Scientific Journal of Impact Factor (SJIF): 4.72

e-ISSN : 2348-4470
p-ISSN : 2348-6406

International Journal of Advance Engineering and Research Development

National Conference On Nanomaterials, (NCN-2017)

Volume 4, Special Issue 6, Dec.-2017 (UGC Approved)

PHYSICAL PROPERTIES OF SULFUR BASED BINARYCOMPOSITES FOR LITHIUM SULFUR BATTERIES

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ABSTRACT:- *In recent years, considerable effort has been made to improve the electrochemical performance of sulfur cathodes for the development of high-energy Li/S batteries. As a light- weight element, sulfur can react with metallic lithium to form Li_2S by a two-electron reaction, leading to a high theoretical capacity and energy density in lithium/sulfur battery system, almost one order of magnitude higher than that of conventional Li- ion batteries. Particular attention has been devoted to the cycle stability and the utilization of a sulfur cathode by means of improving the conductivity of the sulfur and minimizing the solubility of the lithium polysulfides.Polymers are also a good alternative candidate for fabricating sulfur/polymer composites, based on their conductivity and good compatibility with sulfur. Hence, in this work the positiveelectrode with different sulfur ratios of sulfur/ poly (acrylonitrile) composites have been successfully prepared by a solid state reaction method. The XRD results confirm that the sulfur was completely dispersed as fine nano particles into the polymer matrix. The SEM images clearly show the distributions of the particles with less cluster formation. Furthermore, PAN plays an important role in structural stability and chemical confinement settings for elemental sulfur with different loading of the as prepared composites.*

Keywords:*sulfur/ poly (acrylonitrile) composites,positiveelectrode, lithium-sulfur battery*

INTRODUCTION

Among the replacements under development, thelithium-sulfur(Li-S) battery offers one of the highest specificenergy (2600 Wh kg^{-1}), attainable by the complete reaction oflithiumwith sulfur to form Li_2S which carries a theoretical capacityof 1672 mAh g^{-1}. In addition to high specificcapacity, elementalsulfur also has advantages of natural abundance, nontoxic and lowcost,which are all important factors for the upcoming generation of lithium rechargeable batteries [1-4].However,complete discharge of a Li-S battery with bare sulfur cathode iscompromised by the poor electrical conductivity of sulfur. Additionally, thevolume changes between lithiated and delithiated sulfur speciescompromise the mechanical stability of the electrode and the solubility of intermediate lithium polysulfides in liquid electrolytesleads to loss of active material and so called shuttle effect betweenthe two electrodes [5,6].These limitations cause rapid capacityfade on repeated cycling and restrict the practical application ofLi-S batteries. Hence, sulfur must be combined with conductive agents to form cathode materials withbetter conductivity and cycling stability [7-17]

Composites of sulfur with conductive polymers have beenstrongly investigated because these conditions can accommodatethe sulfur volume change; prevent polysulfide dissolution, and actas conductivity enhancers.Noteworthy,Sulfur-poly(acrylonitrile) (SPAN) composites, wherein sulfur is chemically bond to the polymer backboneand PAN acts as a conducting matrix, have shown some success insuppressing the shuttle effect [18,19].However, due to the limitedelectrical conductivity of poly(acrylonitrile), the capacity retentionand rate performance of the SPAN systems are still very modest.The most commonly used method for preparation of composite involves high energy ball milling which may lead tobreakage of the PAN long chains, and in turn reduce theabsorption ability of the polymer towards sulfur and polysulfides. In this present study,the preparation of binary composite with different ratios of sulfur with mild manual mixing components are described.

EXPERIMENTAL PROCEDURE

The binary composite of sulfur /poly (acrylonitrile) is prepared by solid state reaction. In this method sulfur and poly (acrylonitrile) are taken in three different ratios of 3:1, 4:1 and 5:1respectively. These different ratios of S and PAN are grinded together in mortar manually for an hour. Then the precursor was transferred to the Teflon boat and kept at simple heat treatment in Muffle furnace.The final products of composites are denoted as SN31, SN41 and SN51 for 3:1, 4:1 and 5:1 ratios respectively. The different ratios of the obtained composite materials are characterized by XRD (PANalytical XPERT-PRO with Cu Kα radiation), RAMAN (SEKI focal) and SEM (FEG QUANTA 250) analysis.

RESULTS AND DISCUSSION

XRD analysis

The results of XRD measurements are presented in Fig. 1. It shows the XRD patterns of bare S, PAN, and different ratios of SN binary composite. The reflection of the raw sulfur was indexed to an orthorhombic structure.The diffraction patterns of pristine PAN demonstrated a major peak at a $2\theta = 17°$ corresponding to the (110) plane of the PAN crystal structure[20].

After heat treatment, all the composites display an amorphous profile showing only one broadfeature at around$2\theta=26°$.These results not only disclose the chemical reactions between sulfur and PAN but also reveals the embedding of sulfur into poly(acrylonitrile) matrix.Additionally, the active material is uniformly distributed in all binary composites. From XRD analysis of the as prepared composites, it is confirmed that PAN plays a significant part in structural stability and chemical confinement settings for elemental sulfur with different loading.

RAMAN analysis

Raman spectroscopy is a useful tool to further investigate the structural features of binary composites with different ratio of sulfur.The Raman spectra of the obtained binary composites (SN31,SN41 and SN51) are shown in Fig. 2.Two obvious bands can be observed in theRaman spectrum of all the composites, which are due to the D band andG band of carbon. The D band, with a peak at around1320 cm^{-1}, represents a splitting of the E_{2g} stretching mode ofthe carbon atoms, whereas the G band, at around 1588 cm^{-1}corresponds to the breathing mode of k-point phonons withA_{1g} symmetry of the carbon atoms in all samples.The integral intensity ratio(I_D/I_G) can be used to show the extent of the defects anddegree of graphitization for the SN binary composites.The intensity ratio of D band and G band (*I*D/*I*G) for SN41 is 0.9, indicatinga higher electronic conductivity [21].*I*D/*I*G reaches 1.07and 1.02 for SN31and SN51 respectively, which implying that more lattice defects emerge [22].As shown in Figure 2, ID/IG values increases from 1.07 (SN31) to 1.02 (SN51), which indicates thatthe degree of graphitization decreases, thus resulting in inferior conductivity of the obtained composites [23].

No peaks belonging to sulfur which isgenerally located in the range from 300 to 500 cm^{-1}[24,25]is found in the Ramanspectrum of the all obtained composite, indicating that elementalsulfur infiltrates in to polymer matrix, which is in consistent with the conclusion fromXRD.Furthermore, the intensity ratio of0.90 between the two bands (ID/IG) specifies the addition of sp2 hybridization duringcarbonization. This peculiar property subsequently enriches the conductivity by means of π-electron cloud. This defect might arise in the SN41 binary composite due to the partial replacement of carbon atom by thenitrogen [26].

SEM analysis

The morphologies of the samples prepared by manual mixing and after heat treatment are depicted in Fig. 3. Strong agglomerationwas observed in the SN31 and SN51sample.The morphology of the SN41 composite displaysa uniform distribution of sulfur. The long PAN chains prevent the wide agglomeration ofdispersed sulfur but do not inhibit the formation of anchoredpolymer/sulfur nanoparticles.

CONCLUSIONS

A nanostructured sulfur polymer composite was successfullyprepared by manual mixing of sulfur and poly(acrylonitrile) followedby simple heat treatment in argon atmosphere. The preparation method issimpler, faster, and more economical than conventional ball milling.From XRD analysis, PAN shows a significant part in structural stability and chemical confinement settings for elemental sulfur with different loading of the as prepared composites. The intensity ratio of D band and G band (*I*D/*I*G) for SN41 binary composite is 0.9, indicatinga higher electronic conductivity.The morphology of the SN41 composite displays a uniform distribution of sulfur. The long PAN chains prevent the wide agglomeration ofdispersed sulfur but do not inhibit the formation of anchoredpolymer/sulfur nanoparticles.From the investigation of physical properties of the composites, it is confirmed that SN41sample may not only increase the electrical conductivity of the composite, but alsoallows convenient transfer of Li-ion in the composite structure.Based on above mentioned analysis, it can be concluded that SN41 binary composite is theeffective cathode material in Li-S battery.

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FIGURE CAPTIONS
Figure1. XRD patterns for (a) pristine sulfur (b) PAN (c) SN31 (d) SN41 (e) SN51 binary composite
Figure 2. Raman spectra of the obtained binary composites
Figure 3.SEM images of the prepared composite using simple heat treatment.

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Figure 1

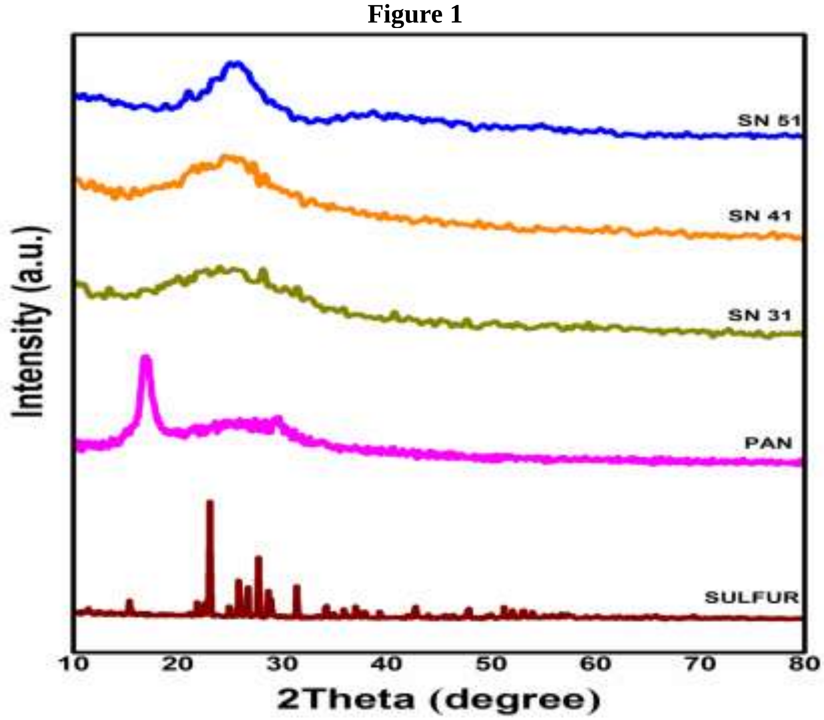

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Figure 2

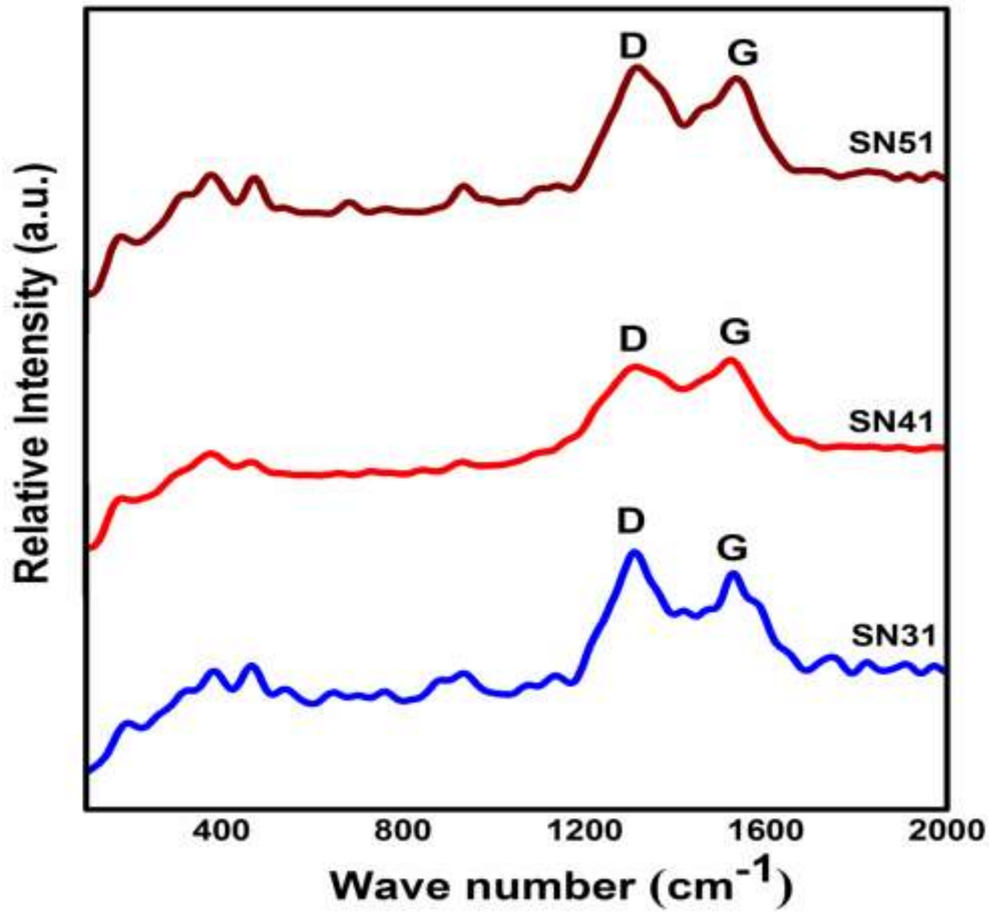

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Figure 3