

**OPTIMIZATION OF S/MnO<sub>2</sub> COMPOSITE CATHODE MATERIAL FOR  
LITHIUM SULFUR BATTERIES**

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**Abstract:**-Development of the cathode materials for lithium-sulfur batteries is vital to meet the demand of the portable devices, power tools, future usage of electric vehicles etc..Sulfur is a promising inexpensive cathode material with a high energy density, environmental acceptability and also are more abundant in nature. Lithium-sulfur batteries possess a higher theoretical capacity of 1672 mAh g<sup>-1</sup> than the commercial Lithium Ion batteries. In spite of these advantages, dissolution of the intermediate polysulfides is hindered the realization of the lithium-sulfur batteries. A simple solid state reaction method has been tried for the preparation of the SMN cathode material by varying the proportion of MnO<sub>2</sub> and sulfur. The effect of MnO<sub>2</sub> in the as prepared composites electrodes on their physical and morphological properties were investigated. In XRD, the peak intensity of sulfur gradually decreases with the increasing content of MnO<sub>2</sub>.The present results suggest that the SMN73 composite is a good candidate for the cathode of Li-S battery.

**INTRODUCTION**

The progress of mobile electronics needs a higher energy density of batteries. For the past few decades, Lithium sulfur batteries have intent in the power sources for wide variety of electronic devices and as motive power battery for electric vehicles (EVs) or hybrid electric vehicles (HEVs) [1-3]. The rechargeable lithium-sulfur (Li-S) battery has attracted immense assiduity in the last several years [4-6] owing to its high energy density (theoretically 2567 Wh/kg) and high theoretical specific capacity (1675 mAh/g). It exhibits higher specific capacity and specific energy (with lithium anode) than any other known cathode active materials [7, 8]. In addition to, sulfur is abundant in nature, inexpensive and environmental harmless. Thence, there is a strong impetus to develop Li/S batteries [9]. Apart from these; sulfur has some drawbacks in the practical usage. However the cyclic stability of lithium-sulfur batteries is not high, which is ascribed to the low electric conductivity of sulfur [14] and dissolution of lithium polysulfides in electrolyte [15, 16]. Lithium polysulfides are intermediate products of electrochemical reactions between sulfur and lithium ions. In the process of charge, dissolved high-order lithium polysulfides diffuse through the separator to the anode (lithium metal). They react with lithium and are deoxidized to low-order lithium polysulfides which migrate back to the cathode and are oxidized to high order lithium polysulfides. Reoccurrence of those processes results in low columbic efficiency and capacity fading [18]. In order to accomplish high performance of Li/S battery, the sulfur particles is reduced with carbon black and metal oxides is brought in as a conductive agent who is an eloquent for current collection, the rate performance and sulfur utilization [10-13]. Lee et al. [17] prepared  $\alpha$ -MnO<sub>2</sub> nanowires by a hydrothermal method and then mixed with agglomerated sulfur powders. Homogeneous  $\alpha$ -MnO<sub>2</sub>-coated sulfur particles were obtained by utilizing heat treatment intended to melt and recrystallize the sulfur.  $\alpha$ -MnO<sub>2</sub> nanowire lead to the suppression in re-agglomeration of sulfur powders during heat treatment and result in successful coating as well as decreased size in parent sulfur powder and improved rate capability compared to apistine sulfur cathode. Cetinkaya et al. [19] prepared Graphene/ $\alpha$ -MnO<sub>2</sub> nanocomposite cathodes containing various amount of  $\alpha$ -MnO<sub>2</sub> catalysts (10 wt.%, 30 wt.%, 50 wt.%) using planetary ball milling in order to the investigate lithium oxide formation and decomposition reactions on the Graphene/ $\alpha$ -MnO<sub>2</sub> cathode. In this present work, an attempt is made to perform a MnO<sub>2</sub> as an additive to the sulfur material and optimize the physical properties of S/MnO<sub>2</sub> composite for lithium-sulfur batteries.

**EXPERIMENTAL WORK**

The composite of sulfur/MnO<sub>2</sub> is prepared by solid state reaction. In this method, Sulfur and MnO<sub>2</sub> were taken respectively in three different ratios, viz, 6:4, 7:3, and 8:2. These different ratios of S and MnO<sub>2</sub> were grinded together in mortar manually for an hour. Then the precursor was transferred to the Teflon boat and kept at 155°C in furnace for 20 h in Argon atmosphere. The SMN composites obtained were characterized by XRD (PANalytical XPERT-PRO with Cu K $\alpha$  radiation), RAMAN (SEKI focal) and SEM (FEG QUANTA 250).

## RESULTS AND DISCUSSION

### X-RAY DIFFRACTOMETER

X-ray diffraction (XRD) analysis has been conducted for the obtained SMN composite with different ratios. The Fig. 1 shows XRD pattern of a) elemental sulfur, b) SMN64, c) SMN73 and d) SMN82. By comparing the XRD patterns, all the composites exhibit peaks that are perfectly matching with those of pure sulfur, thereby indicating the presence of sulfur in the composites. The SMN64 composite exhibits significantly lower peak intensities than the SMN73 and SMN82 composite, thereby suggesting a low content of the sulfur. This finding demonstrates that high content of MnO<sub>2</sub> are intercalated in the sulfur layer, thus affecting the well-defined crystal structure during sulfur precipitation<sup>[20]</sup>.

### MICRO-RAMAN

Raman Spectroscopy was conducted to further confirm that as prepared powders of SMN at different ratios had been successfully produced. Fig. 2 shows the RAMAN spectra of a) SMN64, b) SMN73 and c) SMN 82 composite. In SMN82 and SMN73 composite the peaks at 220 cm<sup>-1</sup> and 476 cm<sup>-1</sup> exhibits the presence of sulfur in the composite and it indicates that the sulfur is fully dispersed in the composite. The pure sulfur exhibit a characteristic peak below 500 cm<sup>-1</sup> that is originated from A1 symmetry of S-S bond<sup>[21]</sup>. The peak at 520 cm<sup>-1</sup> exhibits the presence of MnO<sub>2</sub>. The absence of sulfur peak in SMN64 composite indicates that a fraction of sulfur are dispersed into the MnO<sub>2</sub> structure and the sulfur formed crystal structure in the cooling process which is consistent with the XRD pattern with low intensity peak.

### SCANNING ELECTRON MICROSCOPE

From Fig. 3(a) small islands were observed on the surface could be sulfur, considering that a small amount of sulfur might not be infused into the pores due to high a mass loading of sulfur in SMN82 composite<sup>[22]</sup>. From Fig. 3(b), it was observed that no discrete sulfur particles can be found outside of the SMN73 composite particles which offer the full embodiment of sulfur into the channel of MnO<sub>2</sub><sup>[23]</sup>. After the incorporation of sulfur, no large bulk sulfur particles can be easily observed on the surface of the composite implying the sulfur particles are also embedded in the MnO<sub>2</sub> particles. The existence of sulfur is difficult to identify in SMN 64 composite. It means that the MnO<sub>2</sub> have completely restricted the sulfur and it seems a cluster of particles with inhomogeneous structure.

### CONCLUSION

The positive electrodes with different ratios of additives have been successfully prepared by a simple solid state reaction method. The prepared composites have been characterized by XRD, RAMAN and SEM analyses. The powder XRD pattern of pristine sulfur exhibited orthorhombic structure with F<sub>ddd</sub> space group. A RAMAN spectrum exhibits the presence of sulfur in the composite and it indicates that the sulfur is fully dispersed in the composite. From SEM images it is observed that the disappearance of sulfur in the coating material, suggesting that the sulfur was enclosed into the pores of MnO<sub>2</sub>. Thus it is concluded that the positive electrode of sulfur was prepared successfully. The coating material overruling in the dissolution of polysulfides may enhance the conductivity of Li-S batteries.

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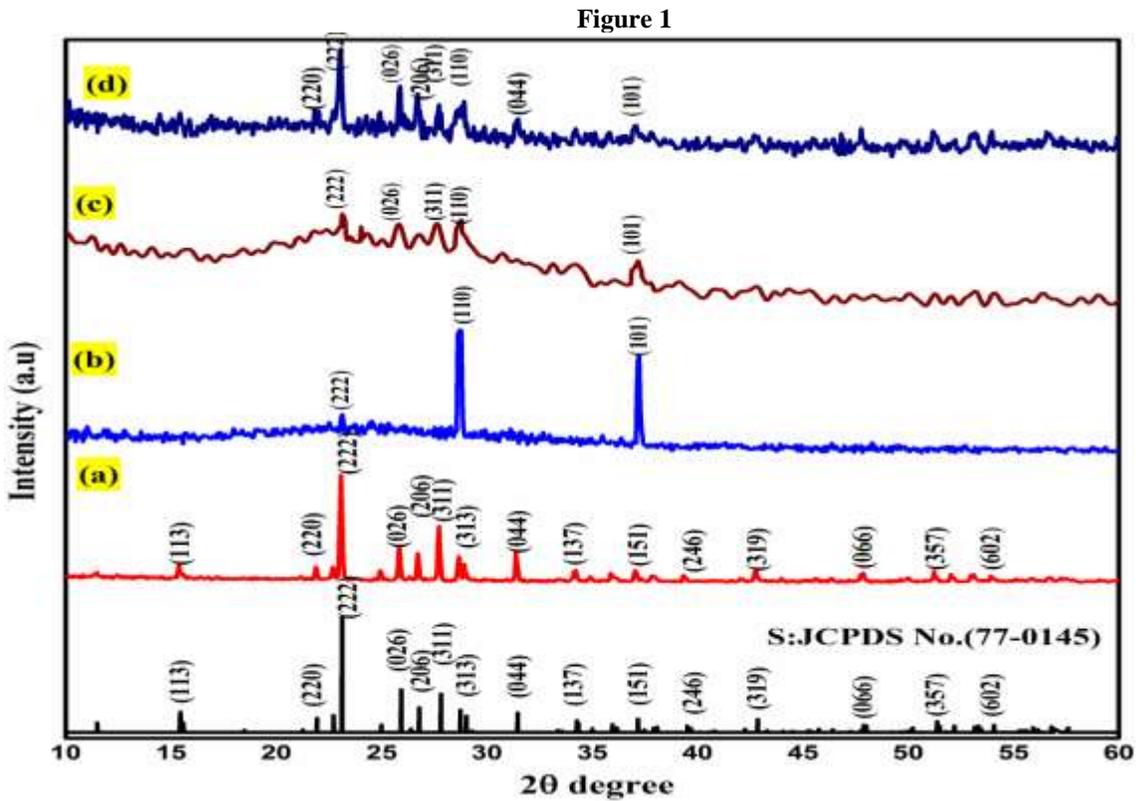
**FIGURE CAPTIONS**

**Figure 1.** XRD pattern of a) Pure sulfur, b) SMN 64, c) SMN 73 and d) SMN 82 composites

**Figure 2.** RAMAN spectra of a) SMN 64, b) SMN 73 and c) SMN 82 composites

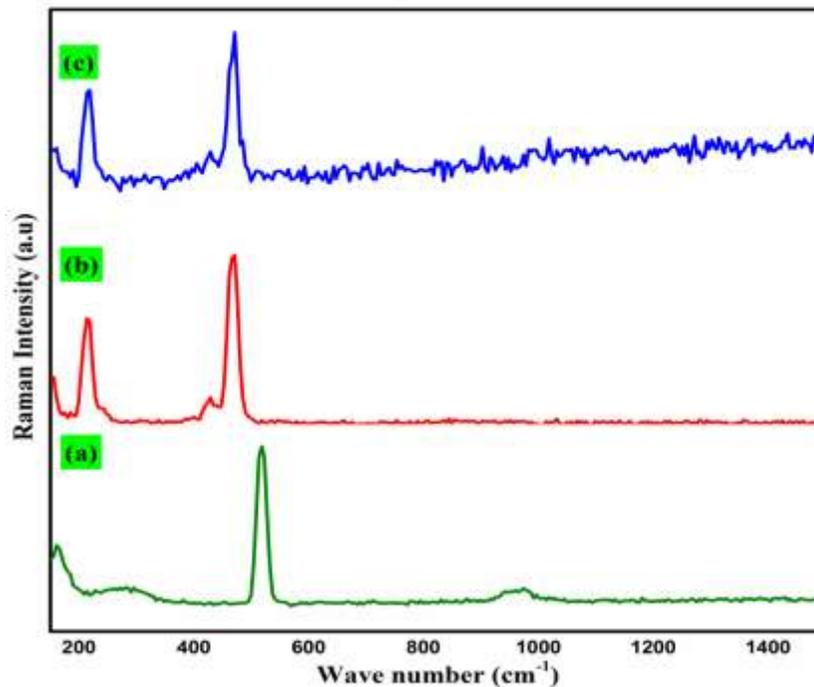
**Figure 3.** SEM images of a) SMN 64, b) SMN 73 and c) SMN 82 composites

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Figure 2



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Figure 3

