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STUDIES ON SILICA WRAPPINGSULFUR ELECTRODE MATERIAL FOR LITHIUM SULFUR BATTERIES

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ABSTRACT:-*Sulfur is a promising cathode material with a high theoretical specific capacity of 1675 mAh g^{-1}, but the challenges of the low electrical conductivity of sulfur and the high solubility of polysulfide intermediates still hinder its practical application. Common choice to overcome these problems is by adding conductive carbons, conductive polymers and metal oxides with sulfur. Among them, metal oxide can help to prevent the dissolution of polysulfide intermediates. Particularly, silica is found to be an abundant material and served as polysulfide absorber through chemical bonding. In this work, SiO_2/Sulfur composites cathode material has been synthesized via solid state reaction. The prepared composites have characterized for structural and morphological analyses using XRD, FTIR, RAMAN and SEM. From the XRD analysis no impurities has been observed in the as-prepared compositesand also found well matched with the standard pattern of sulfur. Raman analysis confirms the presence of sulfur in the as-synthesized composites. The vibrational bands of silicon have been confirmed through the Fourier Transform Infrared Spectroscopy. From these results, it is inferred that the wrapping of SiO_2does not impart any lattice changes and it is expected to give changes in electrochemical properties rather than physical structure.*

Keywords: *sulfur, specific capacity, cathode material, composites*

INTRODUCTION

Energy storage plays a crucial role in our day-to-day life, and has rapidly growing importance in numerous applications. So far, batteries are considered as of the great solutions for energy storage sectors [1-3]. Particularly, secondary li-ion batteries (LIBs) are considered to be the greatest favorable energy technology, and have drawn extensive courtesy from the viewpoint of energy and environmental concerns [4, 5]. Unluckily, the current LIBs cannot entirely meet the ever-increasing power sources necessities for large-scale applications in developing EVs, HEVs, and portable electronic devices due to its high cost, relatively low specific capacity and unsatisfying energy density. Therefore, investigation and improvement of new electrode materials with high specific capacity have become a more key challenge in the future [6-8].

To encounter the fast increasing demands of high power sources, rechargeable Li-S batteries are one of the most promising candidates due to their high theoretical specific capacity of 1675 mAh g^{-1} and high theoretical energy density of 2600 Wh kg^{-1}.In addition, elemental sulfur isinexpensive, abundance on earth and eco-friendly [9-14].Besides these advantages, Li-S batteriessuffered from a serious problem associated to the dissolution of the lithium polysulfide intermediates into the electrolyte. The dissolved lithium polysulfides encourage a polysulfide shuttle during the charging process. This occurrence causes a loss of active material, polarization of the Li anode and corrosion of the Li metal [15, 16]. Numerous studies have addressed this problem, in which some proposed for coating a conductive additive or using a solid or gel electrolyte to avoid the direct interaction between sulfur and the liquid electrolyte. Alternative approach involved is the addition of polysulfide adsorbents to adsorb the long-chain polysulfides. Among these approaches, the use of an adsorbent is a one of the simple method for reducing the shuttle effect of the lithium sulfur batteries. Consequently, several materials have been used as polysulfide adsorbents[17-19].In many cases SiO_2 is called as a “polysulfide reservoir,” it has intermediate polysulfide absorber through weak bonding. It is proved that the function of porous silica as a polysulfide reservoir for reversible electrochemical process, increase long-term cycling stabilization and enhance coulombic efficiency [20-22].

In this study, silica wrapped sulfur composites have been prepared with different weight ratios via solid state reaction. Silica is chosen for the polysulfide adsorbent material, it plays a role in constraining the “shuttle effect” of polysulfide. The prepared composites are characterized for their physical properties using XRD, FTIR, Raman and SEM.

EXPERIMENTAL

Preparation of SiO_2/S composites

SiO_2/Sulfur composite cathode materials were prepared via simplistic solid state reaction. The starting materials, sulfur and silicon dioxide were taken in three different weight ratios of 6:4, 7:3 and 8:2 respectively. Firstly, the starting materials were manually mixed using the mortar and pestle. The mixed powder was heat treated for 20 h without any special atmosphere using muffle furnace. Finally, SiO_2/S composite materials were obtained and labeled as SS64, SS73 and SS82 for the three different weight ratios 6:4, 7:3 and 8:2 respectively.

Material characterization

The prepared composites were characterized for their physical structure. The crystalline phases of the as-synthesized composites were identified by powder X-ray diffraction using PANalyticalX'pert pro diffractometer with Cu K_α radiation. The functional group vibrations were analyzed through Fourier Transform Infrared Spectroscopy (Thermo Nicolet – 380 FTIR spectrophotometer using KBr pellets) and Raman spectrometer (SEKI focal, Japan). The morphology of the prepared composites was observed by using scanning electron microscopy (SEM, FEG Quanta 250) analysis.

RESULTS AND DISCUSSION

X-ray Diffraction Analysis:

Fig.1 demonstrates the X-ray diffraction (XRD) patterns of bare sulfur, bare SiO_2 and as-prepared composites (SS64, SS73 and SS82) with the standard pattern of sulfur.The pure sulfur and all the prepared composites are well accorded with standard pattern of sulfur (JCPDS: 08-0247) and belongs to orthorhombic structure with the space group of F_{ddd}. No changes in diffraction patterns have been observed upon wrapping with SiO_2 on sulfur, which can be attributed to the low content and amorphous nature of silicon dioxide.From the XRD results, the SiO_2has not given any changes in the structure of sulfur and it confirms the structural stability of the sulfur after wrapping with SiO_2.

Fourier Transform Infrared Spectroscopy:

FTIR spectroscopy is used to determine the functional group vibrations of the as-prepared composites. Fig.2 depicts the FTIR spectra of SS64, SS73 and SS82 composites in the range of 2000 to 400 cm^{-1}. From the spectrum, the peak at 465 cm^{-1} represents the bending vibration of Si-O-Si and the vibrational bands at 1091 and 801 cm^{-1} belongs to the asymmetric and symmetric vibrations of Si-O-Si. The peak at 1633 cm^{-1} corresponds to the vibration of C=O stretching. The existing results indicate the presence of SiO_2 content in the as-prepared composites.

Raman spectroscopy:

Fig.3 shows the Raman spectra of as-synthesized SS64, SS73 and SS82 composites. Generally, the sulfur and metal oxides' peaks in Raman spectrum are observed in the range below 500 cm^{-1}. The Raman spectrum displays a high Raman bands in all composites at 216, 153 and 472 cm^{-1}. Those Raman bands are consistent with reported result and correspond to aggregated sulfur [23].It indicates the presence of elemental sulfur in the as-prepared composites, and also these results are in good accordance with the XRD results.

SEM analysis:

Surface morphology of the composites can be determined using scanning electron microscopy. Fig.4 depicts the SEM images of the as-prepared SS64, SS73 and SS82 composites.From SEM images, the SS64 composite shows the inhomogeneous mixture sulfur and SiO_2, which insist the sulfur accumulation on the rough surface in particular region. SS82 composite displays cloud like formation of sulfur which may be due to the high content of sulfur in the composite. Compared to SS64 and SS82, SS73 composite formed a uniform surface morphology, owing to the homogeneous mixture of SiO_2 and sulfur. From these results, the uniform morphology of the SS73 composite may be expected to enhance the electrochemical performance of the lithium sulfur battery.

CONCLUSION

The silica wrapped sulfur composites were successfully synthesized via solid state reaction without any special atmosphere. From the XRD analysis, it is ascertained that the prepared composites are in typical orthorhombic structure of sulfur (JCPDS card no: 08-0247). The functional group vibration confirms the presence of silicon dioxide in the composites and Raman spectrum delivers the sulfur peaks of all the prepared composites. From the SEM analysis, the SS73 composite displays a uniform morphology compared to SS64 and SS82 composites. Finally,it could be concluded that the wrapping of SiO_2 could not affect the structure of sulfur and homogeneous morphology may be predictable to improve the electrochemical properties of Li-S battery.

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FIGURE CAPTIONS

Figure1. XRD patterns of Standard sulfur (JCPDS card no: 08-0247) (a) pure sulfur (b) pure SiO_2(c) SS64 (d) SS73 (e) SS82 composites

Figure 2.FTIR spectra of as-synthesized SS64, SS73 and SS82 composites

Figure 3. Raman spectra of the SS64, SS73 and SS82 composites

Figure 4.SEM images of the prepared composites SS64, SS73 and SS82

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Figure 1

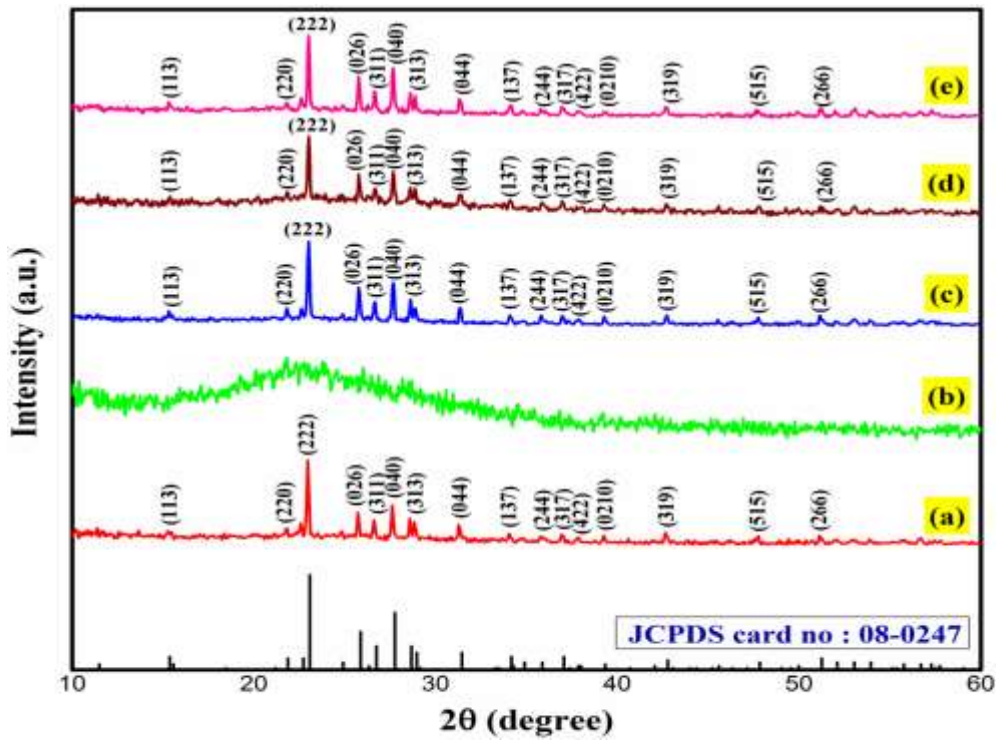

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Figure 2

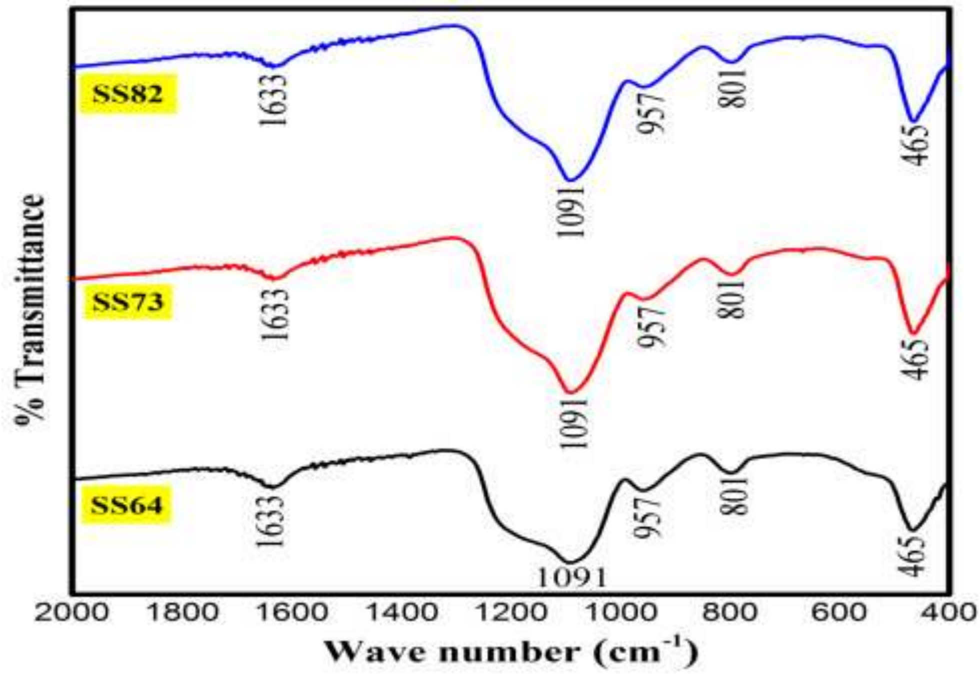

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Figure 3

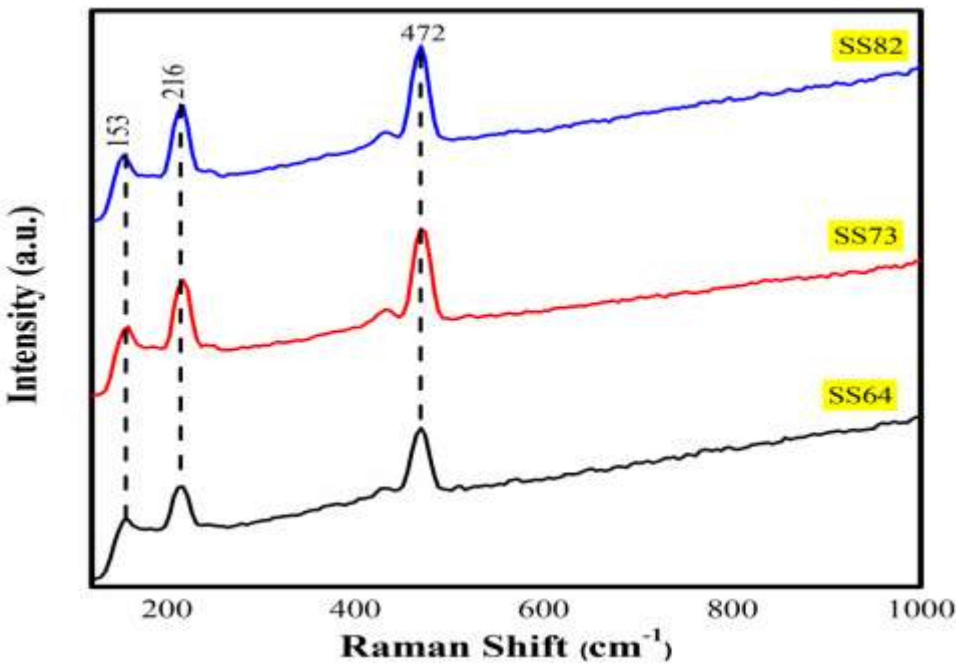

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Figure 4