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Novel chemical synthesis of sulfur thin film for supercapacitor application

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Abstract
Binder less and additive free sulfur thin film is prepared at room temperature (300 K) first time in literature from simple chemical route. The X-ray diffraction (XRD) study analyzed formation of crystalline orthorhombic sulfur. Scanning electron microscopy (SEM) revealed micro-spheres composed surface morphology. Supercapacitive properties of sulfur thin film are analyzed through cyclic voltammetry (CV) and galvanostatic charge-discharge techniques. Large potential window of 0 to +1.6 V is achieved for sulfur electrode in neutral 1 M $LiClO_4$-propylene carbonate ($LiClO_4$-PC) electrolyte. The highest specific capacitance and specific energy of 25 Fg^{-1} and 0.48 $Whkg^{-1}$ is achieved, respectively at 5 mVs^{-1} scan rate. After 600 consecutive CV cycles of sulfur, 90 % capacitance is retained in PC-$LiClO_4$. An electrochemical impedance measurement shows supercapacitive behavior of sulfur.
Keywords: Sulfur, Thin film, Supercapacitor, Cyclic voltammetry, Chemical bath deposition.

Introduction
Burning issue of whole world is harvesting pollution free and high efficient renewable energy and preserving it for a long term. Since renewable energies are accessible in interval, energy storage has become necessary thing. Distinct energy storage systems available for separate purpose, as battery deliver high energy density at low power density rate and conventional capacitor possesses low energy density with very high power density [1]. Supercapacitors alternately known by ultracapacitors or electrochemical capacitors, have been attracting researchers as exceptional energy storage device. It is gifted with high energy density than capacitor and high power density than battery [1-4]. Supercapacitors are predominantly sorted as electrochemical double layer capacitors (EDLCs) and pseudocapacitors from energy storage principles. In EDLCs, energy storage is sustained with electrostatic charge accumulation at the interface of electrode and electrolyte forming Helmholtz double layer [1]. EDLCs prepared from carbon derivatives, capable of great electrochemical cycling stability (above 100,000 charge discharge cycles) owing to no net charge transfer between electrolyte and electrode during charging-discharging cycles [5]. Pseudocapacitor at the other side works with reversible fast redox transitions at the electrode surface [1]. Multiple oxidation states of electrode accountable for reversible redox activities in pseudocapacitor. RuO_2, [6] CuO [7], Co_3O_4 [8] etc. metal oxides, polymers such as polyaniline [9] metal sulfide like MoS_2 [10] are pseudocapacitive electrodes utilized in the past. Nowadays, many research groups are attracted towards novel electrode synthesis for supercapacitor application such as metal sulfide or ternary metal sulfides other than routine metal oxide electrodes.

Sulfur is environment friendly, abundant (10^{th} most common element in the universe), cheap earth element and can be recognized as a good candidate for supercapacitor due to high theoretical energy density (2500 $Whkg^{-1}$) [11]. Multiple oxidation states of sulfur (+6, 5, 4, 3, 2, 1, -1 and -2) are useful for reversible redox response for energy storage. However, from broad literature survey through literature, sulfur thin film preparation is carried out using binders such as carboxy methyl cellulose. No report is found with binder less sulfur thin film preparation and its application in supercapacitor [15]. Contrary sulfur electrode has been investigated extensively for battery application [12-14]. Present article reports preparation of binder less, additive free sulfur film using cost-effective chemical bath deposition (CBD) method first time in literature. Moreover, sulfur film is analyzed for structural and morphological study and examined for supercapacitive application in 1 M PC-$LiClO_4$.

Experimental
Sulfur thin film is prepared from solution growth method. Analytical reagent (AR) grade sodium sulfide (Na_2S) and ammonium per sulfate (APS) ($(NH_4)_2S_2O_8$) chemicals were purchased from SD fine chemicals Ltd. and used without purification. Na_2S was well dissolved in double distilled water (DDW) under constant stirring for 5 min. Then, APS was added to oxidize sulfur (S^{2-}) ions in the solution for maintained pH at about 3. Well cleaned stainless steel substrate was mounted vertically in reaction bath at 300 K temperature for 48 h. A mass of 1.7 mg of sulfur was deposited on 1 cm^2 area of stainless steel substrate. As deposited sulfur film was further studied for structural and morphological analyses.

Crystal structure of sulfur film was determined from x-ray diffractometer using Cu K_α (λ= 1.54 A^0) radiation. IR

spectrum of sulfur was obtained using ALPHA 100508 model. Surface microstructure of sulfur film is scanned through SEM model of JEOL-JSM-6360. Wettability nature of film with $LiClO_4$-PC electrolyte was examined from contact angle measurement using Rame-hart model. Supercapacitive properties were tested using 8 channels battery cycler (Wonatech WBCS-3000 model). Cyclic voltammetry and galvanostatic charge-discharge analyses of sulfur were performed in 1 M $LiClO_4$-PC electrolyte system with conventional three electrode system, which consists of sulfur film as a working, platinum as a counter and saturated calomel as standard reference electrodes. The electrochemical impedance measurement of sulfur electrode was performed using electrochemical work station (ZIVE SP5) within frequency range of 100 kHz to 100 mHz**.**

Results and discussion

Thin film formation and reaction mechanism

Thin film formation in CBD method takes place via controlled precipitation operation. When ionic product in saturated solution exceeds solubility product, precipitate is established in the solution [16]. The precipitate formation in the solution is highly controlled from various reaction parameters such as time of deposition, temperature etc. Homogeneous precipitation occurs in bulk of solution competes with heterogeneous precipitation, and on exceeding rate of later precipitation guides to thin film formation on solid surface in contact with solution. Nucleation, aggregation and coalescence are the fundamental molecular level actions are taken place while growing thin film [16]. In present work, APS is used as an oxidizing agent for S^{2-} ions in the well dissolved Na_2S solution in DDW. S^{2-} ions in the solution are oxidized to form sulfur precipitate. At the optimized concentrations of APS and Na_2S, faint yellow colored sulfur thin film were formed at 300 K on the stainless steel substrate. The possible reaction mechanism for the formation of sulfur thin film is given below.

$$Na_2S+(NH_4)_2S_2O_8 \longrightarrow S + Na_2SO_4+ NH_3+ NaOH \quad (1)$$

Schematic to form sulfur thin film is prepared in **Figure 1**.

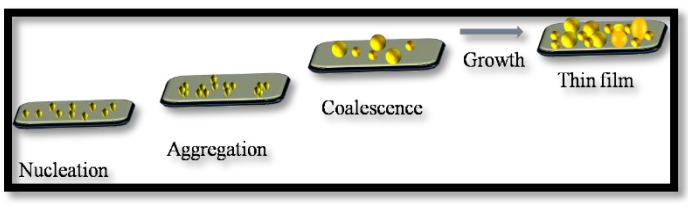

Figure 1:The Schematic of different steps (a), (b), (c), (d) and (e) involved to grow sulfur film in chemical bath deposition method.

Morphological study

Surface texture of sulfur film is examined from SEM technique. Since charge storage in supercapacitor is surface phenomenon, surface morphology of electrode play a vital role. Surface area of thin film has more electrochemical active sites, as compared with bulk material; moreover, pores present on thin film surface provide more active sites for redox interactions [12]. **Figure 2**(A) and (B) discloses the surface microstructure of sulfur thin film at 2,000X and 10,000X magnifications respectively. Microspheres of 1 to 5 µm diameter size observed on the surface of film, moreover the small pits and valleys on the each spheres also contributes to enhance effective surface of material. Such type of surface morphology of electrode is useful for supercapacitor application, since electrolyte ions easily reach to pits and valleys on micro-spheres that enhances redox activity at the surface of sulfur electrode.

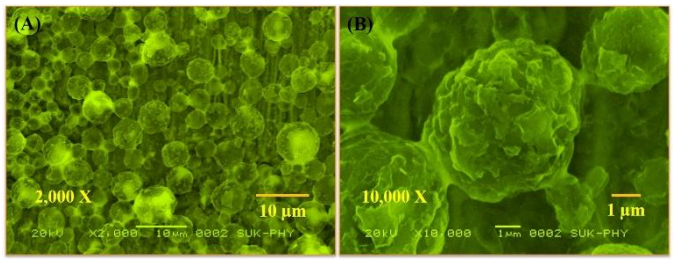

Figure 2: SEM images of sulfur film at two magnifications of (A) 2,000X (B) 10,000X.

Structural study

XRD pattern in **Figure 3**(A) shows well resolved peaks in the region 2θ = 200 to 300 that shows single phase crystalline orthorhombic crystal structure of elemental sulfur matched with JCPDS card no.00-008-0248 without any impurity peaks [11, 14]. It is observed from Fig. 3(A) that most of the sulfur crystals have grown along (101) plane and intensity signifies good crystallinity of sample. Average crystallite size (D) of particles along (101) plane is 23.7 nm calculated using Sherrer formula as below.

$$D = \frac{0.9\,\lambda}{\beta\,Cos\theta} \quad (2)$$

where, D is the diameter of crystalline particle, β is the full width half maximum (FWHM) of intense peak, θ is the angle of diffraction, λ is the wavelength of Cu Kα X- ray.

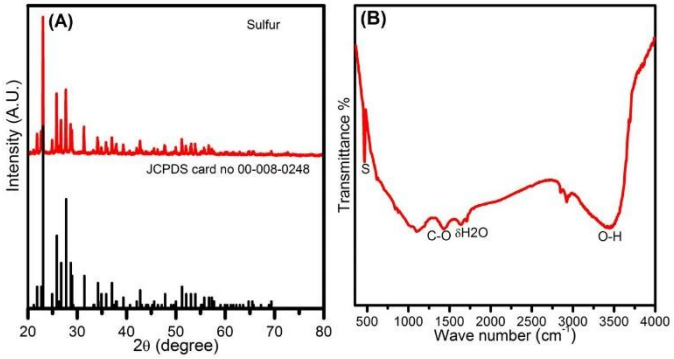

Figure 3:(A)XRD pattern of sulfur film matching with JCPDS card no. 00-008-0248 and (B)IR spectrum of sulfur.

Infrared (IR) study

Figure 3(B) displays IR spectrum of sulfur powder peeled out from thin film deposited at 300 K temperature. Sharp peak at

463 cm^{-1} confirms formation of sulfur. The broad peak at 3430 cm^{-1} is associated with -OH bonding from water content in sample. Moreover small band at 1441 cm^{-1} indicate presence of carbonate bond may be due to exposure of sample to atmosphere. 1628 cm^{-1} wave number corresponds to bending vibration mode of water molecule.

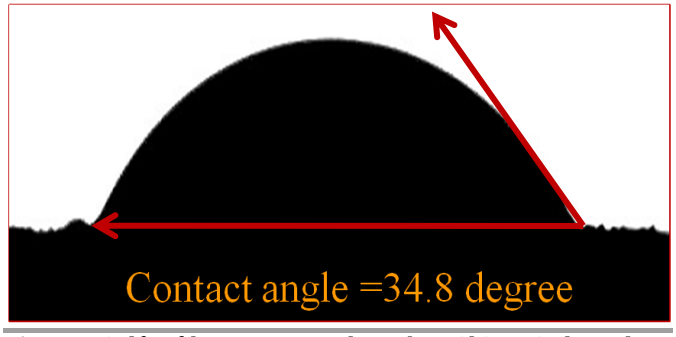

Figure4: Sulfur film contact angle with $LiClO_4$-PC electrolyte.

Wettability study

Wettability test is performed to investigate the interaction between sulfur electrode and $LiClO_4$-PC electrolyte at room temperature. Acute contact angle (34.8^0) shown in **Figure 4**. between sulfur electrode and electrolyte indicates hydrophilic nature of $LiClO_4$-PC with sulfur thin film. Hydrophilic nature helps electrolyte to make intimate contact with electrode surface and therefore extra number of electrolyte ion reaches to electrochemical active sites and maximum electrode material is utilized for energy storage operation. Hydrophilic nature of electrolyte facilitates Li^+ ions to reach at electro-active sites at electrode surface and consequently enhances capacitance.

Cyclic voltammetry (CV) study

As prepared sulfur film is considered as sulfur electrode. Supercapacitive test of sulfur electrode is explored from CV and galvanostatic charge-discharge analyses in 1 M $LiClO_4$-PC electrolyte using three electrodes system. CV technique is employed to acquire specific capacitance and capacitive retention of sulfur thin film in an optimized positive potential window of 0 to +1.6 V/SCE at various scan rates.

Sulfur electrode is employed for different scan rates from 5 to 100 mVs^{-1} in CV analysis to test rate capability. **Figure 5**(A) presents capacitive behavior of sulfur, as nature of all CV curve is maintained almost overlapping for all scan rates. Increasing scan rate of CV curves enhances oxidation and reduction peak currents towards negative and positive directions, respectively, implying capacitive behaviour of sulfur [13, 17, 18]. **Figure 5** (B) shows decrease in capacitance at higher scan rates of material attributes to the less utilization of electrochemical active sites present on electrode surface [18]. Maximum specific capacitance obtained at lower scan rate indicates the maximum utilization of material. Proposed reaction mechanism of intercalation/de-intercalation of electrolyte ions is as follows.

$$xLi^+ + xe^- + S \quad \underset{}{\overset{}{\longleftrightarrow}} \quad Li_xS \qquad (3)$$

The highest specific and interfacial capacitances of sulfur are calculated as 25.16 Fg^{-1} and 0.04276 Fcm^{-2} respectively at 5 mVs^{-1} scan rate. Capacitance (C), specific capacitance (C_s) and interfacial capacitance (C_i) of electrode are calculated using following expressions [19], respectively.

$$C = \frac{I}{dV/dt}, \quad C_S = \frac{C}{m}, \quad C_i = \frac{C}{A} \quad (4)$$

where, dV/dt is scan rate, m is mass of deposited active material, A is area of thin film dipped in electrolyte.

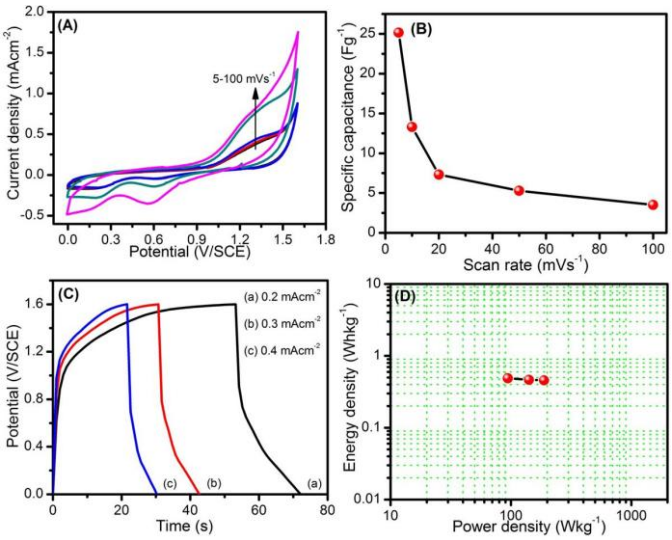

Figure 5: (A) Cyclic voltammetry (CV) curves of sulfur at different scan rates ranging from 5 to 100 mVs^{-1} between 0 to +1.6 V potential window in 1 M $LiClO_4$-PC, (B) Specific capacitance versus scan rate curve, (C) Galvano-static charge discharge curves for 0.2, 0.3 and 0.4 $mAcm^{-2}$ constant current densities and (D) Ragone plot of sulfur.

Galvanostatic charge-discharge study

Figure 5(C) displays galvanostatic asymmetric charge-discharge profile of sulfur electrode at 0.2, 0.3 and 0.4 $mAcm^{-2}$ constant current densities in 1 M $LiClO_4$-PC electrolyte. Discharge curve consist of initial IR drop raised, is combination of ionic resistance of electrolyte, intrinsic resistance of electrode and contact resistance between electrode and current collector. Non-linear portion in discharge curve suggests pseudocapacitive contribution of sulfur [18], which strongly supports to the observed CV plots. The maximum energy density of 0.48 $Whkg^{-1}$ obtained for 0.2 $mAcm^{-2}$ current density at the power density of 188.23 Wkg^{-1}. The energy power density of sulfur electrode are obtained from following expressions [16].

$$E = \frac{0.5 \times C_s \times (V_{max}^2 - V_{min}^2)}{3.6}, P = \frac{E \times 3600}{T_d} \quad (5)$$

where, T_d is discharging time, $V_{max}$and V_{min} are maximum and minimum potentials during galvanostatic charge discharge.

Figure 5(D) is a Ragone plot of sulfur relating its energy and power densities. Values obtained in plot sits midway between values for capacitor and battery materials. Hence the sulfur thin film can be considered for supercapacitor application.

This is our first attempt towards low temperature synthesis of binder free sulfur thin film. Although C_s and E values of sulfur electrode deposited by CBD method are poor in comparison with other supercapacitive material such as MoO_3 [20], values can be increased by making composite of sulfur with polymer or carbon derivatives. Polymers (Polyaniline

and polypyrrole: ~1×10^{-10} Sm^{-1}) [21] are more conducting than sulfur (1x10^{-14} Sm^{-1}) and carbon derivatives offers high surface area (1654 m^2g^{-1}) [22] for charge accumulation. However, large potential window of sulfur in $LiClO_4$-PC electrolyte is useful to motivate energy density of sulfur, since potential window of electrode contributes major part in energy density calculation, since square of potential term raised in calculating capacitance of material (1).

Electrochemical stability study

Long term working capability of electro active sulfur electrode is assessed for 600 CV cycles at 100 mVs^{-1} scan rate. The gradual inflation in capacitance is observed at the beginning cycles which, is associated with increase in the exposure of electro active material up to 300 cycles. Thereafter, capacitance reduces due to the loss of active material in an electrolyte solution during redox activities take place at the electrode surface [23]. Sulfur thin film demonstrates 90 % capacitive retention as shown in **Figure 6** (A) for 600 CV cycles. Inset of the Fig.6 (A) CV plots are displayed at 100 mVs^{-1} scan rate of 1st, 300th, 500th and 600th cycles. It retains peak positions of oxidation and reductions even after 600 cycling, reflecting good reversible redox response of sulfur electrode in $LiClO_4$-PC electrolyte.

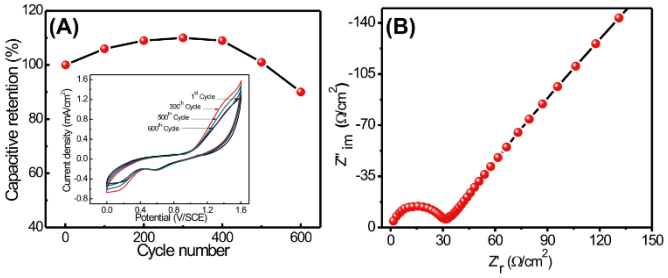

Figure 6: (A) Capacitive retention curves of sulfur electrode for 600 CV cycles. Inset shows CV curves of electrode for 1st, 300th, 500th and 600th CV cycles at 100 mVs^{-1} scan rate, and (B) Nyquist plot of sulfur electrode.

Electrochemical impedance spectroscopy (EIS)

The ion transfer properties of electrode and electrolyte system are scrutinized with electrochemical impedance technique. Nyquist plot of the sulfur in 1 M $LiClO_4$-PC electrolyte is obtained using three electrodes system in 100 kHz to 100 mHz frequency range at 10 mV ac amplitude. Nyquist plot is the graph of an imaginary and real part of impedance. First intercept on the real axis in **Figure 6**(B) attributes to the equivalent series resistance (R_s) of 1.95 Ωcm^{-2}, that consist of ionic resistance of electrolyte, intrinsic resistance of electrode and contact resistance between current collector and electrode [18, 19]. Semicircle present in the higher frequency region represents charge transfer resistance (R_{ct}) of 29.55 Ωcm^{-2}, which reflects electrochemical reactions occurs at the electrode surface. Rct is known as faraday resistance as well [24, 25]. Lower frequency response of electrode explores Warburg resistance. The straight line inclined near 45° with real impedance axis in lower frequency region indicates supercapacitive nature of electrode.

Conclusions

Sulfur thin film is prepared from simple chemical route for first time. Good crystallinity of pure sulfur secured in XRD pattern without any secondary phase at low temperature (300 K). Electrochemical analysis of sulfur thin film is tested in non-aqueous 1 M $LiClO_4$-PC electrolyte provided high operating potential window of 1.6 V/SCE. 600 CV cycles of sulfur are performed with 90 % capacitive retention. Highest energy and power densities are obtained from galvanostatic charge-discharge profile are 0.48 $Whkg^{-1}$ and 188.23 $Wkg^{-1,}$ respectively. We conclude that chemically synthesized sulfur thin film can be considered as the good candidate for supercapacitor application in non-aqueous $LiClO_4$-PC electrolyte.

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[1] B.E. Conway. "Electrochemical Supercapacitors, Scientific Fundamentals and Technological Applications", Kluwer Academic/Plenum Press, New York, 1999.

[2] G.S. Gund, D.P. Dubal, S.S. Shinde, C.D. Lokhande. "Architectured morphologies of chemically prepared NiO/MWCNTs nanohybrid thin films for high performance supercapacitors", ACS Appl Mater Interfaces, vol. 6, pp. 3176-3788, 2014.

[3] T. Zhao, H. Jiang, J. Ma. "Surfactant-assisted electrochemical deposition of α-cobalt hydroxide for supercapacitors", J Power Sources, vol. 196, pp. 860-864, 2011.

[4] B. Ming, J. Li, F. Kang, G. Pang, Y. Zhang, L. Chen, J. Xu, X. Wang. "Microwave-hydrothermal synthesis of birnessite-type MnO_2 nanospheres as supercapacitor electrode materials",J Power Sources,vol. 198, pp. 428-431, 2012.

[5] L. Li, E. Liu, J. Li, Y. Yang, H. Shen, Z. Huang, X. Xiang, W. Li. "A doped activated carbon prepared from polyaniline for high performance supercapacitors", J Power Sources, vol. 195, pp. 1516-1521, 2010.

[6] T.P. Gujar, V.R. Shinde, C.D. Lokhande, W.Y. Kim, K.D. Jung, O.S. Joo. "Spray deposited amorphous RuO2 for an effective use in electrochemical supercapacitor", ElectrochemCommun, vol. 9, pp. 504-510, 2007.

[7] D.P. Dubal, W.B. Kim, C.D. Lokhande. "Galvanostatically deposited Fe: MnO2 electrodes for supercapacitor application", J PhysChem Solids, vol. 73, pp. 18-21, 2012.

[8] S.G. Kandalkar, J.L. Gunjakar, C.D. Lokhande. "Preparation of cobalt oxide thin films and its use in supercapacitor application", Appl Surf Sci, vol. 254, pp. 5540-5544, 2008.

[9] S. Giri, D. Ghosh, C. Das. "In situ synthesis of cobalt doped polyaniline modified graphene composites for high performance supercapacitor electrode materials", J ElectroanalChem, vol. 697, pp. 32-45, 2013.

[10] K. Huang, L. Wang, Y. Liu, Y. Liu, H. Wang, T. Gan, L. Wang. "Layered MoS2–graphene composites for supercapacitor applications with enhanced capacitive performance", Int J Hydrogen Energ, vol. 38, pp. 14027-14034, 2013.

[11] X. Cui, Z. Shan, L. Cui, J. Tian."Enhanced electrochemical performance of sulfur/carbon nanocomposite material prepared via chemical deposition with a vacuum soaking step",ElectrochimActa,vol. 105, pp. 23-30, 2013.

[12] Y. Sun, S. Wang, H. Cheng, Y. Dai, J. Yu, J. Wu."Synthesis of a ternary polyaniline@acetylene black-sulfur material by continuous two-step liquid phase for lithium sulfur batteries", ElectrochimActa,vol. 158, pp. 143, 2015.

[13] H. Zhao, Z. Peng, W. Wang, X. Chen, J. Fang, J. Xu."Reduced graphene oxide with ultrahigh conductivity as carbon coating layer for high performance sulfur@reduced graphene oxide cathode", J Power Sources,vol. 245, pp. 529, 2014.

[14] S. Chen, J. Zhu, Q. Han, Z. Zheng, Y. Yang, X. Wang."Shape-Controlled Synthesis of One-Dimensional MnO2 via a Facile Quick-Precipitation Procedure and its Electrochemical Properties",Cryst Growth Des,vol. 9, pp. 4356-4361, 2009.

[15] Y. Su and A. Manthiram."A facile in situ sulfur deposition route to obtain carbon-wrapped sulfur composite cathodes for lithium–sulfur batteries", ElectrochimActa, vol. 77,pp. 272-278, 2012.

[16] N.R. Chodankar, D.P. Dubal, G.S. Gund, C.D. Lokhande. "Flexible all-solid-state MnO_2 thin films based symmetric supercapacitors", Electrochim Acta,vol. 165, pp. 338-347, 2015.

[17] R. Elazari, G. Salitra, A. Garsuch, A. Panchenko, D. Aurbach."Sulfur-impregnated activated carbon fiber cloth as a binder-free cathode for rechargeable Li-S batteries", Adv Mater, vol. 23, pp. 5641-5644, 2011.

[18] S.B. Kulkarni, A.D. Jagadale, V.S. Kumbhar, R.N. Bulakhe, S.S. Joshi, C.D. Lokhande."Potentiodynamic deposition of composition influenced Co1−xNix LDHs thin film electrode for redox supercapacitors", Int J Hydrogen Energ,vol. 38,pp. 4046-4053, 2013.

[19] V.S. Kumbhar, A.D. Jagadale, C.D. Lokhande."Supercapacitive evaluation of soft chemically deposited α-Sm_2S_3 thin films", J Power Sources,vol. 234,pp. 107-110, 2013.

[20] DOI: 10.1007/s10854-015-4160-3.

[21] G. Ning, Z. Fan, G. Wang, J. Gao, W. Qianc, F. Wei."Gram-scale synthesis of nanomesh graphene with high surface area and its application in supercapacitor electrodes", ChemCommun, vol. 47,pp. 5976-5978, 2011.

[22] H.S. Abdulla, A.I. Abbo. "Optical and electrical properties of thin films of polyanilineand polypyrrole", Int J ElectrochemSci, vol. 7,pp. 10666-10668, 2012.

[23] F. Tao, Y. Zhao, G. Zhang, H. Li."Electrochemical characterization on cobalt sulfide for electrochemical supercapacitors", ElectrochimCommun, vol. 9, pp. 1282-1287, 2007.

[24] S. Bao, C. Li, C. Guo, Y. Qiao."Biomolecule-assisted synthesis of cobalt sulfide nanowires for application in supercapacitors", J Power Sources, vol. 180, pp. 676-681, 2008.

[25] Y. Zhang, J. Li, F. Kang, F. Gao, X. Wang."Fabrication and electrochemical characterization of two-dimensional ordered nano-porous manganese oxide for supercapacitor applications", Int J Hydrogen Energ,vol. 37,pp. 860-866, 2012.