

Synthesis and Characterization of a Novel Nanoporous Composite Based on Elemental Sulfur and Graphitic Mesoporous Carbon

Bahrami Adeh, Narmin*⁺; Mohammadi, Nourali; Khorramjah, Fatemeh

Iranian Institute for Research & Development in Chemical Industries(IRDCI), Academic Center for Education, Culture and Research (ACECR), Karaj, I.R. IRAN

ABSTRACT: A novel sulfur nanocomposite was fabricated based on graphitic mesoporous carbon. The graphitic mesoporous carbon was synthesized using sucrose as carbon precursor, nano CaCO_3 as a hard template and nickel nitrate as graphitization catalyst. The structural properties of the prepared material were characterized using powder X-Ray Diffraction (XRD), N_2 -adsorption/desorption and Scanning Electron Microscopy (SEM) techniques. The mesoporous solid with the high surface area of $710 \text{ m}^2/\text{g}$, average pore size of 2.7 nm and high graphitization degree was applied as the nanoreactor for infiltration of molten sulfur at $150 \text{ }^\circ\text{C}$ in an inert gas atmosphere. The properties of prepared nanocomposite were investigated by XRD, BET, SEM and cyclic voltammetry methods. The obtained results showed that the desired nanocomposite with enhanced conductivity successfully was synthesized.

KEYWORDS: Graphitic mesoporous carbon; Electrical conductivity; Sulfur nanocomposite; Hard template; Cyclic voltammetry.

INTRODUCTION

Elemental sulfur has advantages of being inexpensive and widely available both naturally and in the form of industrial by-product, having low equivalent weight and being environmentally friendly [1]. One of the most important applications of elemental sulfur is in the manufacture of cathode for rechargeable lithium batteries. Li / S (Li-S) battery is highly regarded because of high theoretical capacity (1675 mAh/g) and specific energy density (2600 Wh/kg) of sulfur [1]. However, it is not possible to utilize elemental sulfur on its own, as reversible positive electrode materials in the lithium- sulfur batteries. Despite the mentioned advantages, there are

still a number of major obstacles for the commercialization of Li-S batteries [2], including low active material utilization rate, poor long term cycle life and low coulombic efficiency [3]. It is well known that very low electrical conductivity of sulfur ($5 \times 10^{-30} \text{ S/cm}$) and high solubility of high-order poly-sulfide (Li_2S_n , $4 \leq n \leq 8$) in the electrolyte, which are generated during charging and discharging of the battery, are responsible for these limitations [4]. To overcome these challenges, diverse conductive carbonaceous materials have been designed to increase conductivity of the cathode [5] and suppress the dissolution of polysulfide intermediates into the electrolyte

* To whom correspondence should be addressed.

+ E-mail: b_adeh@gmail.com

1021-9986/2016/4/1

9/\$/5.90

during cycling. [1, 6]. Various materials such as mesoporous carbon [7-10], microporous carbon [11, 12], Porous spherical carbon [5], carbon nanotubes [1, 13, 14], MultiWalled Carbon NanoTubes (MWCNTs) [15, 16], graphene [17, 18], porous hollow carbon [19, 20] and hollow carbon nanosphere[21] have been applied to achieve the purpose.

During the past decade, Mesoporous Carbons (MC) materials have been receiving significant attention because of their high specific surface area, large pore volume, excellent conductivity, as well as chemical inertness and good mechanical stability[22,23]. Generally there are two methods to synthesize of mesoporous carbons [24, 25]. The conventional and widely strategy is hard-templating method (i.e. nano casting) using various hard templates such as zeolites, alumina membranes [26], colloidal silica, SBA-15 and MCM-48[27-30]. Soft- templating is another strategy to preparation of mesoporous carbon. However, this method requires higher demands on the synthesis conditions. Among different hard templates used for the synthesis of mesoporous carbon, nano-CaCO₃ with unique mechanical/optical properties and low price attracted many attentions to easy and effective synthesis of mesoporous carbons [26, 31].

Non-graphitized mesoporous carbons showed low electrical conductivities which limited their applications; therefore enhancing the graphitization degree of mesoporous carbon is of interest to increasing their electrical conductivity [32, 33]. High temperature treatment is effective method to form graphitic structure, but high energy consumption is inevitable during the high temperature treatment [33]. Graphitic carbonous materials with high crystallinity can be prepared at relatively low temperatures (<1000°C) by means of heterogeneous graphitization carried out with the aid of various transition-metal catalysts such as Fe, Co, Ni, Mn ions [31, 32].

To the best of our knowledge, there is no report about preparation of sulfur composite based on graphitic mesoporous carbon. In the present study, we report, the synthesis and characterization of a Graphitic Mesoporous Carbon (GMC) using cheap nano-CaCO₃ as hard template, sucrose as inexpensive carbon precursor, nickel nitrate salt as graphitization catalyst and dilute HCl as template removing agent by hard template method. Then,

fabrication of a novel nanocomposite, with enhanced electrical conductivity, based on sulfur and Graphitic Mesoporous Carbon (GMC) is discussed.

EXPERIMENTAL SECTION

Chemicals

Sucrose (as carbon precursor) and paraffin oil were purchased from Samchun Pure Chemical Co., Ltd. (South Korea). Graphite powder, nickel (III) nitrate (as graphitization catalyst) and HCl (as template removing agent) were supplied by Merck. Nano-CaCO₃ (average particle size: 50nm; surface area: 150 m²/g; purity> 99%) was purchased from Shijiazhuang Jinli Mineral. All other chemicals were of analytical reagent grade and were used as received.

Apparatus

The electrochemical measurements were carried out by the potentiostat/galvanostat (Zive sp2, Wonatech, South Korea). A traditional three-electrode system was used including carbon paste electrodes modified with mesoporous carbon as the working electrode, Ag/AgCl electrode (saturated with KCl) as the reference electrode and platinum wire as the auxiliary electrode. N₂-adsorption/desorption isotherms were measured at 77 K, using a Belsorp Mininll analyzer. Samples were degassed at 523 K for 8 h before measurements. Specific surface areas were calculated using the Brunauer-Emmett-Teller (BET) model [34]. Pore volumes were estimated at a relative pressure of 0.94 (P/P₀), assuming full surface saturation with nitrogen. Pore size distributions were evaluated from desorption branches of nitrogen isotherms using the Barret-Joyner-Halenda (BJH) model [35]. Powder X-Ray Diffraction (XRD) patterns were recorded on Brulcer AXS-D8 Advance diffractometer (40 kV, 30 mA) using Ni-filtered Cu Ka radiation. Scanning Electron microscopy (SEM) micrographs were obtained using a Tescan Vega microscope.

Synthesis of graphitic mesoporous carbon

In order to synthesize of Graphitic Mesoporous Carbon (GMC), first, the solution containing 3g sucrose was prepared, then 4 g of nano-CaCO₃ and 1.5 g of nickel nitrate were added and stirred about 120 minutes in room temperature. The obtained mixture was dried in an 80 ° C oven over night. The resulting powder was carbonized

at 800°C under nitrogen atmosphere. The product was added to 0.5M hydrochloric acid solution which has been stirred for 8 hours to remove the calcium carbonate template. After washing and filtration by deionized water, the desired Graphitic Mesoporous Carbon (GMC) was prepared. The optimization of nano- CaCO_3 to sucrose ratio and amount of nickel nitrate carried out by cyclic voltammetry method.

Fabrication of sulfur-graphitic mesoporous carbon composite

As shown in the literature [3, 4, 7], the sulfur-mesoporous carbon composites are a class of materials with elemental sulfur impregnated into the pores. These materials are generally prepared by infiltrating of molten sulfur into the pores of carbon near the critical temperature (about 150°C), at which the molten sulfur has lowest viscosity. A post treatment by heating the product above boiling point of sulfur for a few hours is often applied to vaporize the residual sulfur on the outer surface of carbon particles. For this purpose, an around 300°C temperature has been widely used. Therefore at the present study, first of all, 1 gram of GMC and 7 grams sulfur powders were mixed and heated in an oven at 150°C under inert gas atmosphere for 1 hour. Molten sulfur was adsorbed into the pores of carbon. At the second step, heating temperature was increased to 300 °C and remained at this temperature for about 3 hours to remove sulfur particles that absorbed at the outer surface of GMC particles. As a result sulfur remains only at the pores as adsorbed material. Furnace temperature programed with a gradient of 3°C per minute. The weight of product was 2.12 grams which indicated the S-GMC composite consists of 52.8 wt% sulfur and 47.2 wt% GMC. Also the result of CNHS analysis showed that about 51 wt% of the prepared composite is sulfur.

Preparation of working electrode

In order to study and compare the electrochemical behavior, the working electrodes were made from GMC, S-GMC composite and sulfur. The conventional Carbon Paste Electrode (CPE) was prepared by hand-mixing of graphite powder and paraffin oil (with a 30/70 paraffin oil/graphite ratio (w/w)) in a mortar and pestle and a portion of the composite mixture was packed firmly into one end of a poly-amide tube (diameter 4.7 mm).

The electrical contact was provided by inserting a copper wire into the carbon paste. Appropriate packing was achieved by pressing the surface against a soft paper until a smooth surface was obtained. The sulfur/CPE, GMC/CPE and sulfur - S-GMC composite /CPE was fabricated by mixing 0.35g of any of the material (sulfur, GMC, S-GMC composite), 0.35 g of graphite powder and 0.3 g of paraffin oil using the same procedure.

RESULTS AND DISCUSSION

Synthesis of graphitic mesoporous carbon

Cyclic voltammetry is powerful technique to characterize conductive materials. In order to synthesize of desired nanoporous carbon material, first, the amounts of nano- CaCO_3 and sucrose were optimized by utilizing cyclic voltammetry (CV) method. As indicated in the Table 1 and Fig. 4; the intensity of anodic and cathodic peaks was decreased by increasing the ratio of nano- CaCO_3 to sucrose (run1 to run 7). Also along with decreasing of peak heights, ΔE_p was increased. The obtained results show that, the electrical conductivity was increased in the resulting materials with the enhancement of the ratio of nano- CaCO_3 to sucrose. However, as indicated in the Table 1, the amount of the resulting material is greatly reduced by increasing of the ratio of nano- CaCO_3 to sucrose, therefore the amount of nano- CaCO_3 and sucrose were determined as run 3.

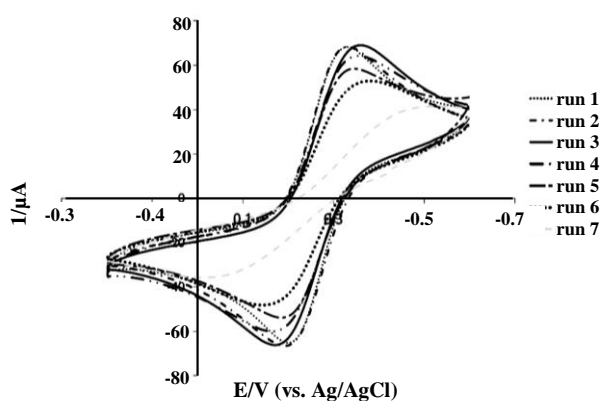
As previously explained, in order to catalytic graphitization; varying amounts of nickel nitrate (III) was added to the reaction medium during the synthesis process. As shown in Table 1 and Fig. 5 peak intensities were strongly enhanced as increasing the amount of nickel nitrate. Also the anodic and cathodic peak separation (ΔE_p) was declined. It is noteworthy that the increasing of anodic and cathodic peak intensity and ΔE_p reduction happens strongly in run 8 to run 11, while only a slight change was observed from run 11 to run 12. Hence desired graphitic mesoporous carbon was synthesized as run 11.

N₂-adsorption/desorption analysis

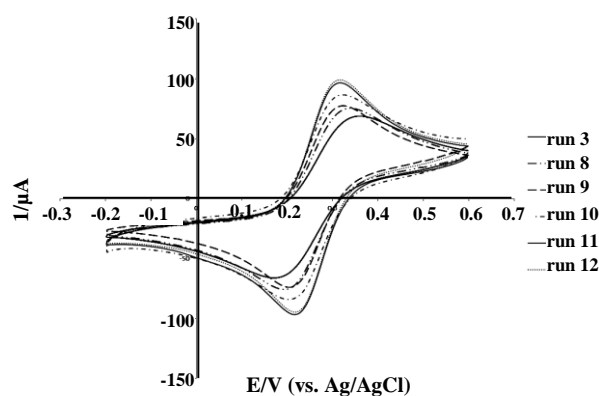
In order to investigate the surface area, pore size and pore size distribution of the synthesized materials, the results of the N_2 adsorption/desorption were discussed. As shown in Fig. 3, the N_2 adsorption/desorption isotherm of GMC and S-GMC composite belongs to type

Table 1: obtained parameters in order to synthesize of graphitic mesoporous carbon.

Prepared material	ratio of nano-CaCO ₃ sucrose (gram/gram)	Amount of added nickel nitrate (gram)	Amount of prepared mesoporous carbon (gram)	I _{p c} (μA)	I _{p a} (μA)	ΔE _p (mV)
Run 1	5/2	-	0.10	65.1	56.0	130.5
Run 2	4.5/2.5	-	0.18	63.1	59.0	145.6
Run 3	4/3	-	0.35	62.6	55.7	185.5
Run 4	3.5/3.5	-	0.44	54.8	48.9	185.7
Run 5	3/4	-	0.53	51.2	41.1	173.6
Run 6	2.5/4.5	-	0.61	43.8	37.9	235.5
Run 7	2/5	-	0.69	16.9	14.3	355.7
Run 8	4/3	0.10	0.35	72.9	66.7	145.5
Run 9	4/3	0.50	0.33	74.0	73.1	123.3
Run 10	4/3	1.00	0.33	84.1	83.5	122.1
Run 11	4/3	1.50	0.30	91.6	89.4	100.5
Run 12	4/3	2.00	0.30	92.5	90.1	100.4

**Fig. 1: Comparison of cyclic voltammery curves of prepared carbon paste electrodes obtained by different ratio of nano- CaCO₃ and sucrose.**

IV profiles, which indicates the mesoporous nature of the prepared materials [37]. According to BET method, the specific surface areas (S_{BET}) of GMC and S- GMC composite are estimated to be 710 m²/g and 15 m²/g, respectively; which indicates that much of the GMC pores are filled with sulfur. However, space with magnitude of 15m²/g remains within the pores of final nano-composite, which is suitable for the intended applications of the project. Also utilizing BJH method [35] the average pore size of GMC and S- GMC estimated as 2.7nm and 2.8nm respectively.

**Fig. 2: Comparison of cyclic voltammery curves of prepared carbon paste electrodes obtained by different amount of nickel nitrate as graphitization catalyst.**

In Fig. 4 SEM images of GMC and S-GMC were compared. It can be seen that particle size of both materials is about 2 micrometers that means particles sizes have not been changed in the process of preparation of composite. In order to determine the presence of sulfur in S-GMC composite, SEM images of sulfur and composite with different magnification depicted in Fig. 4. It can be seen that there is no accumulation of sulfur. It can be concluded that in S-GMC composite preparation process during heating at 300 °C, surface sulfur has been desorbed and just the sulfur which has been absorbed within the pores of the GMC is not desorbed.

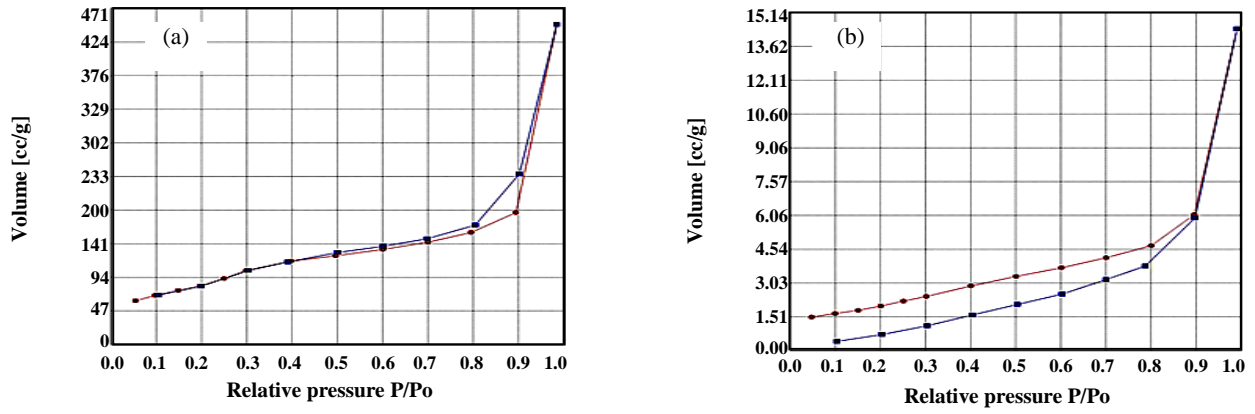


Fig. 3: N_2 adsorption- desorption isotherms (a) GMC (b) S-GMC composite.

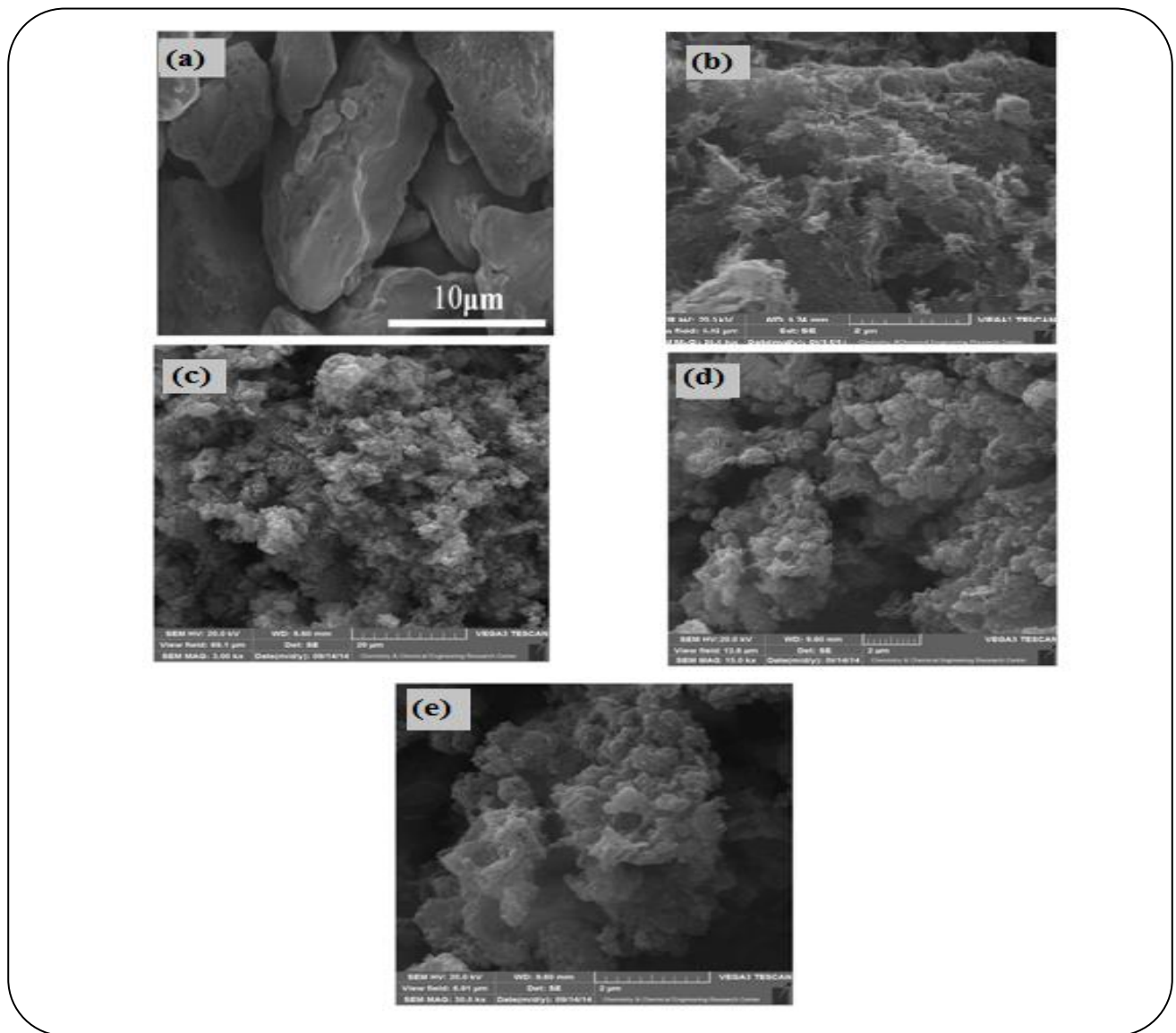


Fig. 4: SEM images of (a) elemental sulfur (b) GMC, (c), (d), (e) S-GMC composite with different magnification.

X-Ray Diffraction (XRD) analysis

X-ray diffraction is a very useful way to examine graphitization degree of graphitic carbon materials. Wide-angle XRD patterns of the obtained GMC, S-GMC and sulfur are shown in Fig. 5. As can be seen in Fig. 5a, X-ray diffraction spectra of GMC shows 3 diffraction peaks in $2\theta=26.2, 44.3, 54.8$, which can be attributed to the (002), (100) and (004) planes of graphitic structures [38, 39]. A literature survey showed that existence of all three peaks in carbon materials represents a high graphitization degree in the desired material [38, 39]. The results indicate successful synthesis of graphitic mesoporous carbon. The XRD pattern of S-GMC composite is identified in Fig. 5b. Due to the fact that the X-ray diffraction spectra of sulfur (Fig.5c) has numerous peaks in 2θ range between 20 to 70 and the subject that the dominant component of the obtained composite is sulfur (about 52%), the XRD pattern of S-GMC is logical.

It shall be mentioned, filling the pores of a nanostructured material reduces the intensity and sharpness of X-ray diffraction peaks, nevertheless the 0 0 2 diffraction peak of the composite can be seen in the Fig. 5b.

cyclic voltammetry

In order to investigate the electrochemical behavior of prepared carbon paste electrodes, the Cyclic Voltammetry (CV) at the surface of GMC/CPE, S-GMC/CPE, S/CPE electrodes were performed in 1mM $K_3 [Fe (CN)_6]$ / 0.1 M KCl solution with a scan rate of 100 mV/s and the obtained results are shown in Fig. 6 and Table 2.

As shown in the figure and the table, anodic and cathodic electrochemical response currents at GMC/CPE are larger in comparison with S-GMC/CPE. Regarding to filling of GMC pores with sulfur particles and a decrease in the surface area, the current decline seems logical. Electrodes made from a mixture of sulfur - Graphite in comparison with electrodes made from S-GMC composite and GMC, with a significant decline, show a current about $35\mu A$ for reduction and oxidation peaks. The results show the significance of porosity and graphitization in the GMC. Furthermore, the peak separation between the potential of anodic and cathodic peaks is 101mV and 110mV for GMC/CPE and S-GMC/CPE, respectively; while peak separation for S/CPE is 407 mV. The very high distance of peaks in S/CPE is due to very low electrical conductivity of sulfur,

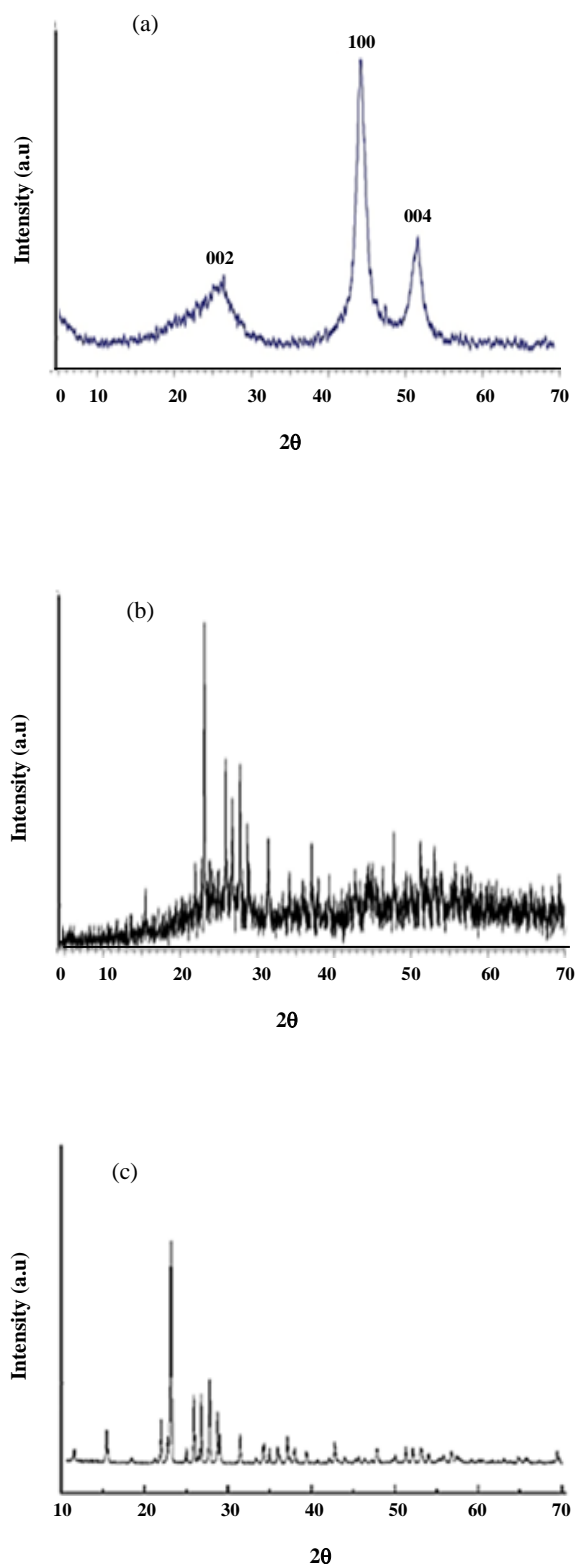


Fig. 5: XRD patterns of a) GMC b) S-GMC c) elemental sulfur.

Table 2: comparison of peak current of prepared electrodes.

electrode	Anodic peak current(μA)	Cathodic peak current(μA)	Anodic & cathodic peak separation(mV)
S/CPE	35.14	34.81	407
GMC/CPE	89.34	91.2	101
S-GMC/CPE	78.5	78.9	110

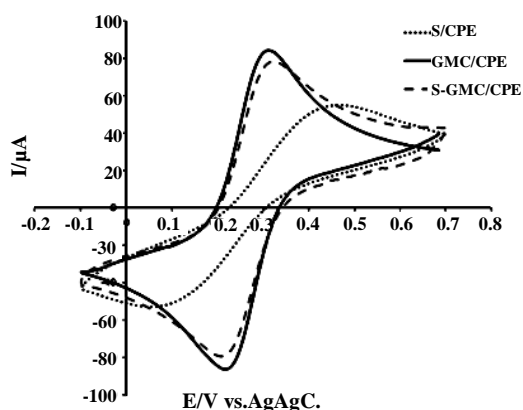


Fig. 6: Cyclic voltammetry curves of prepared carbon paste electrodes.

which caused carbon paste electrodes constructed from sulfur to have low electrical conductivity and the distance of oxidation and reduction peak to increase. Similar peak separation of electrodes made from S-GMC and sulfur composite indicates that the electrical conductivity of two materials is very close. The results suggest that the addition of insulation sulfur into the pores of the S-GMC material didn't decrease electrical conductivity significantly, so it can be concluded that nanocomposite of sulfur-graphitic mesoporous carbon with improved electrical conductivity successfully was synthesized.

CONCLUSIONS

In this study, synthesis and characterization of a novel nanocomposite based on sulfur and graphitic mesoporous carbon was reported. GMC with high electrical conductivity was synthesized using nano calcium carbonate as hard template, sucrose as a carbon precursor and nickel nitrate as graphitization catalyst. The result of XRD analysis confirmed the high graphitization degree of synthesized material. Also, N_2 adsorption/desorption analysis showed that average pore size of GMC is about 2.7nm. Hence it can be concluded that the synthesized graphitic mesoporous carbon belongs to mesoporous

group of nanoporous materials. SEM studies showed that particle size of synthesized GMC is about 2 micrometers. GMC with large particle and appropriate pore sizes and high electrical conductivity was used for fabrication of sulfur nanocomposite. S-GMC composite was prepared by penetration of sulfur to GMC pores. For this purpose, sulfur was melted at 150°C and infiltrated to the pores of the GMC due to capillary forces and was absorbed to the surface. SEM and BET studies showed that sulfur is well distributed in the vast areas of GMC material. Also there are no degradation and changes in the structure of GMC during this process. The cyclic voltammetry data showed that the electrical conductivity of S-GMC composite is far higher than the elemental sulfur. Therefore the desired nanocomposite with improved electrical conductivity successfully has been fabricated.

Received : Nov. 23, 2015 ; Accepted : May 18, 2016

REFERENCES

- [1] Cheng X-B., Huang J-Q., Zhang Q., Peng H-J., Zhao M-Q, Wei F., Aligned Carbon Nanotube/Sulfur Composite Cathodes with High Sulfur Content for Lithium-Sulfur Batteries, *Nano Energy*, **4**:65-72 (2014).
- [2] Guo J., Xu Y., Wang C., Sulfur-Impregnated Disordered Carbon Nanotubes Cathode for Lithium-Sulfur Batteries, *Nano. Lett.*, **11**:4288-4294 (2011).
- [3] Ma G., Wen Z., Jin J., Lu Y., Rui K., Wu X., Wu M., Zhang J., Enhanced Performance of Lithium Sulfur Battery with Polypyrrole Warped Mesoporous Carbon/Sulfur Composite, *J. Power Sources.*, **254**: 353-359 (2014).
- [4] Liang X., Wen Z., Liu Y., Zhang H., Huang L., Jin J., Highly Dispersed Sulfur in Ordered Mesoporous Carbon Sphere as A Composite Cathode for Rechargeable Polymer Li/S Battery, *J. Power Sources.*, **196**(7): 3655-3658 (2011).

- [5] Sohn H., Gordin M. L., Xu T., Chen S., Lv D., Song J., Manivannan A., D. Wang, Porous Spherical Carbon/Sulfur Nanocomposites by Aerosol Assisted Synthesis: The Effect of Pore Structure and Morphology on Their Electrochemical Performance As Lithium/Sulfur Battery Cathodes, *ACS Appl Mater Interfaces.*, **6**(10): 7596-606 (2014).
- [6] Fedorková A., Oriňáková R., Čech O., Sedlaříková M., New Composite Cathode Materials for Li/S Batteries: A Review, *Int. J. Electrochem. Sci.*, **8**: 10308-10319 (2013).
- [7] Choi H., Zhao X., Kim D-S., Ahn H-J., Kim K-W., Cho K-K., Ahn J-H., A Mesoporous Carbon-Sulfur Composite as Cathode Material for High Rate Lithium Sulfur Batteries, *Mater. Res. Bull.*, **58**: 199-203 (2014).
- [8] Schuster J., He G., Mandlmeier B., Yim T., Lee K. T., Bein T., Nazar L. F., Spherical Ordered Mesoporous Carbon Nanoparticles with High Porosity for Lithium-Sulfur Batteries, *Angew. Chem. Int. Ed.*, **51**: 3591(2012).
- [9] Xu T., Song J., Gordin M. L., Sohn H., Yu Z., Chen S., Wang D., Mesoporous Carbon-Carbon Nanotube-Sulfur Composite Microspheres for High-Areal-Capacity Lithium-Sulfur Battery Cathodes, *ACS Appl. Mater. Interfaces.*, **5** (21): 11355-11362 (2013).
- [10] Jin J., Wen Z., , Ma G., Lu Y., Rui K., Mesoporous Carbon/Sulfur Composite with Polyaniline Coating for Lithium Sulfur Batteries, *Solid State Ionics*, **262**: 170-173(2014).
- [11] Zhang W., Qiao D., Pan J., Cao Y., Yang H., Ai X., A Li⁺-Conductive Microporous Carbon-Sulfur Composite for Li-S Batteries, *Electrochim. Acta.*, **87**: 497-502 (2013).
- [12] Zhang B., Qin X., Li G.R., Gao X.P., Enhancement of Long Stability of Sulfur Cathode by Encapsulating Sulfur Into Micropores of Carbon Spheres, *Energy Environ. Sci.*, **3**(10): 1531-1537 (2010).
- [13] Dörfler S., Hagen M., Althues H., Tu'bkke J., Kaskel S., Hoffmann M.J., High Capacity Vertical Aligned Carbon Nanotube/Sulfur Composite Cathodes for Lithium-Sulfur Batteries, *Chem. Commun.*, **48**(34): 4097-4099 (2012).
- [14] Jin K., Zhou X., Zhang L., Xin X., Wang G., Liu Z., Sulfur/Carbon Nanotube Composite Film as a Flexible Cathode for Lithium-Sulfur Batteries, *J. Phys. Chem. C*, **117**(41): 21112-21119 (2013).
- [15] Ahn W., Kim K. B., Jung K. N., Shin K. H., Jin C. S., Synthesis and Electrochemical Properties of a Sulfur-Multi Walled Carbon Nanotubes Composite as A Cathode Material for Lithium Sulfur Batteries, *J. Power Sources*, **202**: 394- (2012).
- [16] Yuan Z., Peng H-J., Huang J-Q., Liu X-Y., Wang D-W., Cheng X-B. , Zhang Q., Hierarchical Free-Standing Carbon-Nanotube Paper Electrodes with Ultrahigh Sulfur-Loading for Lithium-Sulfur Batteries, *Adv. Funct. Mater.*, **24**(39): 6105-6112 (2014).
- [17] Gao X., Li J., Guan D., Yuan C., A Scalable Graphene Sulfur Composite Synthesis for Rechargeable Lithium Batteries with Good Capacity and Excellent Columbic Efficiency, *ACS Appl. Mater. Interfaces*, **6** (6):4154-4159 (2014).
- [18] Zhang Y., Zhao Y. , Bakenov Z., A Novel Lithium/Sulfur Battery Based on Sulfur/Graphene Nanosheet Composite Cathode and Gel Polymer Electrolyte, *Nanoscale. Res. Lett.* , **9**: 137- (2014).
- [19] Jayaprakash N., Shen J., Moganty S. S., Corona A., Archer L. A., Porous Hollow Carbon@Sulfur Composites for High-Power Lithium-Sulfur Batteries, *Angewandte. Chemie. International. Edition.*, **50**(26): 5904-5908 (2011).
- [20] Zhang K., Zhao Q., Tao Z., Chen J., Composite of Sulfur Impregnated in Porous Hollow Carbon Spheres as the Cathode of Li-S Batteries with High Performance, *Nano. Res.*, **6**(1): 38-46 (2013).
- [21] Zheng J., Yan P., Gu M., Wagner M.J., Hays K. A., Chen J., Li X., Wang C., Zhang J-G., Liu J. , Xiao J., Interfacial Reaction Dependent Performance of Hollow Carbon Nanosphere-Sulfur Composite as a Cathode for Li-S Battery , *Front. Energy. Res.*, **3**(25): 1-8 (2015).
- [22] Liu L-L, Tian S., Zhu Y-S., Tang W., Li L-L. , Wu Y-P., Nanoporous Carbon as Anode Material of High Rate Capability for Lithium Ion Batteries, *J. Chin. Chem. Soc.*, **59**(10): 1216-1219(2012).

- [23] Srinivasu P., Islam A., Singh S.P., Han L., Kantam M.L., Bhargava S.K., [Highly Efficient Nanoporous Graphitic Carbon with Tunable Textural Properties for Dye-Sensitized Solar Cells](#), *J. Mater. Chem.*, **39**(22): 20866-20869 (2012).
- [24] Xia Y., Yang Z., Mokaya R., [Templated Nanoscale Porous Carbons](#), *Nanosci.*, **2**: 639–659(2010).
- [25] Ma T., Liu L., Yuan Z. Y., [Direct Synthesis of Ordered Mesoporous Carbons](#), *Chem. Soc. Rev.*, **42**(9):3977-4003(2013)
- [26] Wu X., Hong X., Luo Z., Hui K.S., Chen H., Wu J., Hui K.N., Li L., Nan J., Zhang Q., [The Effects of Surface Modification on the Supercapacitive Behaviors of Novel Mesoporous Carbon Derived from Rod-Like Hydroxyapatite Template](#), *Electrochim. Acta*, **89**: 400-406 (2013).
- [27] Gierszal K. P., Jaroniec M., [Carbons with Extremely Large Volume of Uniform Mesopores Synthesized by Carbonization of Phenolic Resin Film Formed on Colloidal Silica Template](#), *J. Am. Chem. Soc.*, **128**(31): 10026-10027 (2006).
- [28] Delahaye E., Escax V., Hassan N. El., Davidson A., Aquino R., Dupuis V., Perzynski R., Raikher YL., [Nanocasting: Using SBA-15 Silicas as Hard Templates to Obtain Ultrasmall Monodispersed Gamma-Fe₂O₃ Nanoparticles](#), *J. Phys. Chem. B.*, **110**(51): 26001-26011 (2006).
- [29] Ying F., Wang S., Au C-T., Lai S-Y., [Highly Active and Stable Mesoporous Au/CeO₂ Catalysts Prepared from MCM-48 Hard-Template](#), *Microporous Mesoporous Mater.*, **142**(1): 308–315(2011).
- [30] Petkovich N.D., Stein A., [Controlling Macro- and Mesostructures with Hierarchical Porosity Through Combined Hard and Soft Templating](#), *Chem. Soc. Rev.*, **42**: 3721-3739 (2013).
- [31] Yang G., Han H., Li T., Du C., [Synthesis of Nitrogen-Doped Porous Graphitic Carbons Using Nano-CaCO₃ as Template, Graphitization Catalyst, and Activating Agent](#), *Carbon*, **50**: 3753-3765 (2012).
- [32] Sevilla M., Fuertes A. B., [Catalytic Graphitization of Templated Mesoporous Carbons](#), *Carbon*, **44**: 468-474 (2006).
- [33] Jiang L., Yan J., Hao L., Xue R., Sun G., Yi B., [High Rate Performance Activated Carbons Prepared from Ginkgo Shells for Electrochemical Supercapacitors](#), *Carbon*, **56**: 146-154 (2013).
- [34] Brauner S., Emmet P.H., Teller E., [Adsorption of Gases in Multimolecular Layers](#), *J. Am. Chem. Soc.*, **60**: 309–319(1938).
- [35] Barrett E.P., Joyner L.G., Halenda P.P., [The Determination of Pore Volume and Area Distributions in Porous Substances. I. Computations from Nitrogen Isotherms](#), *J. Am. Chem. Soc.* **73**(1): 373–380(1951).
- [36] Zhou G., Wang D-W., Li F., Hou P-X., Yin L., Liu C., Lu G.Q.(M.), Gentlec I.R., Cheng H-M., [A Flexible Nanostructured Sulphur–Carbon Nanotube Cathode with High Rate Performance for Li-S Batteries](#), *Energy Environ. Sci.*, **5**: 8901(2012).
- [37] Chai, G.S., Shin I.S., Yu J.S., [Synthesis of Ordered, Uniform, Macroporous Carbons with Mesoporous Walls Templated by Aggregates of Polystyrene Spheres and Silica Particles for Use as Catalyst Supports in Direct Methanol Fuel Cells](#), *Adv. Mater.*, **16**(22): 2057-2061(2004).
- [38] Kicinski W., Bystrzejewski M., Mummeli M. H., GEmming T., [Porous Graphitic Materials Obtained from Carbonization of Organic Xerogels Doped with Transition Metal Salts](#), *Bull. Mater. Sci.*, **37**(1): 141-150 (2014).
- [39] Joshi S., Shrestha L. K., Kamachi Y., Malgras V., Pradhananga M. A., Pokhrel B. P., Raja T.N., Pradhananga R. Ariga, K., Yamauchi Y., [Synthesis and Characterizations of Nanoporous Carbon Derived from Lapsi \(Choerospondias Axillaris\) Seed: Effect of Carbonization Conditions](#), *Adv. Powder. Tech.*, **26**(3): 894-900 (2015).