An Advanced Lithium-Sulfur Battery

Junghoon Kim, Dong-Ju Lee, Hun-Gi Jung, Yang-Kook Sun, Jusef Hassoun,* and Bruno Scrosati**

A lithium-sulfur battery employing a high performances mesoporous hard carbon spherules-sulfur cathode and a stable, highly conducting electrolyte is reported. The results demonstrate that the battery cycles with very high capacity, i.e., of the order of 750 mAh g^{-1} with excellent retention during cycling. In addition, by exploiting the high conductivity of our selected electrolyte, the battery performs very well also at low temperature, i.e., delivering a capacity of 500 mAh $g^{-1}_{(S)}$ at 0 °C for over 170 charge-discharge cycles. We believe that these results may substantially contribute to the progress of the lithium-sulfur battery technology.

1. Introduction

Particular attention is presently devoted to batteries having prospected energy density values in the range of several hundred watt-hours per kilogram.[1] These advanced power sources, occasionally named "superbatteries", are in fact regarded as the sole electrochemical systems that may efficiently open the door to the success of the electrified road transportation market. Lithium-sulfur and lithium-air are the most common examples of these high- energy, super-batteries; however, while the latter is still in a very initial stage of R&D, the former is in a more advanced state of development due a series of recent breakthroughs that have led to the overcoming of serious operational issues, such as the solubility of the discharge products in common, liquid organic electrolytes and the limited functionality of the carbon-sulfur cathode material.

The most important of these breakthroughs include: i) the identification of stable solvent-free polymer electrolytes to control the solubility issue;[2] ii) the use at the cathode side of lithium sulfide-carbon composite instead of the common sulfur-carbon composite to allow the replacement of the highly reactive lithium metal with alternative anode materials (3); (iii) the development of advanced electrode nanomorphologies, such as sulfur shielded into a carbon matrix, either mesoporous[4] or spherical,[5,6] or polysulfide reservoirs based on porous silica embedded within a carbon–sulfur composite,[7] for improving rate and cycling life.

However, although substantial progress has been marked, the road for making the sulfur-battery a practical reality is still long; further improvements, particularly at the electrode and electrolyte sides, are required. Accordingly, these aspects require particular attention and in this paper we report an advanced lithium-sulfur battery exploiting a morphologically optimized sulfur-carbon composite cathode and a stable, highly conductive electrolyte. We believe that the results here described may substantially contribute to the progress of the lithium-sulfur battery technology.

2. Results and Discussion

The basic electrochemical process of a lithium-sulfur cell is the conversion of lithium and sulfur into lithium sulfide, 16 Li + S_8 = 8 Li_2S, via the formation of a series of intermediate polysulfides, Li_2S_x (1≤ × ≤ 8), to which is associated a voltage of about 2 V and a specific capacity of 1,675 mAh $g^{-1}_{(S)}$, this giving an estimated energy density exceeding 3,000 Wh kg^{-1}, i.e., a value much greater than that achievable by common lithium-ion batteries. Hence, the large attention presently devoted to this Li-S "super-battery".

It is now established that one of the weak points in this battery is the sulfur cathode that, if not properly prepared, looses capacity upon cycling and lacks in rate capability. Accordingly, we have devoted a particular attention to the formulation of proper sulfur-carbon composites and in this work we report a new electrode morphology obtained by refining the procedure recently suggested by Archer and co-workers,[6] namely by developing an hard carbon spherules matrix having a high surface area and a very small pore size into which sulfur can be easily infiltrated, see also the experimental section.

Dr. J. Hassoun, Prof. B. Scrosati
Department of Chemistry
University of Rome Sapienza
Rome, 00185 (Italy)
Department of WCU Energy Engineering
Hanyang University
Seoul 133-791, Republic of Korea
E-mail: jusef.hassoun@uniroma1.it;
Bruno.scrosati@uniroma1.it
Prof. Y.-K. Sun
Department of WCU Energy Engineering
Department of Chemical Engineering
Hanyang University
Seoul 133-791, Republic of Korea
E-mail: yksun@hanyang.ac.kr
Mr. J. Kim, Mr. D.-J. Lee, Mr. H.-G. Jung
Department of WCU Energy Engineering
Hanyang University
Seoul 133-791, Republic of Korea
Mr. H.-G. Jung
Department of Chemical Engineering
Hanyang University
Seoul 133-791, Republic of Korea

DOI: 10.1002/adfm.201200689

A special attention has been also devoted in this work to the choice of an electrolyte that could properly be used in connection with the hard carbon spherules-sulfur electrode (HCS-S) for the development of an effective lithium-sulfur battery. As well known, liquid organic carbonate electrolytes, e.g., the typical $LiPF_6$ solution in an ethylene carbonate-dimethyl carbonate (EC-DMC) mixture, are excluded because of their high dissolution power for polysulfides.[9,10] In addition, due to their reactivity as strong Lewis bases, these carbonate electrolytes tend to form undesired, highly resistive passivation films on the electrode surface.[11] Therefore, it is now generally recognized that these liquid organic electrolytes are not suitable for use in lithium-sulfur cells. More stable media such as gel[3] or solid[2] lithium-conducting polymer membranes have been proposed as efficient alternatives; however, especially in the solid case, the range of applicability is limited because of the temperature dependence of the conductivity.[12] As preferred electrolyte for our Li/HCS-S battery we have chosen a solution of lithium triflate, $LiCF_3SO_3$ in tetraethylene glycol dimethyl ether, TEGDME, at the $(TEGDME)_4LiCF_3SO_3$ molar composition. We are aware that the use of end capped glycols as electrolytes in lithium-sulfur cells has been already reported.[13,14] The novelty of our version is in its special design and composition, involving the use of a very stable lithium salt ($LiCF_3SO_3$) and an appropriate composition ratio of the elements that form it. These improvements result in an electrolyte having a conductivity of the order of 1 mS cm^{-1} in a range of temperature extending from −10 °C to 60 °C,[8] namely with values rarely obtained in the past. The conductivity of the selected electrolyte that maintains an appreciable and stable value over a wide temperature range provides the condition necessary for operating the $Li/(TEGDME)_4LiCF_3SO_3/HCS\text{-}S$ battery even at low temperatures, see later.

Figure 1 shows the pore size distribution (A) and the SEM image morphology (B) of the precursor carbon spherules. The data evidence the high pore distribution at the lower pore diameters, reflecting in a high surface area of 854.18 m^2 g^{-1} and pore size of about 1.5 nm. In addition, since its total pore volume is 0.372 cc g^{-1}, the hard carbon precursor has a highly nanoporous structure, that is expected to be very beneficial for assuring optimized morphology and fast kinetics to the final HCS-S electrode, as in fact experimentally confirmed, see later.

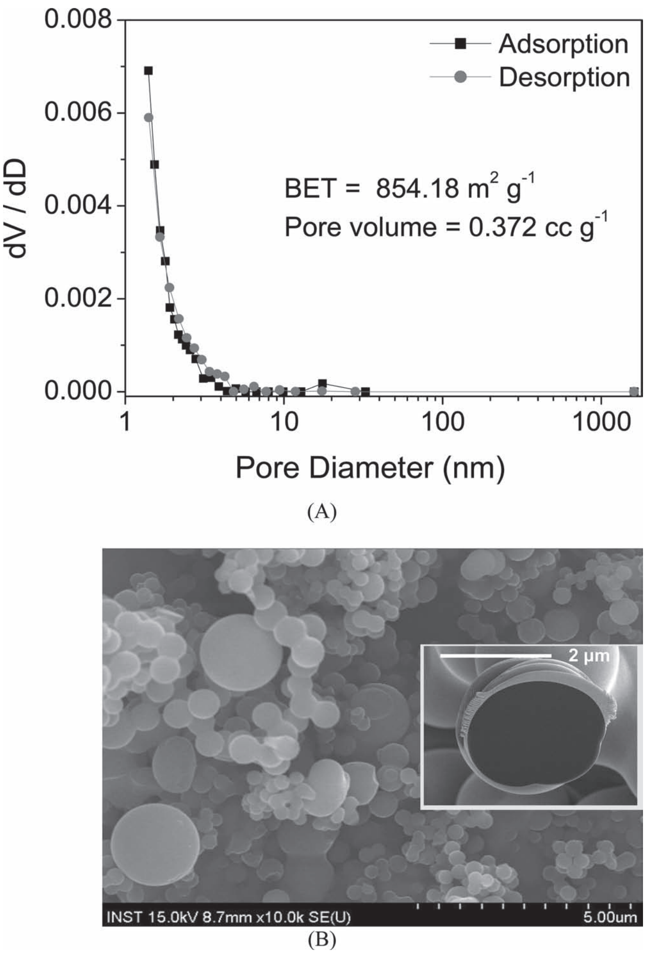
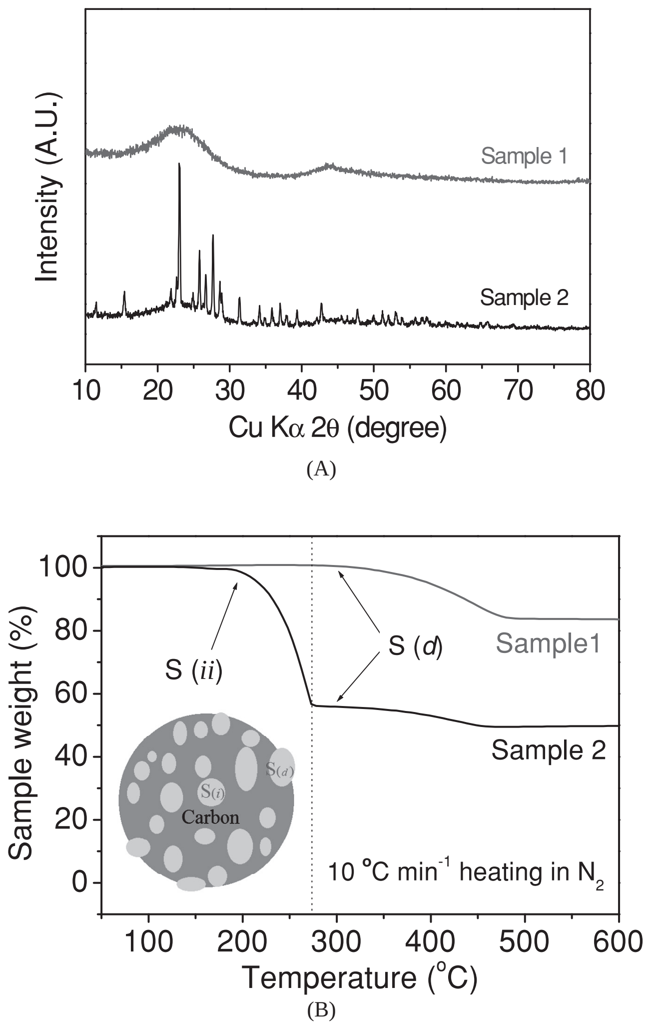


Figure 1. (A) BET analysis showing the pore size distribution and (B) SEM image showing the morphology of the carbon spherules precursor used for the synthesis of the HCS-S electrode.

By monitoring the synthesis conditions, i.e. by properly selecting the reciprocal amount of the mesoporous carbon spherules and sulfur precursors, and by carefully controlling the final vaporization step at 300 °C (see experimental), the procedure here adopted allows to modulate the sulfur loading of the final HCS-S electrode. Accordingly, we have prepared two HCS-S electrode samples, varying by the sulfur content, i.e., 20% w:w for a sample 1 and 52% w:w for a sample 2. **Figure 2**A shows the XRD patterns of the two samples. All the original diffraction peaks of crystalline sulfur are retained in sample 2, confirming that sulfur is indeed dispersed throughout the carbon particles, while sample 1 shows only a broad profile with an amorphous shape. We then conclude that in sample 1 sulfur is confined in the very internal part of the carbon spherules precursor, this shielding the diffraction patterns. This conclusion finds extra support by the TGA response, see Figure 2B. The trace of sample 1 shows only a limited weight loss at 260 °C attributed to release of sulfur confined within the inner part of the carbon spherules. Quite different is the response of sample 2, showing an initial weight loss at around 160 °C, followed by a second at around 260 °C; the former associated with the loss of the sulfur situated at the surface and throughout the hollow carbon particles (sulfur melting point, 118 °C) and the latter matching that observed for sample 1 and analogously attributed to the release of the sulfur confined within the carbon particles, see also the schematic representation in inset of the Figure 2B where the internal sulfur is marked as S*(i)* and the diffused sulfur as S*(d)*.

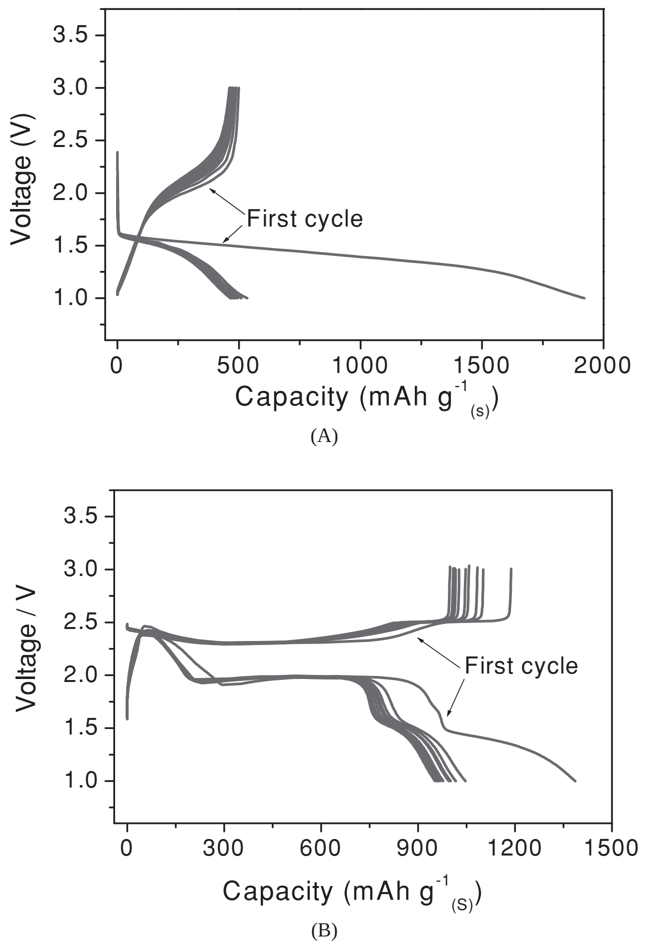
The amount of the active species is an important factor for attaining good performance with any electrode material. The same applies for the two HCS-S electrodes here examined. **Figure 3** compares their voltage profiles when galvanostatically cycled in a lithium cell using our selected $(TEGDME)_4LiCF_3SO_3$ electrolyte. Figure 3A reveals that, as expected, sample 1, where most of the sulfur is situated in the inner part of the electrode, cycles with a limited capacity of 500 mAh $g^{-1}{}_{(S)}$ at the low rate of 0.1 A $g^{-1}{}_{(S)}$. A very large irreversible capacity is also observed, probably caused by the reactive, large surface area carbon exposed to the electrolyte.



(A)

(B)

Figure 2. XRD patterns (A) and TGA profiles (B) of the two HCS-S sample electrodes studied in this work. Sample 1 contains 20% w:w of sulfur mostly concentrated in the inner part of the carbon spherules while sample 2 has 52% w:w of sulfur uniformly diffused within the spherules. A schematic representation of the two samples is shown in the inset (S*(i)* = internal sulfur; S*(d)*= diffused sulfur)



(A)

(B)

Figure 3. Voltage profiles of the charge-discharge galvanostatic cycles of lithium cells using the HCS-S sample 1 (A) and sample 2 HCS-S (B). Current rates: 0.1 A $g^{-1}_{(S)}$ for cell with sample 1 and 1 A $g^{-1}_{(S)}$ for cell using sample 2. Voltage limits: 1.0 V–3.0 V. Room temperature.

Quite different is the response of sample 2 for which the capacity increases to 1 000 mAh $g^{-1}_{(S)}$ with a voltage profile that assumes the multi-plateau signature typical of a high performance lithium-sulfur cells[14] and at rate of 1 A $g^{-1}_{(S)}$, i.e. 10 times higher than that exhibited by sample 1, see Figure 3B. We see from this figure that, during the first discharge process of the HCS-S electrode sample 2, all the expected sulfur reduction plateaus at 2.4, at 2.0 V and at about 1.5 vs. Li, are observed. Most likely, the first two plateaus can be attributed to the electrochemical process of the sulfur hosted in the more external part of the carbon spherules (S*(d)* in scheme of Figure 2B), while the plateau at the lower voltage to the more resistive internal sulfur (S*(i)* in scheme of Figure 2B), namely matching the only one observed for the sample 1 (compare Figure 3A). Another bonus of the sample 2 electrode is in the limited value of the first cycle irreversible capacity that is much smaller than that observed for sample 1. This difference is most likely associated with a less carbon-activated electrolyte decomposition, since in sample 2 the reactivity of carbon is shielded by the presence of sulfur that covers its surface. The results above described and the differences in the electrochemical behavior of the two samples highlight the key importance of the electrode morphology in determining the response of lithium-sulfur cells. Accordingly, we may conclude that in sample 2 all the available sulfur is electrochemically active and thus, that it can be rated as a very efficient sulfur electrode.

The excellent electrochemical behavior of our HCS-S electrode is confirmed by **Figure 4**A that shows the derivative dQ/dV profiles of the galvanostatic test reported in Figure 3B. The figure shows a complete overlapping of the anodic and cathodic peak profiles of the first and of the second cycle, as well as peak sharpness, these evidences suggesting high reversibility and very fast electrode kinetics. Figure 4B shows the impedance response and the SEM images of the HCS-S electrode compared with those of a conventional, ball milled, mixed S-C electrode. Both spectra evolve along two semicircles, the one at high frequency associated with a pristine Solid Electrolyte

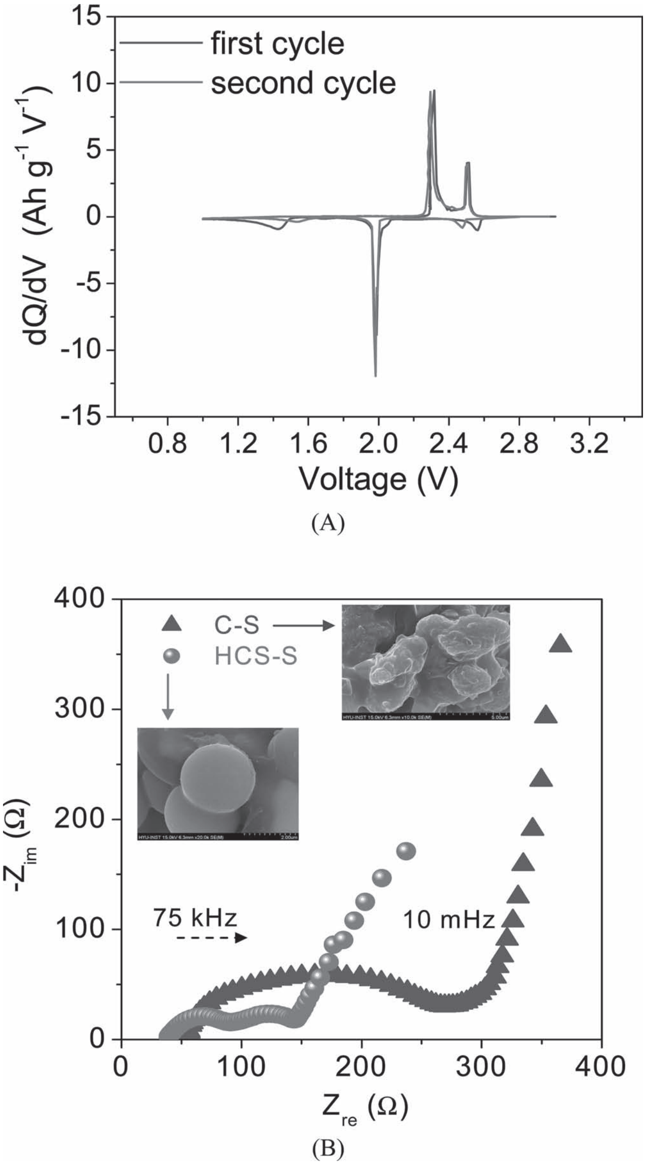


Figure 4. Derivative dQ/dV profiles of the first two galvanostatic cycles of the HCS-S sample 2 lithium cell cycled at a current rate of 1 A $g^{-1}{}_{(S)}$ (A) and impedance spectroscopy response, with an inset of SEM images, of the HCS-S sample 2 in comparison with a conventional S-C electrode (B). Room temperature.

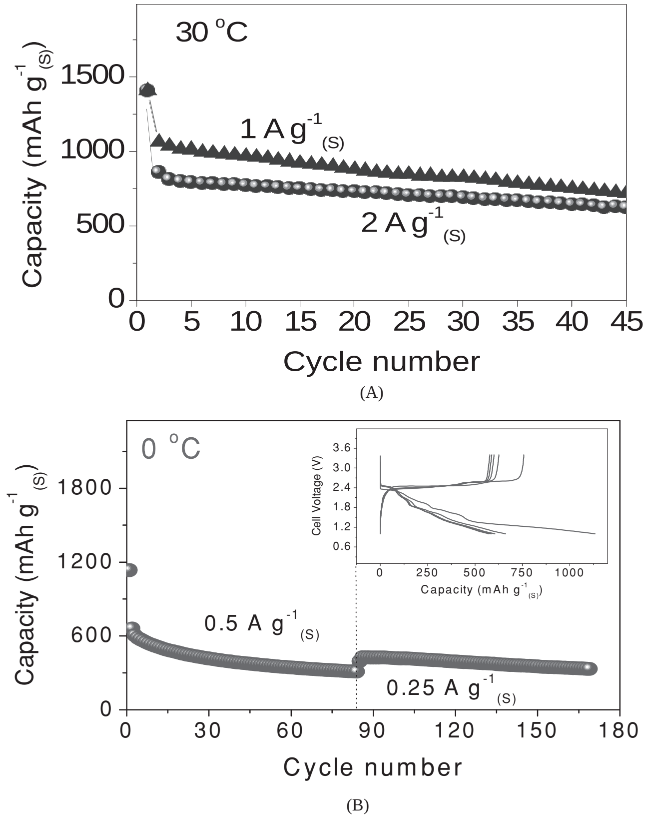


Figure 5. Capacity versus cycle number of a Li/(TEGDME)$_4$LiCF$_3$SO$_3$/HSC-S sample 2 battery cycling at various current rates at 30 °C (A) and at 0 °C (B). Voltage limits: 1.0 V–3.0 V.

Interface, SEI film formed on the electrodes' surface and the other at lower frequency associated with the charge transfer impedance.[11] The latter is consistently smaller for our HSC-S electrode and this finally demonstrates that the adopted special hollow morphology indeed favors fast charge-transfer response and, ultimately, very high rates.

Figure 5A shows the cyclic behavior of our Li/(TEGDME)$_4$LiCF$_3$SO$_3$/HSC-S sample 2 battery at various current rates. The results highlight the promising response of this battery that can cycle at a rate as high as 2 A $g^{-1}{}_{(S)}$ for 45 cycles with a specific capacity of the order of 750 mAh $g^{-1}{}_{(S)}$. Furthermore, by exploiting the high conductivity of our selected electrolyte, the battery performs very well also at low temperature, i.e., by delivering a capacity of about 500 mAh $g^{-1}{}_{(S)}$ at 0 °C for 170 cycles. To our knowledge, there are not many other reported Li/S batteries capable to match this performance.

3. Conclusions

In this paper the importance of the electrode morphology in determining the electrochemical response of a lithium sulfur cell is outlined by comparing the behavior of two cells having different hard carbon spherules-sulfur cathodes. We show that the cell exploiting an electrode having a well-controlled spherical and compact morphology with a 52% w:w sulfur fully infiltrated within the pores of the carbon hollow particles in combination with a stable and highly conducting electrolyte, has an excellent electrochemical performance. Indeed, we demonstrate that this cell cycles at high rates with a capacity of the order of 750 mA g^{-1} and an average voltage of 2 V, this giving a theoretical energy density of 1,500 Wh kg^{-1}, i.e., three times higher than that achievable with the state-of-art lithium ion batteries. It is of relevance to point out that the particular morphology adopted in this work assures a high tap density to the HSC-S electrode, namely of the order of 1.04 g cm^{-3}. Therefore, also a high value of volumetric energy density is expected for the Li/HCS-S battery here reported. Finally, we anticipate that by further optimizing the morphology of the HCS-S electrode, e.g. by enlarging specific surface area, pore volume, and pore size, a substantial increase in sulfur loading and, accordingly, in the overall electrode capacity, can be obtained. This work is in progress in our laboratories.

4. Experimental Section

Synthesis of the HCS-S composite cathode: The HCS-S composite was prepared by mixing mesoporous hard carbon spherules (HCS) described in previous paper[8] with sulfur in a 1:5 weight ratio. The mixture was heated at 150 °C for 7 h in a sealed round flask under an argon atmosphere in order to infiltrate the low-viscosity molten sulfur into the pores. Then, the excess sulfur outside the carbon spherules was vaporized by a heat treatment at 300 °C for 2 h. Two samples, i.e. differing by the final vaporization step, have been prepared. The first sample, labeled as Sample 1 and characterized by sulfur content of 20%, has been vaporized under argon flow. The second sample, labeled Sample 2 and characterized by sulfur content of 52%, has been vaporized in a sealed stainless steel reactor under an argon atmosphere.

Electrolyte: the electrolyte, a solution of lithium trifluoromethane sulfonate, $LiCF_3SO_3$ (Aldrich), in tetraethyleneglicole dimethylether (TEGDME, Aldrich) with a $LiCF_3SO_3$ to TEGDME molar ratio of 1:4 was prepared in argon-filled glove box.

Material characterization: The sulfur content in the HCS-S composite material was determined by thermo-gravimetric analysis (TG 209 F3, Netch) performed in a nitrogen atmosphere with a heating rate of 10 °C min^{-1}. The morphology and crystalline phase were analyzed by field-emission scanning electron microscopy (S-4800, Hitachi), focalized ion beam (KICET instrument), and x-ray diffraction (Rint-2000, Rigaku) with Cu-Kα radiation. The diffraction data were obtained at 2θ ranging from 10° to 80°, with a step size of 0.03°. The BET analysis has been performed on the HCS powder using Nitrogen adsorption technique with a Quantachrom Autosorb-1 after degassing the sample at 200 °C for 4 h.

Electrode film preparation and electrochemical tests: The HCS-S electrode film was prepared by mixing in acetonitrile the active materials with a carbon black conducting agent (acetylene black) and a polyethylene oxide ($Mw = 6 \times 10^5$, Aldrich) binder in a 60:20:20 weight ratio. The resulting slurry was then coated on an Al foil to obtain a film with approximately 40 μm thickness. The electrode was roll-pressed and subsequently dried at 50 °C to remove the residual solvent. The electrochemical tests of the Li/HCS-S battery were performed with R2032 coin-type cells formed by contacting, in an argon-filled glove box, a lithium foil anode with a HCS-S cathode separated by the selected $LiCF_3SO_3$-TEGDME electrolyte solution soaked in a porous polyethylene separator. The response of the cell was determined by galvanostatic cycling at different rates (1C rate (sulfur mass) = 1.68 A $g^{-1}{}_{(S)}$) using a TOSCAT-3100 instrument. The electrochemical impedance spectroscopy (EIS) has been performed using a Swagelok 3-electrode cell combining the HCS-S electrode with lithium foil counter and reference electrode, in the $LiCF_3SO_3$-TEGDME electrolyte solution, in the frequency range of 75 kHz–10 mHz, using a signal amplitude of 10 mV with a VMP instrument.

Acknowledgements

This work was performed within the Project “REALIST” (Rechargeable, advanced, nano-structured lithium batteries with high energy storage) sponsored by the Italian Institute of Technology (IIT), and the Human Resources Development of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Korea government Ministry of Knowledge Economy (No. 20114010203150).

Received: March 13, 2012
Published online: May 29, 2012

---

[1] B. Scrosati, J. Hassoun, Y.-K. Sun, *Energy Environ. Sci.* **2011**, *4*, 3287.
[2] J. Hassoun, B. Scrosati, *Adv. Mater.* **2010**, *22*, 5198.
[3] J. Hassoun, B. Scrosati, *Angew. Chem. In. Ed.* **2010**, *49*, 2371.
[4] X. Ji, K. T. Lee, L. F. Nazar, *Nat. Mater.* **2009**, *8*, 500.
[5] B. Zhang, X. Qin, G. R. Li, X. P. Gao, *Energy Environ. Sci.* **2010**, *3*, 1531.
[6] N. Jayaprakash, J. Shen, S. S. Moganty, A. Corona, L. A. Archer, *Angew. Chem. Int. Ed.* **2011**, *50*, 5904.
[7] X. Ji, S. Evers, R. Black, L. F. Nazar, *Nat. Comm.* **2011**, *2*, 325.
[8] J. Hassoun, J. Kim, D.-J. Lee, H.-G. Jung, S.-M. Lee, Y.-K. Sun, B. Scrosati, *J. Power Sources* **2012**, *202*, 308.
[9] D. Peramunge, S. A. Licht, *Science* **1993**, *261*, 1029.
[10] J. Shim, K. A. Stribel, E. J. Cairns, *J. Mater. Chem.* **2010**, *20*, 9821.
[11] D. Aurbach, *J. Power Sources* **2003**, *119–121*, 497.
[12] G. B. Appetecchi, F. Croce, J. Hassoun, B. Scrosati, M. Salomon, F. Cassel, *J. Power Sources* **2003**, *114*, 105.
[13] M.-S. Song, S.-C. Han, H.-S. Kim, J.-H. Kim, K.-T. Kim, Y.-M. Kang, H.-J. Ahn, S. X. Dou, J.-Y. Lee, *J. Electrochem. Soc.* **2004**, *151*, A791.
[14] C. Liang, N. J. Dudney, J. Y. Howe, *Chem. Mater.* **2009**, *21*, 4724.