International Research Journal of Engineering and Technology (IRJET) **e-ISSN: 2395-0056**
Volume: 04 Special Issue: 09 | Sep -2017 **www.irjet.net** **p-ISSN: 2395-0072**

One Day International Seminar on Materials Science & Technology (ISMST 2017)
4th August 2017
Organized by
Department of Physics, Mother Teresa Women's University, Kodaikanal, Tamilnadu, India

INVESTIGATIONS ON PHYSICAL PROPERTIES OF SULFUR BASED COMPOSITE CATHODES IN LITHIUM SULFUR BATTERY FABRICATION

G.Radhika[1], K.Krishnaveni[2], R.Subadevi[3], M.Sivakumar[4]

[1,2,3,4] *#120, Energy Materials Lab, Department of Physics, Alagappa University, Karaikudi-630 003,*
Tamil Nadu, India.
(Corresponding Author: susiva73@yahoo.co.in (M.Sivakumar))*

***

Abstract: *Sulfur is a promising cathode material with a high theoretical capacity of 1672 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. The use of conductive carbon framework is efficient and effective to obtain advanced composite cathodes for lithium–sulfur batteries. However, the loading amount of sulfur less than 70 wt% induces a limited energy density, which hinders the practical application of lithium–sulfur batteries. Herein, a scalable and one-step method is employed for carbon nanotube/sulfur composite cathode, in which aligned CNTs served as interconnected conductive frameworks to accommodate sulfur. The results of the SEM and XRD measurements reveal that the CNTs serve as the cores and are dispersed individually into the sulfur matrices; the sulfur with a high loading content was efficiently utilized for a lithium–sulfur cell with a much improved energy density.*

Key Words: *sulfur battery; carbon nanotube; XRD; SEM; energy density.*

1. INTRODUCTION

Lithium-ion batteries are being increasingly used for large-scale energy storage systems, driven by the growth of markets such as electric vehicles and large scale energy storage systems [1, 2]. Their practical use in these new applications is still challenging, however, as long as the attainable energy density of Li-ion batteries is limited to their current forms. In this respect, intercalation-based cathode materials have almost approached their theoretical energy density limit [3-5]. It is anticipated that breakthroughs will probably come from chemical transformation or conversion chemistry, similar to the evolution of anodes from carbonaceous materials that function on the basis of intercalation chemistry, to conversion chemistry based on metal oxides or lithium alloys [6]. Li-S batteries become one of the most attractive candidates for the next generation high-energy rechargeable battery because of their high theoretical specific capacity (1675 mAh g^{-1}), high theoretical energy density (2600 Wh kg^{-1}), and economic cost [7-10].

Additionally, sulfur is abundant, low cost, and environmentally friendly. Therefore, lithium sulfur batteries have great potential for the next generation of high energy density lithium batteries. However, the lithium/sulfur battery systems investigated previously have some critical problems [11-13]. First, elemental sulfur is electrically and ironically insulating at room temperature, which leads to poor electrochemical performance and the low utilization of sulfur in the cathode. Second, Li_2S and other insoluble compounds are generated and cover the active compounds during cycling, which inhibit access to lithium ions. Third, since the discharge process of the battery is composed of many steps and generates various forms of soluble intermediate lithium polysulfide, the liquid electrolyte can dissolve and cause a rapid irreversible loss of sulfur active materials over repeat cycles. Furthermore, the spread of these polysulfide's to the anode can lead to the shuttle mechanism and this may cause more serious capacity loss. Consequently, the battery suffers because of the low utilization of active materials and because of poor cycle life. Over the past few decades, these above issues have been mitigated by moving from conventional electrodes to sulfur–carbon composites, in which the elemental sulfur is efficiently trapped within protecting carbon matrixes of various configurations (such as grapheme, [14,15] porous carbon, [16] and CNTs [17]).

Alternatively, it has also been proposed to contain sulfur in hollow carbon nanoparticles, as a method of targeted design of porous materials that could; allow for higher sulfur content while still retaining the benefits of a porous carbon shell that inhibits polysulfide dissolution [18-19]. Such mesoporous hollow carbon capsules might offer advantages over other porous carbon materials, presenting a very attractive conducting matrix for encapsulating sulfur.

Carbon nanotubes and carbon nanofibers, as attractive matrices for sulfur, have attracted considerable attention [20-23]. The intimate contact between conductive nanotubes and sulfur can enable fast electron and lithium ion transport in electrodes [24]. In addition, flexible carbon nanotubes can accommodate the volume expansion of sulfur during cycling. Ji, Lee and Nazar [25] have reported highly ordered mesoporous carbon-sulfur electrodes exhibiting high pore volume, uniform pore diameter and interconnected porous structure by employing CMK-3, a well-known mesoporous material. Their result shows that this cathode renders a highly enhanced performance. Yuan et al. [26] have taken advantage of the capillary effect between the sulfur and MWCNTs to construct a novel electrode with carbon nanotube as the core. This composite show a good cycle life compared to the counterpart made by simply mixing sulfur with MWCNTs [22].

2. EXPERIMENTAL WORK

The composite of sulfur carbon nanotube is prepared by solid state reaction. In this method sulfur and carbon nanotube are taken for two different ratios, which are as follows 6:4, 7:3 respectively. These different ratios of S and CNT were ground together in mortar manually for fifteen minutes. Then the precursor is transferred to Teflon boat and kept at 155° C in furnace for 20 hours under argon atmosphere. The S-CNT composites are characterized by Fourier-transform infrared (FT-IR) spectra were recorded using a (Thermo Nicolet 380 Corporation and KBr pellets). XRD measurements were performed using a (PANalytical XPERT-PRO with Cu Kα radiation) (XRD). The surface morphology of the composites was obtained by scanning electron microscopy SEM (FEG QUANTA 250).

3. RESULTS AND DISCUSSION

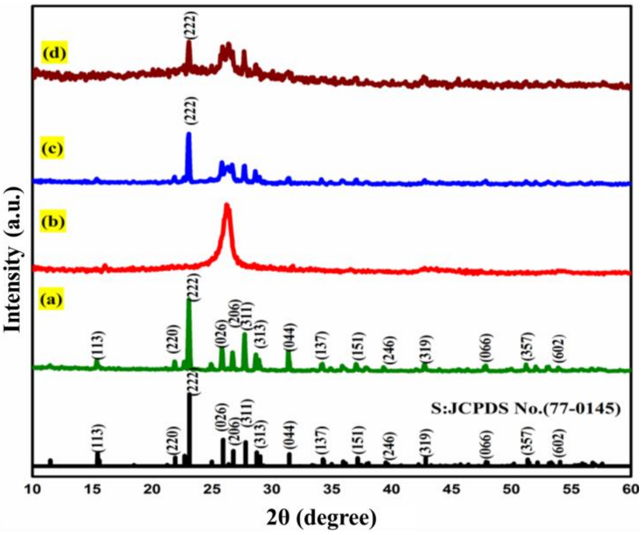

Fig -1: XRD Pattern of a) elemental sulfur, b) CNT, c) SCNT 64 and d)SCNT 73 composite

Figure 1 shows characteristic XRD spectra of related materials. The reflections of the raw sulfur are consistent with Fddd orthorhombic structure. Compared with the pattern of the raw elemental sulfur, the XRD spectra of the S-coated CNTs did not exhibit many changes except for the appearance of the slight and broad CNTs peaks centered at $2\ \theta = 26^{\circ}$. An XRD analysis of elemental sulfur showed two prominent peaks at $2\theta = 23^{\circ}$ and 28°that correspond to an Fddd orthorhombic structure. This indicates that no phase transformation of sulfur occurs during the preparation steps, and crystal structure of sulfur still remains Fddd orthorhombic structure [26] and reveals that the sulfur particles coated the surface of the CNTs well.

Fig. 2 shows the FTIR spectra of the pristine CNTs, S-CT73 and S-CT64 composite. The characteristic vibrational modes of CNTs, C-C (~1650 cm^{-1}) and O-H (~3400 cm^{-1}) were identified in all the composite and the existence of O-H groups might be from ambient atmospheric moisture tightly bound to CNTs [27]. The peak around 1632cm^{-1} and 1463 cm^{-1} indicating the existence of C-C stretching mode. The peak around 2922 cm^{-1} assigned to C-H asymmetric vibration which exists in all the composites. The S-CT composite showed similar characteristic peaks with the CNTs, manifesting no chemical reaction occurring between sulfur and CNTs during the melt-diffusion process [28].

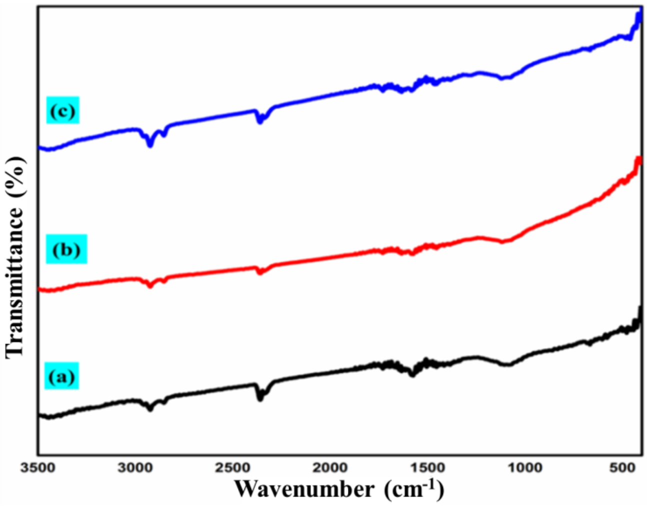

Fig -2: FTIR Spectrum of a) CNT, b) SCNT64 and c)SCNT73 composite.

Scanning electron microscopy (SEM) images (Figure 3 & 4) show that the S and CNT are well intertwined. This network facilitates electron transfer and provides large interspaces to accommodate diverse materials, including the active materials. In addition, CNT provide a highly conductive, mechanically robust structure that enables efficient sulfur utilization. The mechanical robustness indicates its potential application for flexible energy storage devices [29]. In contrast, the S-CNT64, CNTs are aggregated in a small region with diverse structure. In this structure, the aggregated CNT having many interconnected pores is formed on the sulfur, indicating a loosely packed nanostructure on the surface. It can be seen that the CNT layer may affect the enhancement of the electrochemical performance of the composite [30].

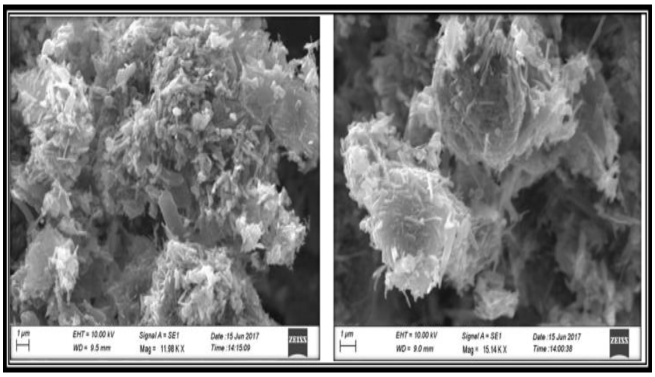

Fig -3 and 4: SEM images of SCNT64 and SCNT 73 composite

3. CONCLUSIONS

In summary, the sulfur/carbon nanotube composites were synthesized by solid state reaction method with different sulfur loadings. The structural characteristics are beneficial for loading sulfur as well as ensuring good conductivity of the carbon tube. This indicates that no phase transformation crystal structure of sulfur still remains Fddd orthorhombic structure. In morphological study, the SCNT 73 composite implying the sulfur particles are also embedded in the CNT matrix. The favorable CNT may also increase the electrical conductivity of the composite, but also allows convenient transfer of Li-ion in the composite structure.

REFERENCES

[1]. Zaghib K, Mauger.A.;Groult.H, Goodenough.JB, Julien,CM. Advanced Electrodes for High Power Li-ion Battery.Materials2013, 6, 1028–1049.

[2]. Liu. J, Zhang JG, Yang. Z, Lemmon.JP,Imhoff. C, Craff.GL, Li. L, Hu.C,Xiao.J, Xia.G,
Materials Science and Materials Chemistry for Large Scale Electrochemical Energy Storage: From Transportation to Electrical Grid.Adv.Funct. Mater.2013, 23, 929–946

[3]. Ellis.B, Lee.KT, Nazar.LF, Positive Electrode Materials for Li-ion and Li- Batteries, Chem.Mater.2010, 22, 691–714.

[4]. Scrosati. B, Garche.J, Lithium Batteries: Status, Prospects and Future. J. Power Sources2010, 195, 2419–2430.

[5]. Whittingham.MS, Lithium Batteries and Cathode Materials, Chem. Rev.2004, 104, 4271–4301.

[6].Choi.NS, Chen.Z, Freunberger.SA, Ji.X, Sun.YK,Amine.K, Yushin..G, Nazar.LF, Cho.J, Bruce.PG, Challenges Facing Lithium Batteries and Electrical DoubleLayer capacitors. Angew. Chem., Int. Ed.2012, 51,9994–10024.

[7]. Zhang.Y,Zhao.Y, Yermukhambetova. A, Bakenov. Z, Chen.P,Ternary Sulfur / Polyacrylonitrile / Mg0.6Ni0.4O Composite Cathodes for High Performance Lithium/Sulfur Batteries, J. Mater.Chem.A 2013, 1, 295-301.

[8]. Kolosnitsyn.VS, Karaseva.EV, Lithium-Sulfur Batteries: Problems and Solutions. Russ. J. Electrochem. 2008, 44, 506-509.

[9].Hassoun. J, Scrosati.B, Moving to a Solid-State Configuration: A Valid Approach to Making LithiumSulfur Batteries Viable for Practical Applications, Adv. Mater. 2010, 22, 5198-5201.

[10]. Jayaprakash. N, Shen. J, Moganty. SS, Corona. A, Archer. LA, PorousHollowCarbon@SulfurComposites for High-Power Lithium-Sulfur Batteries.Angew. Chem. Int. Ed. 2011, 50, 5904-908.

[11].Cheon.SE, Ko.KS, Cho.J H, Kim.SW, Chin.EY, Kim.HT,Rechargeable Lithium Sulfur Battery,I. Structural Change of Sulfur Cathode During Discharge and ChargeJ. Electrochem.Soc.2003, 150, A796.

[12]. Cheon SE, Ko.K S, Cho. JH, Kim.SW, Chin.EY, Kim.HT, RechargeableLithium Sulfur BatteryII. Rate Capability and Cycle Characteristics, J. Electrochem. Soc.2003, 150, A800.

[13].Mikhaylik. YV, Akridge. JR, Polysulfide shuttle study in the Li/S battery system, J. Electrochem. Soc. 2004, 151, A1969.

[14]. Sun. H, Xu.GL,Xu.YF,Sun.SG,ZhangX,Qiu.Y, Yang, S, A CompositeMaterial of Uniformly Dispersed Sulfur on Reduced Graphene Oxide: Aqueous One-Pot Synthesis, Characterization and Excellent Performance as the Cathode in Rechargeable Lithium−Sulfur Batteries.Nano Res.2012, 5, 726−738.

[15]. Wang.H, Yang Y, Liang. Y, Robinson.J T, Li. Y, Jackson.A, Cui.Y, Dai. H, Graphene-Wrapped Sulfur Particles as a Rechargeable Lithium−Sulfur Battery Cathode Material with High Capacity and Cycling Stability.Nano Lett.2011, 11, 2644−2647.

[16]. Jung.D S, Hwang.TH, Lee, J. H,Koo.HY,Shakoor.RA, Kahraman.R, Jo.YN, Park.MS, Choi.JW, Hierarchical Porous Carbon by Ultrasonic Spray Pyrolysis YieldsStable Cycling in Lithium−Sulfur Battery.Nano Lett.2014, 14, 4418−4425.

[17].Yuan.Z, Peng.HJ, Huang.JQ, Liu.XY, Wang.DW, Cheng.XB, Zhang.Q, Hierarchical Free-Standing Carbon-Nanotube Paper Electrodes with Ultrahigh Sulfur-Loading for Lithium−Sulfur Batteries, Adv. Funct.Mater.2014, 24, 6105−6112.

[18].Jayaprakash.N, Shen. J,Moganty.SS, Corona. A, Archer. AA, Porous HollowCarbon@Sulfur Composites for HighPower Lithium-Sulfur Batteries. Angew.Chem., Int.Ed.2011, 50, 5904–5908

[19]. Zhang.C, Wu.HB, Yuan.C,Guo.Z, Lou. XW, Confining Sulfur in Double-ShelledHollow Carbon Spheres for LithiumSulfurBatteries.Angew. Chem., Int. Ed.2012, 51,9592–9595

[20]. M. Rao, X. Song, H. Liao, E.J. Cairns, Carbon nanofiber-sulfur composite with different binders for secondary Li-S cellsElectrochim. Acta 65 (2012) 228-233.

[21]. M. Rao, X. Song, E.J. Cairns, Nano-carbon/sulfur composite cathode materials with carbonnanofiber as electrical conductor for advanced secondary lithium/sulfur cellsJ. Power Sources 205 (2012) 474-478.

[22].W. Ahn, KB. Kim, KN. Jung, KH. Shin, CS. Jin,Synthesis and electrochemical properties of a sulfur-multi walled carbon nanotubes composite as a cathode material for sulfur batteries, J. Power Sources 202 (2012) 394-399.

[23]. J. Guo, Y. Xu, C. Wang,Sulfur-impregnated disordered carbon nanotubes cathode for lithium-sulfur batteries,Nano Lett. 11 (2011) 4288-4294.

[24].SC. Han, MS. Song, H.Lee, HS. Kim, HJ. Ahn, JY. Lee,Effect of mutiwalled carbon nanotubes on electrochemical properities of lithium/sulfur rechargeable batteries,J. Electrochem.Soc. 150, (2003) A889-A893.

[25].X. Ji, KT. Lee, LF. Nazar, A highly ordered nanostructured carbon sulphur cathode lithium Sulphur batteries forNat. Mater. 8 (2009) 500-506

[26].L. Yuan, H. Yuan, X. Qiu, L. Chen, W. Zhu, Improvement of cycle property of sulfur-coated multi-walled carbon nanotubes composite cathode for lithium/sulfur batteries, J. Power Sources 189 (2009) 1141-1146.

[27]. Titus E, Ali N, Cabral G, Gracio J, Babu PR, Jackson MJ, Chemically functionalized carbon nanotubes and their characterization using thermogravimetric analysis, fourier transform infrared, and raman spectroscopy. J Mater Eng Perform 2006;15:182-186.

[28]. L. Chen, , H. Zhou, C. Fu, Z. Chen, C. Xu, Y. Kuang, Chemical modification of pristine carbon nanotubes and their exploitation as the Carbon hosts for lithium-sulfur batteries,International journal of hydrogen energy xxx , (2016) 1-1

[29]. H. Xu, L. Qie, A. Manthiram, An Integrally-designed, Flexible Polysulfide Host for High -performance Lithium-sulfur Batteries with Stabilized Lithium-metal Anode, http: / /dx.doi .org/10.1016/ j .nanoen .2016.05.028

[30]. KS.Kim, SJ. Park, Synthesis of carbon-coated graphene electrodes and their electrochemical performance, ElectrochimicaActa 56 (2011) 6547–6553.

BIOGRAPHIES

Radhika Govindaraju is pursuing Ph.D., in Alagappa University, Karaikudi. Her research interests focus on Nano materials and electrode materials for high energy density batteries.

Krishnaveni Kalaiappan is a Research scholar in Alagappa University, Karaikudi. Her research interests are electrolytes and electrodes for Li-ion and Li-S batteries.

Subadevi Rengapillai received his Ph.D. in Alagappa University, and currently she is working Assistant professor in Alagappa University, Karaikudi. Her research interests focus on rechargeable Batteries, Super capacitors, Nano materials and Bio-diesel. She has published more than 39 papers in international journals.

Sivakumar Marimuthu received his Ph.D. in Alagappa University, and then Post-Doctoral Fellow in National Taiwan University, Taipei. Currently, he is working as Assistant professor in Alagappa University, Karaikudi. His research interests are in the areas of Batteries (Li-ion, Li-S and Na-ion), Super capacitors, Bio-fuels and Nano materials. He has published more than 41 papers in international journals.

`