

Review

New Composite Cathode Materials for Li/S Batteries: A Review

Andrea Fedorková^{1,2,*}, Renáta Oriňáková¹, Ondřej Čech², Marie Sedlářková²

¹Department of Physical Chemistry, Faculty of Science, P.J. Šafárik University, Moyzesova 11, SK–04154 Košice, Slovak Republic

²Department of Electrical and Electronic Technology, Faculty of Electrical Engineering and Communication, Brno University of Technology, Technická 10, Brno 616 00, Czech Republic

*E-mail: andrea.fedorkova@upjs.sk

Received: 6 June 2013 / Accepted: 4 July 2013 / Published: 1 August 2013

This paper reviews the state-of-art of composite cathode materials for the applications in lithium/sulfur (Li/S) batteries. An attempt is made to highlight those key issues in previous work that have stimulated further research toward practical application of Li/S batteries. Detailed information on the advanced developments on carbon and polymer composite cathodes are presented. Their implementation holds the greatest promise in a number of applications ranging from portable electronics to electric vehicles. Fundamental scientific advances in understanding the reactions occurring in the cells as well as new materials are key to overcoming all the drawbacks related to Li/S batteries. In this review article we focus on some of the recent achievements in boosting the cyclability, power density and performance of Li/S batteries through the development of new cathode composite materials.

Keywords: Lithium-sulfur, polymer, carbon, MWNCTs, batteries

1. INTRODUCTION

The lithium-sulfur (Li/S) battery is a “conversion” type battery, because the electrochemical reactions which take place during charging and discharging of the battery result in new chemical compounds [1-3]. By contrast, lithium-ion batteries operate in accordance with the “insertion” principle. This means that lithium ions occupy spaces in the crystal structure of the cathode, without substantially changing the structure of the cathode material. The new Li/S batteries can hold up to three times more energy than current lithium ion batteries, yet it is made with safer and efficient processes that use very little energy, demand no solvents and produce almost no waste. A new technique mixes lithium, sulfur and carbon nanotubes to make a new conductive electrode. Li/S battery

is attractive for its highest theoretical specific capacity of 1675 mAh/g and high theoretical specific energy of 2600 Wh/kg. Comparison of different cathode materials is shown in Table 1. Drawbacks of Li/S are the low operating voltage of around 2.15 V during discharge, the isolating property of both sulfur and Li₂S, the volume change of approximately 79% based on full transformation of sulfur to Li₂S and a polysulfide (PS) shuttle mechanism first described by Mikhaylik et al. [4].

Table 1. Specific capacity of various cathode materials.

Cathode material	Specific capacity (mAh/g)	Cell voltage (V)	Specific energy (Wh/kg)
LiFePO ₄	140	3.3	578
LiCoO ₂	160	3.7	580
LiMn ₂ O ₄	130	3.9	592
S	1670	2.1	2600

The reaction between lithium and sulfur can be written as:



with the reactions being driven in the reverse direction during charge. Each sulfur atom will accept 2 electrons when fully reacted, immediately doubling the capacity compared to an element that only uses 1 electron. This, when combined with the low atomic mass of sulfur, is why the Li/S battery has the second highest theoretical specific energy of all Li battery chemistries only beaten by the related lithium-air (Li-O₂) battery [1]. Sulfur naturally forms ring shaped molecules of 8 sulfur atoms, meaning that the reaction at least should be written as:



although this equation still manages to hide one of the largest sources of problems for Li/S cells: the polysulfides. The reduction of S₈ to S₈²⁻ goes through a whole zoo of intermediate polysulfide species (Li₂S_n, 2 < n < 8) [5-8]. These reductions occur at different voltages and usually result in two reduction peaks in a cyclic voltammetry (CV) trace, instead of one peak as for simpler systems. The nature of these reactions changes with solvent, electrolyte salt and electrode materials.

Sulfur and its reduction products are non-conductive and they have a relatively low gravity density (2.07 g/cm³ for α-sulfur and 1.66 g/cm³ for Li₂S). In most cases, a large amount of conductive carbon should be mixed with sulfur to obtain the necessary electronic conductivity for the cell's operation. To retain the advantage of sulfur's high energy density, the cathode is required to have a sulfur content of at least 70% by weight and a reasonable sulfur loading of equaling to a specific capacity of 2-3 mAh/cm². Reduction from elemental sulfur to Li₂S leads to a volumetric increase by 79.2%. Therefore, high porosity is required for the conductive carbon to accommodate the increased volume. While high content of the conductive carbon favors increasing the specific capacity and capacity retention of sulfur, it reduces the cell's energy density. In many cases, functional groups on the carbon surface are helpful for increasing the chemical adsorption of PS anions from the PS solution

[9-13]. A variety of strategies have been developed to form sulfur composites with favorable structures and properties to improve the discharge capacity, cyclability, and Coulombic efficiency [1]. Other approaches being pursued include novel cell configurations with trapping interlayers, Li/dissolved polysulfide cells, and efficient electrolytes [14-16].

The main efforts to improve the electrochemical performances of Li/S batteries have been on the development of carbon-based sulfur composites. An ideal carbon matrix for sulphur-carbon composites needs to have (i) high electrical conductivity, (ii) electrochemical affinity for sulfur, (iii) small cells (pores) without large outlets to accommodate polysulfides, (iv) accessibility of liquid electrolyte to active material, and (v) stable framework to sustain the strain generated by the volume changes of the active material during cycling [17].

2. SULFUR-CARBON COMPOSITE ELECTRODES

The extremely low electronic conductivity of sulfur represents the major drawback which makes it impossible to reach the full theoretical potential of lithium-sulfur batteries. The sulfur cathode loses capacity upon cycling and lacks in rate capability, if not properly prepared. To overcome these challenges, many efforts have been dedicated. Carbonaceous materials with high porosity to “wire” and contain the sulfur and good electrical conductivity are the best choice to overcome these challenges and improve cycle life of lithium/sulfur batteries. The carbon matrix serves as an electron transport network and provides reaction sites for sulfur.

During the past decades, various sulfur-carbon composites have been designed using carbon black [18] acetylene black or activated carbons [19-21]. In particular, the application of activated carbon in the form of fibers woven into a cloth as a microporous host for sulfur by Aurbach's group should be noted [21]. A sulfur-impregnated carbon fiber cloth was examined as the binder-free cathode material.

Conducting carbon additives especially carbon with porous structure, were found to significantly enhance the electrical conductivity and effectively prevents the dissolution of lithium polysulfide into the electrolyte during cycling [21-27]. However, most of the previously reported composites have only shown improvements in low rate capability ($< C/2$) and cyclability [28]. Furthermore, the structural changes of the interparticle network were suggested to cause the degradation of sulfur/carbon composite cathodes [29]. The carbon-sulfur cathodes were generally synthesized by the filling of carbon pores with molten sulfur or sulfur-containing liquids. However, the fully filled pores inhibit the fast infiltration of lithium ions and electrolyte as well as increase the cathode polarization and thereby lower the power performance of sulfur cathodes [30].

The synthesis of highly ordered nanostructured polymer-modified mesoporous carbon-sulfur interwoven composites was investigated by Ji et al. [31]. The growth of sulfur nanofiller was strictly steered into the channels of the mesoporous carbon framework. The sulfur fibres had a similar diameter to that of the channels of the mesoporous carbon (3.3 nm), and a comparable diameter to the carbon nanorods that enclose them (6-7 nm). It was possible to infiltrate 70 wt% sulfur. The retaining conductive carbon framework generated electrical contact to the insulating sulfur encapsulated within

and also acted as a minielectrochemical reaction chamber. Moreover, the polymer coating on the carbon surface hindered diffusion of polysulphide out of the electrode, thus inhibited the reduction of the active mass in the cathode and enhanced the cycling stability. The composite materials can supply reversible capacities up to 1320 mAh/g.

The unique spherical ordered mesoporous carbon (OMC) nanoparticles with extremely high bimodal porosities were studied as a sulfur host by Nazar et al. [32]. The spherical mesoporous carbon nanoparticles of 300 nm in diameter with the same pore distribution were obtained in a two-step casting process. The nanoscale morphology of these materials allowed very efficient exploitation of the sulfur content. The C/S spherical electrodes showed a high reversible charge capacity of up to 1200 mAh/g and good cycling stability even at high cycling rates (1 C). The electrodes maintained a high and relatively stable discharge capacity of 850 mA h g⁻¹ at the 100th cycle.

Another promising host materials are porous hollow carbons. A facile, template-based approach for synthesizing mesoporous hollow carbon capsules and vapor phase infusion of elemental sulfur into the carbon framework was reported by Archer et al. [33]. The hollow carbon spheres exhibited a porous outer shell with small 3 nm pores and a large interior cavity around ~200 nm. They were able to hold 70 wt % sulfur and deliver the initial capacity as high as 1071 mAh/g. These materials demonstrated good electrochemical stability and promising electrochemical behavior upon extended cycling for 100 cycles at 850 mA g⁻¹ (0.5 C).

An *in situ* approach of synthesizing lithium sulfide-carbon (Li₂S@C) nanocomposites as cathode materials combined with high-capacity anodes other than metallic lithium was reported recently by Yang et al. [34]. As the precursor for Li₂S@C composites was used a lithium sulfate. A mesoporous, partially graphitic carbon matrix provided a scaffold for sequestration of sulfur and lithium polysulfides and enhanced the electrical conductivity of the cathode. The homogeneous distribution of lithium sulfide in the carbon host promoted the effective inhibition of polysulfide shuttling, advanced the cycling stability and electrochemical properties. An additional improvements in cycling stability and efficiency of the Li₂S@C composite anodes was achieved by using the electrolyte contained a lithium polysulfide as additives.

The effect of the electrode morphology on the electrochemical performance of a lithium-sulfur battery was shown by Kim et al. [35]. The electrochemical behavior of two cells with different sulfur-carbon composite cathodes was compared. The electrode consisting of an hard carbon spherules matrix with a high surface area and a very small pore size into which sulfur can be easily incorporated was obtained by improving the procedure reported by Archer and co-workers [36]. This particular morphology of the hard carbon spherules-sulfur electrode (HCS-S) assures a high tap density. An excellent electrochemical response was demonstrated by employing a stable and highly conducting electrolyte and a composite cathode with well-controlled spherical and compact morphology containing a 52 wt% sulfur. This battery can cycle at high rates with a specific capacity of the order of 750 mAh g⁻¹ and an average voltage of 2 V with excellent retention during cycling. The battery has an excellent electrochemical performance also at low temperature, delivering a capacity of 500 mAh g⁻¹ at 0 ° C for over 170 charge-discharge cycles.

In spite of improvements attained, the uniform distribution of sulfur in the composite is lost during cycling. The cathodes suffered from inhomogeneous contact between the active material and

the electronic conductors, resulting in decreased utilization and poor cycle life time. Moreover, in the electrodes containing porous carbons is overall energy density decreased due to the high carbon content the addition of binders [37]. The higher integrity retention of the conductive framework and thereby the more stable capacities during cycling could be achieved using carbon nanotubes (CNTs) as additives in the slurry. CNTs were found to be superior support materials to prepare sulfur/carbon composites owing to their high aspect ratio and the high intrinsic conductivity [38-44].

The template-directed growth of CNTs with an anodic aluminum oxide (AAO) template has been studied for a long time [45]. The synthesis of sulfur-impregnated disordered carbon nanotubes (DCNTs) by a template wetting technique from polyaniline deposited in an AAO membranes was reported by Wang et al. [46]. A new method of sulfur impregnation into carbon nanotubes was investigated. Through a vapor infusion method was sulfur incorporated into graphitic clusters and smaller voids/defects in amorphous carbon structures. The sulfur-impregnated DCNTs displayed great cycling stability. Moreover, the Coulombic efficiency was improved with increased heating temperature, indicating a new stabilization mechanism of sulfur in carbon induced by heat treatment. The Coulombic efficiencies of SDCNTs cathodes at 0.25C rate were averagely at 89% and 96% during 100 cycles for SDCNT heat treated at 300°C, and 500°C, respectively.

The synthesis of carbon nanotubes containing elemental sulfur (S-CNTs) using a sulphate-containing AAO template was reported by Zhou et al. [30]. The preparation method integrated the template directed chemical vapour deposition of carbon, carbothermal reduction of sulphate and ethanol evaporation-induced assembly. The developed binder-free, highly conductive and flexible nanostructured membrane was used as a self-supporting metal current-collector-free cathode for Li/S batteries. This membrane cathode demonstrated a high electrical conductivity, a long life of sulfur of over 100 charge–discharge cycles due to sulfur confined in the walls of the nanotubes and a high rate performance due to greatly improved cathode kinetics. The high discharge capacities of sulfur at a high current density were attained at 712 mA h g⁻¹ and 520 mA h g⁻¹ and overall capacities of the membrane electrodes reached 163 mA h g⁻¹ and 260 mA h g⁻¹ for the cathodes with 23 wt.% S and 50 wt.% S, respectively. Moreover, because sulfur is confined in the walls of the nanotubes, dissolution of polysulphides is restricted, which gives the material good cyclability. This S-CNT cathode material and its assembly are potentially adaptable for fast, durable and flexible Li/S batteries.

A new approach to exploit the full potential of Li–S batteries in terms of energy density based on binder free vertical aligned (VA) CNT/sulfur composite electrodes was reported by S. Dörfler et al. [37]. In contrast to slurry-based electrodes, vertical-aligned carbon nanotube/sulfur composite electrodes can be directly synthesized using chemical vapor deposition (CVD) on a Ni current collector based on a process developed by Hata et al. [47]. The CNT growth was performed at 730°C using ethene as carbon precursor. Infiltration of elemental sulfur was achieved from sulfur solutions in toluene. The CNT film with the thickness of up to 100–200 nm serves as a stabilizing, conducting framework for the sulfur cathodes. The composite electrodes with high sulfur loadings up to 70 wt% were reported to deliver stable discharge capacities of over 1300 mAh/g (related to sulfur mass) and of over 800 mAh/g (in terms of composite electrode mass) upon 20 cycles. Further, the different methods of sulfur infiltration and cycle tests with several electrolytes (liquid organic, ionic liquid and solid) were performed [48]. The homogenous sulfur coating was obtained by solvent sulfurization with a

heated CNTs cathode or by melting of solid sulfur powder on the CNTs electrode. The sulfur ratio of approximately 90% and much higher loads of sulfur per cm^2 electrode than in slurry made electrodes was obtained. The surface capacity of around 5.5 mAh cm^{-2} was achieved with liquid organic electrolytes, which is now twice as high as in high-energy lithium-ion batteries or regular sulfur electrodes.

By the same authors was recently introduced a binder free thick film electrode based on CNTs, coated on a conductive carbon structure with very high sulfur loads ($3\text{-}20 \text{ mg cm}^{-2}$ electrode) [49]. The sulfur infiltration was performed by melting of sulfur powder. The dependence of achieved capacities on the sulfur load and applied current was observed. The discharge capacity between 800 and 900 mAh/g sulfur were reached at 0.64 mA cm^{-2} . The electrochemical results indicated that the obtained capacities can be stable for 100 cycles and more if short circuit during charging through lithium dendrites are inhibited.

Fabrication of novel graphene/single-walled carbon nanotube (G/SWCNT) hybrid by a direct growth through an one-step high-temperature (over 950°C) CVD of methane on layered double hydroxide (LDH) was reported by Zhao et al. [50]. A high electrical 3D conductive net was constructed by the SWCNTs and the graphene, as well as by the robust connection between them, which ensured the fabrication of conductive agent-free G/SWCNT-S electrodes. The internal spaces between the two stacked graphene layers and among SWCNTs offer room for sulfur storage. The G/SWCNT-S nanocomposites were fabricated following a typical melt-diffusion strategy. The as obtained G/SWCNT-S nanocomposite cathode exhibited excellent rate performance. A capacity of 650 mAh/g can be preserved after 100 cycles even at a high current rate of 5 C.

The multiwalled carbon nanotubes (MWCNTs) in a Li/S cell are useful carbon materials for the dispersion and stabilization of sulfur nanoparticles and might provide a more effective electronically conductive network than the traditional conductive additives and an encapsulation effect for sulfur due to their 1D porous structure [51,52]. It was reported, that the use of MWCNTs instead of acetylene black in the cathode can increase not only rate capability but also the cycle life of the sulfur electrode [42]. Different methods for the preparation of sulfur - MWCNTs (S/MWCNTs) composites were reported, e.g. heat treatment [44, 53], ball-milling [39, 54] and solvent exchange [37, 41, 55].

A well-dispersed S/MWCNTs composite was simply synthesized via direct precipitation method by Ahn et al. [56]. Precipitated sulfur was deposited on the surface and infiltrated into the large pore of MWCNTs by oxidation of sodium polysulfide in the presence of MWCNTs. The S/MWCNTs composite material showed a high initial sulfur utilization with specific capacity up to 1355 mAh g^{-1} but the fairly rapid decrease in capacity was observed over 30 cycles with only 63% capacity retention. These results indicated rather limited effect of MWCNTs on soluble polysulfides retention.

A similar procedure for the preparation of S/MWCNT composite through direct precipitation of sulfur nanoparticles in the MWCNTs was reported by Geng et al. [57]. A conventional S/MWCNT composite prepared by ball-milling was also studied for comparison. The sulfur content in both composite was equivalent, 58.3 wt% and 61.7 wt% for the precipitated S/MWCNTs and ball-milling S/MWCNTs. The homogeneous dispersion of precipitated sulfur nanoparticles within the MWCNTs resulted in better electrochemical performance, good cyclic stability and rate performance than the ball-milling S/MWCNTs. The initial discharge capacities as high as 1299 mAhg^{-1} and 839 mAhg^{-1}

were delivered at 0.02 C for the precipitated S/MWCNTs and ball-milling S/MWCNTs, respectively. The capacity remains 800 mAhg^{-1} for the precipitated S/MWCNTs but only 620 mAhg^{-1} for ball-milling S/MWCNTs at 0.05 C after 50 cycles. The precipitated S/MWCNT composite displays a discharge capacity of 1128 mAhg^{-1} at 0.05 C, which remains 800 mAh g^{-1} after 50 cycles. The ball-milling S/MWCNT cathode displays a discharge capacity of 663 mAhg^{-1} at 0.05 C.

The production of a robust, flexible self-weaving S/MWCNTs composite cathode by a scalable in situ sulfur deposition method and a vacuum filtration process was reported by Su [28]. The formation of binder/current collector-free electrode was enabled owing to the self-weaving behaviour of the MWCNTs when being fabricated as a flexible film. The highly conductive MWCNTs supplied numerous electrical and ionic pathways during the electrochemical reaction and enhanced the active material utilization at high rates. Moreover, the good electrolyte-absorption ability of the cathode framework localizes the electrolyte and suppresses the migration of soluble polysulfides. The developed composite cathode with 60 wt% MWCNTs maintained capacities as high as 1352 mAh/g and 1012 mAh/g at 1C rate and 4C rate, respectively and extraordinarily high-rate cyclability. After 100 cycles, the S/MWCNTs cathode exhibited a reversible capacity of 915 mAh/g at 1C rate.

The preparation of sulfur cathodes for Li/S batteries by ball milling method with the Super-P and MWCNTs as conductive agents was reported by Zhao et al. [58]. The influence of ball milling time and type of binders (poly(ethylene oxide) and poly(vinylidene fluoride)) on the electrochemical properties of Li/- batteries was evaluated. For the sulfur cathode with MWCNTs, the ball milling time of 1 h was appropriate to get homogenous dispersion. The sulfur cathode with MWCNTs generated an initial discharge capacity of 944 mAh/g and a discharge capacity of 300 mAh/g after 20 cycles. For the sulfur cathode with Super-P a lower initial capacity of 794 mAh/g , but a higher capacity of 350 mAh/g after 20 cycles was obtained.

The design and preparation of sulfur-coated MWCNTs composite material (S-coated-MWCNTs) through capillarity between the sulfur and MWCNTs was reported by Yuan et al. [39]. A dense sulfur cathode with well-distributed morphology was expected to admit the mechanical stress caused by volume change due to the charge–discharge cycles. The purified MWCNTs were mixed with the elemental sulfur by mechanical ball milling and then sealed in a PTFE container filled with argon gas and heated at $155 \text{ }^\circ\text{C}$ for 24 h to prepare the S-coated-MWCNTs. The S-coated-MWCNTs have a typical core-shell structure with the MWCNTs cores dispersed individually into the sulfur matrices. When the composite contained 80 wt.% sulfur, its shell thickness was about 30 nm. The electrochemical performance of the composite cathode was compared with a sulfur-coated carbon black composite and a sulfur cathode with simple MWCNTs addition (S/MWCNTs). The S coated-MWCNTs cathode exhibited a reversible capacity of 670 mAh g^{-1} after 60 cycles, showing a greatly improved cycle ability as compared with the other two types of sulfur cathodes. The homogeneous distribution of the MWCNTs in the composite cathode was recognized as the main key factor to the improvement in the electrochemical performance and cycle life of the sulfur cathode.

The reported CNT/S composite electrodes indicate that the utilization of sulfur as a cathode material is improved during the charge–discharge process in particular due to its homogeneous dispersion within carbonaceous framework, but more improvements are still needed at the cathode. The containment of polysulfides is critical to increase cycle life and minimize capacity fading.

3. SULFUR-POLYMER COMPOSITE ELECTRODES

Conducting polymers such as polyaniline (PANI), polypyrrole (PPy), polythiophene (PTh) are very interesting materials for using in Li/S batteries. Polymer modification of the carbon surface facilitates a more complete reaction by providing a chemical gradient that retards diffusion of the polysulfides into the electrolyte. Reversible capacities up to 1320 mAh/g are attained with no shuttle phenomenon on the first cycle, indicating the shuttle mechanism is fully suppressed. This polymer modified composite clearly exhibits better morphological control than the unmodified composite during cycling [31].

Polyethylene glycol coated onto sulfur provides a chemical gradient that retards diffusion of polysulfides out of the electrodes [26,31]. One monolayer of polymer is not enough to fully trap polysulfides. In order to confine polysulfides more effectively, the surface coating layer should be rigid and stable, but not too rigid to break during the expansion of sulfur upon cycling. Moreover, it needs to be both ionically and electronically conductive. Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) is a good choice based on these criteria, as it is stable and moderately rigid in the electrochemical environment [59]. Zhang *et al.* [60] introduced a novel polymer, polyaniline polysulfide (SPAN), which can hold more sulfur in the polymer than the others. The polymer has polyaniline as the backbone chain and 2 four-member rings with S-S bonds as the side chains of aniline. From the structure, it is predicted that the polymer can store high energy when it is used in Li/S battery. The result of Li/S battery with SPAN showed high initial discharge capacity of 980 mAh/g and a stable reversible capacity of 403 mAh/g after 20 cycles.

In the other research group, Ma *et al.* [61] developed polyaniline/sulfur composite cathode, which was synthesized by situ polymerization. The aniline was polymerized to form a layer of polyaniline on the sulfur surface. The results showed that the composites reached 1134 mAh/g at the first cycle, which is relatively low compared to the results from the other polymers containing sulfur. The capacity remained 526.9 mAh/g after 30 cycles.

As one alternatively resolved method, the cathode materials can be well combined with electrical and ionic conducting agent, such as the electro-polymerized conductive polyaniline (PANI) and polypyrrole (PPy), which would improve the battery's rechargeability [62-69].

Conductive PPy coating on the surface of the sulfur can improve the conductivity of S-PPy electrode. At the same time, PPy can also act as a binder, increasing the contact between particles [70]. The capacity of the S-PPy composite electrode is higher than that of the pure S electrode. This may be due to the presence of polypyrrole, which acts not only as a conducting additive but also as an active material contributing to capacity of the electrode during cycling [71,72] PPy nanoparticles coated onto the surface of S powder may also absorb polysulphide due to their porous surface morphology [73] and reduce the dissolution of the polysulphide into the electrolyte. Consequently, the sulfur utilization and cyclic durability were improved [20,65].

Yang *et al.* [74] have demonstrated that conductive polymer PEDOT:PSS coating on the surface of mesoporous carbon/sulfur particles could be used to effectively trap polysulfides and minimize the dissolution of polysulfides and the loss of active mass in cathodes, which leads to a notable improvement of the performance of Li_S batteries. The initial discharge capacity reached 1140 mAh/g, which is ~10% higher than that of the bare counterpart. Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) is a good choice for lithium-sulfur battery, as it is stable and

moderately rigid in the electrochemical environment [75,76]. PEDOT:PSS is also reported to be thermally stable at 85 °C for over 1000 h with minimal change on electrical conductivity [77].

Group of Duan et al. [78] investigated a novel conductive PANI and Ppy coated sulfur composite as cathode materials in lithium–sulfur batteries fabricated by a facile and controllable layer-by-layer assembly technique combined with crosslinking and heating treatment. The as-prepared sulfur shells possess a low permeability, which is permeable for very small molecular weight of Li^+ and slowly or hardly for sulfur and polysulfide during charge and discharge process. The high electric conductivity of sulfur composite materials further provides a well electron conducting paths for the rechargeability of lithium–sulfur battery.

Another strategy to improve the capacity and cyclability of Li/S batteries is the electrolyte optimization so as to reduce the loss of sulfur by dissolution in the liquid electrolyte [79-83]. Among the possible electrolyte modifications, replacement of the common liquid organic electrolytes with polymer electrolytes has proved promising and efficient.

4. CONCLUSIONS

A storage system based on lithium/sulfur might be the most promising candidate for the next generation lithium batteries. Li/S battery has a theoretical capacity of 1672 mAh/g and a theoretical energy density of 2600 Wh/kg, which is about five times higher than that of the $\text{LiCoO}_2/\text{graphite}$ and LiFePO_4/C systems. Additionally, sulfur is abundant in various minerals, cheap and environmental friendly. Significant improvements have been realized in the past decade with Li/S batteries, but challenges still remain. The electrical insulating nature of sulfur and the high solubility of lithium polysulfides as intermediate products generated during the discharge process in traditional organic electrolyte have resulted in very poor cycle life. Development of novel nanocomposite materials with smart engineering design combined with new anode materials, electrolytes and cell configurations will have a significant impact in the field. Promising results have been achieved by modifying the cathode in the Li/S battery with carbon or polymer coating. Also evenly distributing sulfur in the composite cathode material consisting of conductive matrix, enhancing the cyclability and performance of the composite cathode, and stabilizing the retention of polysulfides. Along with the use of silicon instead of metal lithium anode and solid polymer electrolyte will lead to the employment of sulfur based cathode batteries in the commercial world.

ACKNOWLEDGEMENT

The authors wish to acknowledge financial support from the Grant Agency of the Ministry of Education of the Slovak Republic, Grant No. 1/0211/12, Center of Research and Utilization of Renewable Energy Sources, No. CZ.1.05/2.1.00/01.0014, and project CZ.1.07/2.3.00/30.0039 of Brno University of Technology.

References

1. P. G. Bruce, S.A. Freunberger, L. J. Hardwick, J. M. Tarascon, *Nat. Mater.*, 11 (2012) 19.
2. X. Ji, L. F. Nazar, *J. Mater. Chem.*, 20 (2010) 9821.
3. D. Aurbach, E. Pollak, R. Elazari, G. Salitra, *J. Electrochem. Soc.*, 156 (2009) A694.

4. Y. V. Mikhaylik, J. R. Akridge, *J. Electrochem. Soc.*, 151 (2004) A1969.
5. J. Shim, K. A. Striebel, E. J. Cairns, *J. Electrochem. Soc.*, 149 (2002) A1321.
6. W. Zheng, X. G. Hu, C. F. Zhang, *Electrochem. Solid State Lett.*, 9 (2006) A364.
7. B. H. Jeon, J. H. Yeon, K. M. Kim, I. J. Chung, *J. Power Sources*, 109 (2002) 89.
8. X. Yu, J. Xie, J. Yang, K. Wang, *J. Power Sources*, 132 (2004) 181.
9. V. Jourdain, O. Stephan, M. Castignolles, A. Loiseau, P. Bernier, *Adv. Mater.*, 16 (2004) 447.
10. S. B. Fagan, R. Mota, A. J. R. Da Silva, A. Fazzio, *Nano Lett.*, 4 (2004) 975.
11. M. Holzinger, O. Vostrowsky, A. Hirsch, F. Hennrich, M. Kappes, R. Weiss, F. Jellen, *Angew. Chem. Int. Edit.*, 40 (2001) 4002.
12. J. K. Lim, W. S. Yun, M. H. Yoon, S. K. Lee, C. H. Kim, K. Kim, S. K. Kim, *Synthetic Met.*, 139 (2003) 521.
13. J. J. Stephenson, A. K. Sadana, A. L. Higginbotham, J. M. Tour, *Chem Mater.*, 18 (2006) 4658.
14. Y. S. Su, A. Manthiram, *Chem. Commun.*, 48 (2012) 8817.
15. S. S. Zhang, J. A. Read, *J. Power Sources*, 200 (2012) 77.
16. J. Hassoun, B. Scrosati, *Adv. Mater.*, 22 (2010) 5198.
17. A. Manthiram, Y. Fu, Y. S. Su, *Acc. Chem. Res.*, 46 (2013) 1125.
18. J. Shim, K. A. Striebel, E. J. Cairns, *J. Electrochem. Soc.*, 149 (2002) A1321.
19. J. Wang, L. Liu, Z. Ling, J. Yang, C. Wan, C. Jiang, *Electrochim. Acta*, 48 (2003) 1861.
20. J. L. Wang, J. Yang, J. Y. Xie, N. X. Xu, Y. Li, *Electrochem. Commun.*, 4 (2002) 499.
21. R. Elazari, G. Salitra, A. Garsuch, A. Panchenko, D. Aurbach, *Adv. Mater.*, 23 (2011) 5641.
22. Y. L. Cao, X. L. Li, I. A. Aksay, J. Lemmon, Z. M. Nie, Z. G. Yang, J. Liu, *Phys. Chem. Chem. Phys.*, 13 (2011) 7660.
23. C. Lai, X. P. Gao, B. Zhang, T. Y. Yan, Z. Zhou, *J. Phys. Chem. C*, 113 (2009) 4712.
24. S. C. Wei, H. Zhang, Y. Q. Huang, W. K. Wang, Y. Z. Xia, Z. B. Yu, *Energy Environ. Sci.*, 4 (2011) 736.
25. X. Liang, Z. Wen, Y. Liu, H. Zhang, L. Huang, J. Jin, *J. Power Sources*, 196 (2011) 3655.
26. H. L. Wang, Y. Yang, Y. Y. Liang, J. T. Robinson, Y. G. Li, A. Jackson, Y. Cui, H. J. Dai, *Nano Lett.*, 11 (2011) 2644.
27. G. Zheng, Y. Yang, J. J. Cha, S. S. Hong, Y. Cui, *Nano Lett.*, 11 (2011) 4462.
28. Y. S. Su, Y. Fu, A. Manthiram, *Phys. Chem. Chem. Phys.*, 14 (2012) 14495.
29. B. H. Jeon, J. H. Yeon, K. M. Kim, I. J. Chung, *J. Power Sources*, 109 (2002) 89.
30. G. Zhou, D. W. Wang, F. Li, P. X. Hou, L. Yin, C. Liu, G. Qing (Max) Lu, I. R. Gentle, H. M. Cheng, *Energy Environ. Sci.*, 5 (2012) 8901.
31. X. Ji, K. T. Lee, L. F. Nazar, *Nat. Mater.*, 8 (2009) 500.
32. J. Schuster, G. He, B. Mandlmeier, T. Yim, K. T. Lee, T. Bein, L. F. Nazar, *Angew. Chem. Int. Ed.*, 51 (2012) 3591.
33. N. Jayaprakash, J. Shen, S. S. Moganty, A. Corona, L. A. Archer, *Angew. Chem.*, 123 (2011) 6026.
34. Z. Yang, J. Guo, S. K. Das, Y. Yu, Z. Zhou, H. D. Abruña, L. A. Archer, *J. Mater. Chem. A*, 1 (2013) 1433.
35. J. Kim, D. J. Lee, H. G. Jung, Y. K. Sun, J. Hassoun, B. Scrosati, An Advanced Lithium-Sulfur Battery, *Adv. Funct. Mater.*, 23 (2013) 1076.
36. N. Jayaprakash, J. Shen, S. S. Moganty, A. Corona, L. A. Archer, *Angew. Chem. Int. Ed.*, 50 (2011) 5904.
37. S. Dörfler, M. Hagen, H. Althues, J. Tübke, S. Kaskel, M. J. Hoffmann, *Chem. Commun.*, 48 (2012) 4097.
38. W. Zheng, Y. Liu, X. Hu, C. Zhang, *Electrochim. Acta*, 51 (2006) 1330.
39. L. X. Yuan, H. P. Yuan, X. P. Qiu, L. Q. Chen, W. T. Zhu, *J. Power Sources*, 189 (2009) 1141.
40. Y. S. Choi, S. Kim, S. S. Choi, J. S. Han, J. D. Kim, S. E. Jeon, B. H. Jung, *Electrochim. Acta*, 50 (2004) 833.

41. J. J. Chen, X. Jia, Q. J. She, C. Wang, Q. Zhang, M. S. Zheng, Q. F. Dong, *Electrochim. Acta*, 55 (2010) 8062.
42. S. C. Han, M. S. Song, H. Lee, H. S. Kim, H. J. Ahn, J. Y. Lee, *J. Electrochem. Soc.*, 150 (2003) A889.
43. L. Yin, J. Wang, J. Yang, Y. Nuli, *J. Mater. Chem.*, 21 (2011) 6807.
44. W. Wei, J. Wang, L. Zhou, J. Yang, B. Schumann, Y. Nu Li, *Electrochem. Commun.*, 13 (2011) 399.
45. T. Kyotani, L. F. Tsai, A. Tomita, *Chem. Mater.*, 8 (1996) 2109.
46. J. Guo, Y. Xu, C. Wang, *Nano Lett.*, 11 (2011) 4288.
47. K. Hata, D. N. Futaba, K. Mizuno, T. Namai, M. Yumura, S. Iijima, *Science*, 306 (2009) 1362.
48. M. Hagen, S. Dörfler, H. Althues, J. Tübke, M.J. Hoffmann, S. Kaskel, K. Pinkwart, *J. Power Sources*, 213 (2012) 239.
49. M. Hagen, S. Dörfler, P. Fanz, T. Berger, R. Speck, J. Tübke, H. Althues, M.J. Hoffmann, C. Scherr, S. Kaskel, *J. Power Sources*, 224 (2013) 260.
50. M. Q. Zhao, X. F. Liu, Q. Zhang, G. L. Tian, J. Q. Huang, W. Zhu, F. Wei, *ACS Nano*, 6 (2012) 10759.
51. S. Evers, L. F. Nazar, *Acc. Chem. Res.*, DOI: 10.1021/ar3001348
52. Y. J. Choi, K. W. Kim, H. J. Ahn, J. H. Ahn, *J. Alloys Compd.*, 449 (2008) 313.
53. L. Li, L. Y. Li, X. D. Guo, B. H. Zhong, Y. X. Chen, Y. Tang, *J. Solid State Electrochem.*, DOI:10.1007/s10008-012-1864-7
54. D. J. Kim, J. W. Park, J. S. Kim, K. K. Cho, K. W. Kim, J. H. Ahn, M. K. Jo, H. J. Choi, D. H. Bae, H. J. Ahn, *J. Nanosci. Nanotechnol.*, 11(2011) 484.
55. J. J. Chen, Q. Zhang, Y. N. Shi, L. L. Qin, Y. Cao, M. S. Zheng, Q. F. Dong, *Phys. Chem. Chem. Phys.*, 14 (2012) 5376.
56. W. Ahn, K. B. Kim, K. N. Jung, K. H. Shin, C. S. Jin, *J. Power Sources*, 202 (2012) 394.
57. X. Geng, M. Rao, X. Li, W. Li, *J. Solid State Electrochem.*, DOI 10.1007/s10008-012-1959-1
58. X. Zhao, D. S. Kim, H. J. Ahn, K. W. Kim, C. S. Jin, J. H. Ahn, *J. Korean Electrochem. Soc.*, 13 (2010) 169.
59. Y. Yang, G. Yu, J. J. Cha, H. Wu, M. Vosgueritchian, Y. Yao, Z. Bao, Y. Cui, *ACS Nano*, 5 (2011), 9187.
60. S. Ch. Zhang, L. Zhang, W. K. Wang, W. J. Xue, *Synthetic Metals*, 160 (2010) 2041.
61. P. Ma, B. H. Zhang, Y. H. Xu, G. Y. Gong, *Mod. Chem. Ind.*, 27 (2007) 30.
62. Z. P. Guo, J. Z. Wang, H. K. Liu, S. X. Dou, *J. Power Sources*, 146 (2005) 448.
63. A. Du Pasquier, F. Orsini, A. S. Gozdz, J. M. Tarascon, *J. Power Sources*, 81 (1999) 607.
64. B. Veeraraghavan, J. Paul, B. Haran, B. Popoy, *J. Power Sources*, 109 (2002) 377.
65. J. Wang, J. Chen, K. Konstantinov, L. Zhao, S. H. Ng, G. X. Wang, Z. P. Guo, H. K. Liu, *Electrochim. Acta*, 51 (2006) 4634.
66. A. Wu, H. Kolla, S. K. Manohar, *Macromolecules*, 38 (2005) 7873.
67. J. L. Wang, J. Yang, J. Y. Xie, N. X. Xu, *Adv. Mater.*, 14 (2002) 963.
68. M. M. Sun, S. C. Zhang, T. Jiang, L. Zhang, J. H. Yu, *Electrochem. Commun.*, 10 (2008) 1819.
69. J. Suárez-Guevara, O. Ayyad, P. Gómez-Romero, *Nanoscale Research Letters*, 7 (2012) 521.
70. S. Kuwabata, M. Tomiyori, *J. Electrochem. Soc.*, 149 (2002) A988.
71. H. Yoneyama, A. Kishimoto, S. Kuwabata, *J. Chem. Soc. Chem. Commun.*, 15 (1991) 986.
72. J. Wang, C. O. Too, D. Zhou, G. G. Wallace, *J. Power Sources*, 140 (2005) 162.
73. H. Wang, T. Lin, A. Kaynak, *Synth. Met.*, 151 (2005) 136.
74. Y. Yang, G. Yu, J. J. Cha, H. Wu, M. Vosgueritchian, Y. Yao, Z. Bao, Y. Cui. *ASC Nano*, 5 (2011) 9187.
75. C. M. Zhan, L. Z. Zhan, Z. P. Song, J. Y. Zhang, J. Tang, H. Zhan, Y. H. Zhou, *Electrochim. Acta*, 53 (2008) 8319.
76. A. V. Murugan, T. Muraliganth, A. Manthiram, *Electrochem. Commun.*, 10 (2008) 903.

77. A. Elschner, S. Kirchmeyer, W. Lovenich, U. Merker, K. Reuter, *PEDOT: Principles and Applications of an Intrinsically Conductive Polymer*, CRC Press: Boca Raton, FL, USA, 2010.
78. L. Duan, J. Lu, W. Liu, P. Huang, W. Wang, Z. Liu, *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 414 (2012) 98.
79. S. E. Cheon, K. S. Ko, J. H. Cho, S. W. Kim, E. Y. Chin, H. T. Kim, *J. Electrochem. Soc.*, 150 (2003) A796.
80. X. Liang, Z. Wen, Y. Liu, M. Wu, J. Jin, H. Zhang, X. Wu, *J. Power Sources*, 196 (2011) 9839.
81. J. W. Choi, J.K. Kim, G. Cheruvally, J. H. Ahn, H. J. Ahn, K. W. Kim, *Electrochimica. Acta*, 52 (2007) 2075.
82. M. Nadhera, J. Reiter, J. Moskon, R. Dominko, *J. Power Sources*, 196 (2011) 7700.
83. D. R. Chang, S. H. Lee, S. W. Kim, H. T. Kim, *J. Power Sources*, 112 (2002) 452.