_2 bending and CCC skeletal vibration; this peak is parallel to the chain axis [14, 15]. The 494-cm^{-1} band is related to bending and wagging vibrations of the CF_2 group ascribed to the α-PVDF polymorph [15, 16]. Therefore, it could be concluded that the PVDF structure is successfully obtained via solid state reaction on the surface of sulfur particles.

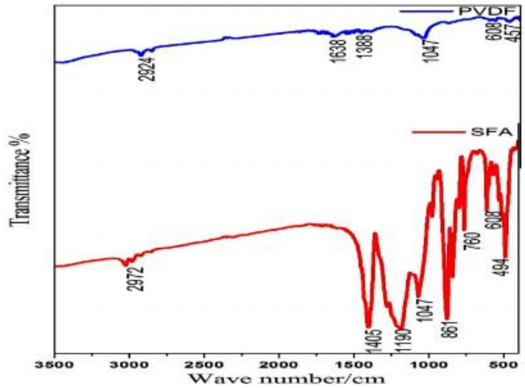


Figure.2.FTIR spectrums of pure PVDF and as-prepared S/PVDF composite (SFA)

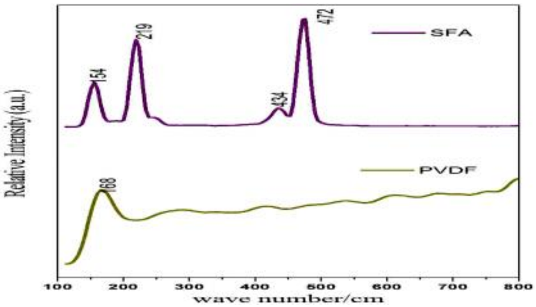


Figure.3. RAMAN spectra of pure PVDF and S/PVDF composite (SFA)

Raman spectroscopy is a spectroscopic technique used to observe vibrational, rotational, and other low-frequency modes in a system .It was carried out to confirm the chemical structure of the as prepared composite (Fig. (3)). The RAMAN spectrum of the after heat treatment of S/PVDF composite displays peaks below 500cm^{-1} because it contains sulfur particles due to the low synthesis temperature. The pure sulfur exhibit a characteristic peak below 500cm^{-1} that is originated fromA1 symmetry of S-S bond [17].

The morphology of S/PVDF composite was investigated by SEM. From Fig.4, after the incorporation of sulfur, no large bulk sulfur particles can be easily observed on the surface of the as prepared composites implying the sulfur particles are also embedded in the polymer matrix. After heat treatment, the composite becomes more homogenous and smoother.

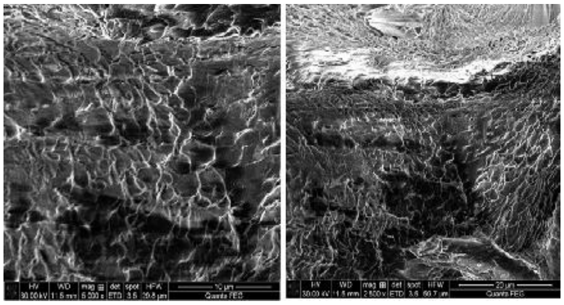
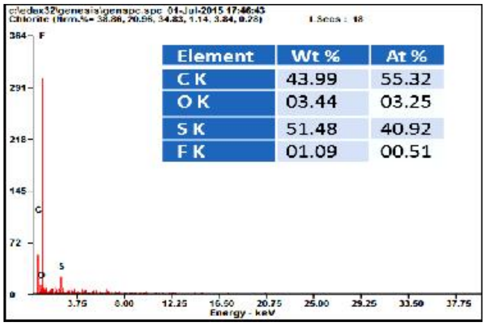


Figure.4 SEM images of S/PVDF composite

Figurre (5) is the EDX spectrum of as prepared composites, confirming the sample consists of five elements(C, O, S, F). It also confirms the presence of high ratio of sulfur in the as prepared sample.



Element	Wt %	At %
C K	43.99	55.32
O K	03.44	03.25
S K	51.48	40.92
F K	01.09	00.51

Figure 5 EDX spectra of the S/PVDF composite

CONCLUSION

A sulfur cathode has been designed with PVDF via solid state reaction method. From XRD, the non- crystalline profile of sulfur has homogeneously well distributed in to the polymer matrix and it also confirmed in HR-SEM. Such a highly distributed state may also result in the good electric conductivity of the composite cathode. The functional group vibrations of the composite materials are confirmed by FTIR. From the above investigation, S/PVDF composite material is a promising matrix for sulfur cathode.

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