Angewandte Chemie

DOI: 10.1002/ange.200907324

Lithium Ion Batteries

A High-Performance Polymer Tin Sulfur Lithium Ion Battery**

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The lithium–sulfur battery, based on the electrochemical reaction $16\,\mathrm{Li}+\mathrm{S}_8 \rightleftarrows 8\,\mathrm{Li}_2\mathrm{S}$, has a theoretical specific energy and energy density of 2500 $\mathrm{W\,h\,kg^{-1}}$ and 2800 $\mathrm{W\,h\,L^{-1}}$, respectively, much greater than those of any conventional lithium battery.[1] The Li–S battery has been investigated by many workers for several decades; however, such studies have been limited to the simplest cell configuration consisting of sulfur as the positive electrode, lithium metal as the negative electrode, and a solution of a lithium salt in an aprotic organic solvent as the electrolyte.[2–6]

The practical development of the lithium–sulfur battery has been hindered to date by a series of shortcomings. A major hurdle is the high solubility in the organic electrolyte of the polysulfides $\mathrm{Li}_2\mathrm{S}_x$ ($1 \leq x \leq 8$) that form as intermediates during both charge and discharge processes. This high solubility results in a loss of active mass, which is reflected in a low utilization of the sulfur cathode and in a severe capacity decay upon cycling. The dissolved polysulfide anions, by migration through the electrolyte, may reach the lithium metal anode, where they react to form insoluble products on its surface; this process also negatively impacts the battery operation.[7] Various strategies to address the solubility issue have been explored. They include the design of modified organic liquid electrolytes[8–10] and the use of ionic-liquid-based electrolytes[11] and polymer electrolytes.[12] However, although interesting, the results are still far from marking real breakthroughs in the field.

Important progress was recently made by Nazar and coworkers, who showed that by fabricating cathodes based on an intimate mixture of nanostructured sulfur and mesoporous carbon, high reversible capacity and good rates can be obtained.[13] However, this battery is also based on conventional chemistry in terms of anode and electrolyte, as it contains a lithium metal foil anode and an organic liquid electrolyte. Lithium metal is very reactive in common lithium battery electrolyte media: the organic solution readily decomposes at the metal surface, thus forming a passivating layer.[14] Nonuniformities in this layer result in dendrite deposition that may eventually extend to short the cell, with negative repercussion for the cycle life of the battery and also for its safety. For this reason, commercial "lithium" batteries do not use a lithium metal anode but rather a material capable of hosting and releasing lithium ions (e.g., graphite) in order to operate by lithium ion transfer only, thus carefully avoiding any lithium metal deposition. It is then surprising that all the strategies attempted to date to achieve progress with the Li–S battery have been concentrated on the cathode problems, totally neglecting those associated with the anode.

The key challenge is then to totally renew the chemistry of this battery such as to achieve an advanced configuration that can consistently provide high capacity, a long cycle life, and safe operation. Herein, we report an example of a lithium-metal-free new battery version and demonstrate that, to a large extent, it can effectively meet these targets. In contrast to most of the Li–S batteries proposed to date, which are fabricated in the "charged" state, that is, using a carbon–sulfur composite cathode that necessarily requires a lithium metal counter electrode (anode) to assure the $16\,\mathrm{Li}+\mathrm{S}_8 \rightarrow 8\,\mathrm{Li}_2\mathrm{S}$ discharge process, we propose to fabricate the battery in the "discharged" state by using a carbon lithium sulfide composite as the cathode.

The battery may be activated by reversing the above process, that is, by converting lithium sulfide back to lithium and sulfur ($8\,\mathrm{Li}_2\mathrm{S} \rightarrow 16\,\mathrm{Li}+\mathrm{S}_8$). We show herein that the charging process may be reversibly turned into a reverse discharge process and that the entire charge–discharge cycle can be efficiently repeated several times.

We also renewed the electrolyte component by replacing the common liquid organic solutions with a gel-type polymer membrane, formed by trapping an ethylene carbonate/dimethylcarbonate lithium hexafluorophosphate (EC:DMC LiPF_6) solution saturated with lithium sulfide in a polyethylene oxide/lithium trifluoromethanesulfonate (PEO/$\mathrm{LiCF}_3\mathrm{SO}_3$) polymer matrix.[15] A dispersed zirconia ceramic filler enhances the mechanical properties of the gel and improves liquid retention within its bulk.[16] For simplicity, we refer to this composite gel polymer electrolyte as CGPE.

The photograph in Figure 1a demonstrates the plastic appearance of the CGPE polymer electrolyte. We can describe this electrolyte as a membrane with liquid zones contained within a polymer envelope. It is expected that when the membrane is used as electrolyte in the cell, the external polymer layer may act as a physical barrier preventing the direct contact of the electrode components with the internal liquid solution. This barrier function will help to control the dissolution of the sulfide anions from the cathode and to prevent the attack of the same anions at the anode. Bearing in mind that the solubility of the sulfide anions is one of the key factors affecting cell life and performance, we have further enforced its control by supplementing the electrolyte with lithium sulfide up to saturation, which leads to a combined physical and chemical barrier to block most the dissolution.

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[**] This work was carried out with the financial support of the Italian ministry of university and research under a PRIN2007 project.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200907324.

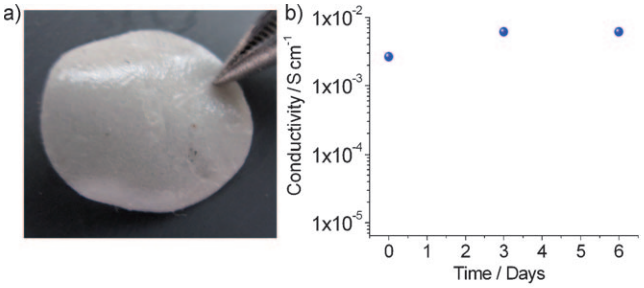

Figure 1. Characteristics of the CGPE membrane to be used as electrolyte separator in the lithium–sulfur battery. a) Appearance of the membrane. b) Time evolution of the conductivity at room temperature. CGPE: Composite gel polymer electrolyte; see text for the composition.

Another key requirement for a battery electrolyte is a high and stable conductivity in order to minimize the ohmic drop during cell operation. This requirement also holds in this case, and care was taken to prepare the gel polymer electrolyte in its most highly conductive form. Impedance studies[17] at room temperature and at increasing storage times indicate that the resistance of the CGPE is low and stable with time; this result is reflected in a high conductivity with values approaching 10^{-2} S cm^{-1} (Figure 1 b). Comparable, stable conductivity values were also obtained at 60 °C.

The electrochemical activity of the Li_2S/C-based electrode in the gel electrolyte was demonstrated by potentiodynamic cycling with galvanostatic acceleration (PCGA) analysis. This technique is powerful for evaluating electrochemical processes, as it operates under quasi-thermodynamic conditions and hence gives valid information on their reversibility.[18] As seen in Figure 2, the anodic scan (charge of the Li_2S/C electrode) develops with a main peak at 3.5 V versus Li, representing the various intermediate steps in the conversion of Li_2S to elemental sulfur. Two additional minor peaks are also observed, quite likely associated with the intermediate steps which accompany the evolution of the electrochemical process.[19] The electrochemical process is reversed in the subsequent cathodic scan (discharge of the working electrode), for which the PCGA trace reveals a series of peaks representing the reconversion of sulfur to the intermediate lithium sulfide species.[20] The integration of the peak areas reveals that the overall capacity related to the charge process matches that of the discharge process, thus demonstrating the reversibility of the overall electrochemical reaction.

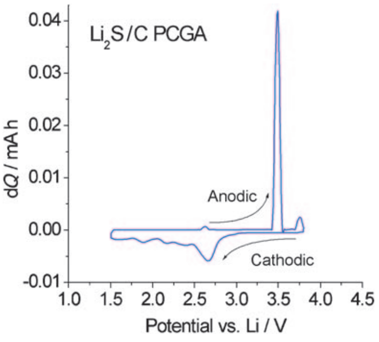

Figure 2. PCGA response of a Li_2S/C electrode in the CPGE electrolyte. Lithium metal counter and reference electrodes. Room temperature.

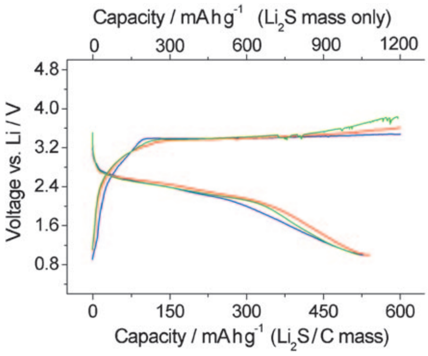

Figure 3. Typical capacity delivery in multiple charge–discharge cycles (1 blue, 2 red, 3 green) of a Li_2S/C electrode in the CGPE electrolyte. Lithium metal counter and reference electrode. Operating temperature 60 °C. Cycling rate *C*/20 ($C = 2.2$ mA cm^{-2}). The capacity is shown both in terms of total electrode mass and in terms of active material mass only.

The favorable electrochemical response of the Li_2S/C electrode is further demonstrated in Figure 3, which shows the voltage profiles of repeated charge–discharge cycles obtained with a cell using CGPE as the electrolyte and lithium metal as the counter electrode. The voltage profiles evolve with charge and discharge plateaus that correspond to the peaks highlighted by the PCGA analysis (cf. Figure 2). The profiles overlap upon cycling, thus demonstrating the electrochemical feasibility and the reversibility of the charge–discharge process using our electrode material. We see that the profiles evolve around 2.5 V versus Li with a total capacity on the order of 600 mA h g^{-1}. Note that the capacity is calculated on the basis of the Li_2S/C electrode mass; if the calculation uses only the Li_2S mass, the capacity reaches values on the order of 1200 mA h g^{-1}. Both the capacity values and the voltage profiles compare well with those reported.[13,20,21] Therefore, the results discussed above confirm the electrochemical activity of our cathode material and demonstrate that it can be efficiently used for the development of rechargeable lithium–sulfur batteries.

An expected key advantage of the configuration adopted herein is that the polymer electrolyte acts as a barrier to prevent lithium sulfide dissolution out of the Li_2S/C electrode and thus helps to avoid capacity losses. To confirm this important assumption, we ran the test depicted in Figure 3 at a relatively low rate (*C*/20) for a total of 12 days. The test was also run at 60 °C to accelerate possible dissolution processes. No sign of dramatic capacity decay was noticed. This behavior was reproducible for various cells, and thus the results seem to be consistent in supporting the rationality of the cathode–electrolyte combination adopted to prevent lithium sulfide dissolution. However, although the liquid component is trapped in the polymer cage, some release cannot be totally excluded, especially in the course of prolonged cycling tests. In such a case, the sulfide ions present in the released liquid solution may reach the lithium metal anode and react there, and this reaction will eventually affect battery operation. In our final battery design, however, this risk is minimized by replacing the lithium metal anode with an alternative, more stable electrode.

Since the lithium ions necessary to drive the electrochemical process are provided by the Li_2S/C cathode, any material capable of accepting and releasing lithium ions can be chosen as anode to replace lithium metal. We have demonstrated this concept by selecting a tin/carbon nanocomposite, Sn/C 1:1 in weight, as the anode material alternative to lithium metal. The volume change that affects lithium-metal alloy electrodes is circumvented by using an optimized morphology in which the nanometric Sn particles are confined in a protective amorphous carbon matrix.[22] The specific capacity of this improved Sn/C electrode matches that of the Li_2S/C electrode, and this feature is very convenient for achieving cell balance when combining the two electrodes in the battery structure. Finally, and most importantly, Sn/C has a high chemical stability,[23] and we do not expect it to react with the sulfide ions that are occasionally released from the electrolyte.

The feasibility of the concept was demonstrated by assembly of a cell in which the Sn/C anode was paired with the Li_2S/C cathode across the CGPE. This arrangement is a new version of a polymer lithium-metal-free/lithium sulfide battery. Figure 4 shows a sketch of the cell.

The electrochemical process is basically the conversion of lithium sulfide into sulfur with the release of lithium ions: $2.2\,Li_2S/C \rightarrow 2.2\,S + C + 4.4\,Li^+ + 4.4\,e^-$. The lithium ions travel through the electrolyte to reach the anode where they form an alloy with the tin metal: $4.4\,Li^+ + Sn/C + 4.4\,e^- \rightarrow Li_{4.4}Sn + C$. The total process is the reversible reaction of the lithium–tin alloy with elemental sulfur to form tin metal and lithium sulfide. Figure 5 shows the voltage profiles of a few charge–discharge cycles of this battery, which gives an energy density of the order of 1000 or 2000 $Wh\,kg^{-1}$, depending whether the mass of Li_2S/C or the mass of the Li_2S active material only is considered.

The sloping trend of the voltage profiles and the large charge–discharge overpotential are likely due to a still not sufficiently high conductivity of the cathode mass. We are currently addressing this issue by optimizing the cathode morphology. Figure 6a shows the low-rate cycling performance of the SnC/Li_2S polymer battery described herein. Although a slight decay in capacity does occur upon cycling, no sign of dramatic capacity failure is observed. This evidence, combined with the fact that the test shown in Figure 6a lasted for several days, is a good indication of the stability of our cathode material. This stability is further confirmed by Figure 6b which shows the cycling of the battery at a relatively high rate: the capacity is lower, owing to rate effects, but the cell keeps its value upon prolonged cycling with an excellent charge–discharge efficiency. The result confirms that the chemistry adopted herein effectively prevents the dissolution of lithium sulfide.

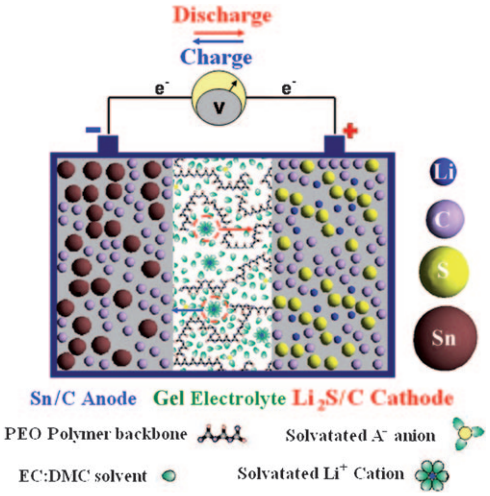

Figure 4. Sketch of the Sn/C/CGPE/Li_2S/C polymer battery developed herein. The battery is formed by a Sn/C composite anode, a PEO-based gel polymer electrolyte, and a Li_2S/C cathode. PEO = poly(ethylene oxide).

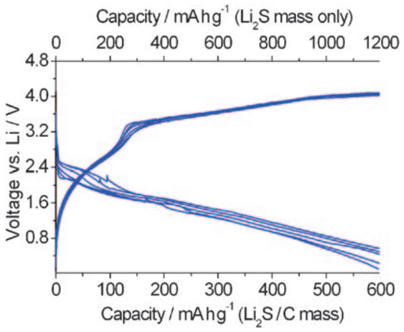

Figure 5. Typical charge–discharge voltage profiles and capacity of a Sn/C/CPGE/Li_2S/C battery. Operating temperature 25 °C. Cycling rate: charge: 76 $mA\,cm^{-2}\,g^{-1}$ (C/10), discharge: 38 $mA\,cm^{-2}\,g^{-1}$ (C/20). The capacity is shown both in terms of Li_2S/C mass and in terms of Li_2S active material mass only.

In summary, we demonstrate that the strategy proposed herein leads to an advanced tin–sulfur lithium ion battery that

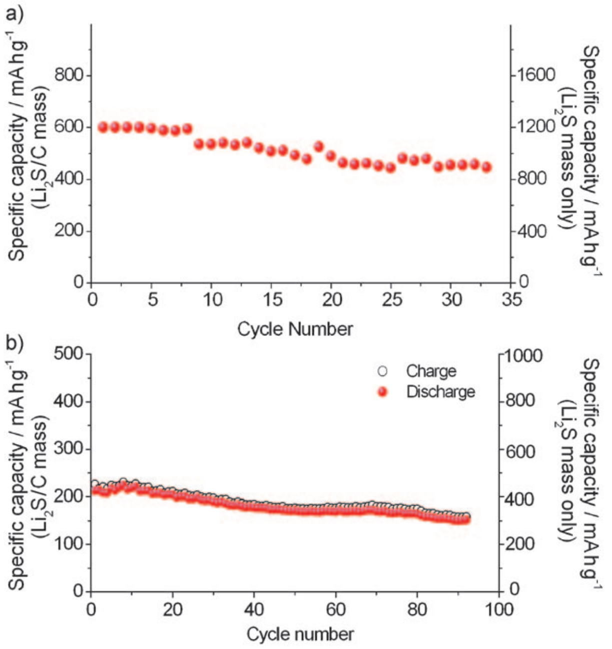

Figure 6. Capacity versus cycle number of a Sn/C/CPGE/Li_2S/C battery a) at 38 $mA\,cm^{-2}\,g^{-1}$ (C/20) in a 0.2–4 V voltage range and b) at 152 $mA\,cm^{-2}\,g^{-1}$ (C/5) in a 0.2–4.6 V voltage range. Operating temperature 25 °C. The capacity is shown both in terms of Li_2S/C mass and in terms of Li_2S active material mass only.

benefits from an entirely new electrode and electrolyte configuration. The materials used in this configuration may have been discussed separately in the literature, but to our knowledge they have never been considered in a single battery system. The reported results show that this innovation is effective in controlling most of the issues that have, to date, prevented practical exploitation of the lithium–sulfur electrochemical system and give rise to a novel tin–lithium sulfide battery that provides a specific energy on the order of 1100 $\mathrm{W\,h\,kg^{-1}}$, a value not previously achieved for a lithium-metal-free battery.

The assembly of the cathode in its discharge state and its combination with a gel electrolyte containing a Li_2S-saturated liquid solution is a valid approach for controlling the dissolution of the polysulfide ions, a major problem affecting the shelf life and cycle life of known lithium–sulfur batteries. The use of a tin/carbon composite eliminates the risk of anode attack by the sulfide anions, which is very high in batteries using a lithium metal anode.

Finally, the replacement of the conventional, liquid-based electrolyte with a polymer membrane gives an extra contribution in improving the overall operation and the safety of the battery. In addition to safety, the use of polymer electrolytes provides to the battery all those advantages that are typical of plastic batteries, such as ease of fabrication and modularity in design. A test run in a battery using a conventional liquid electrolyte showed a very rapid decay in the cycling response (Figure S-2 in the Supporting Information). This result confirms the beneficial role of the polymer electrolyte in preventing Li_2S_x dissolution. Certainly, the road to a practical lithium–sulfur battery is still long: optimization in electrode morphology and cell structure are needed to further improve the cycle life and the rate capability. Nevertheless, we hope that the work reported herein may contribute to the achievement of this technologically important target.

Experimental Section

The Li_2S/C electrode was prepared by low-energy glass ball milling by blending, under an argon atmosphere, pure crystalline lithium sulfide (Li_2S, Aldrich) and Super P carbon (SP) in a 1:1 weight ratio. The sieved and dried components were introduced inside sealed polyethylene bottles, where they were intimately mixed by ball milling for at least 24 h to obtain a homogeneous powder mixture. The Li_2S/C electrode was than fabricated as a thin film by hot pressing on an aluminum support a blend formed by 70 % Li_2S/C (active material) and 30 % $PEO_{20}LiCF_3SO_3$ (binder).

The Sn/C electrode and the $PEO_{20}LiCF_3SO_3 + 10\,\mathrm{wt\,\%}\ ZrO_2$ dry electrolyte membrane were prepared according to published procedures.[22–25] The final gel polymer electrolyte was formed by swelling the $PEO_{20}LiCF_3SO_3 + 10\,\mathrm{wt\,\%}\ S\text{-}ZrO_2$ membrane for 10 min with the EC/DMC 1:1 $LiPF_6$ 1 M solution saturated by Li_2S.

Potentiodynamic cycling with galvanostatic acceleration (PCGA) was performed by setting stepwise potential scans of 10 mV and minimum current limits of 20 μA within a 1.5–3.8 V voltage range using a VMP Biologic Science instrument. A three-electrode cell with Li_2S/C as the working electrode and lithium metal as counter and reference electrodes was used for this test. The charge–discharge test was carried out in a galvanostatic mode using a two-electrode cell similar to the previous one with the exclusion of the reference lithium electrode. The cycling protocol was run and controlled by a Maccor Series 4000 Battery Test System instrument.

The ionic conductivity of the electrolyte was measured by AC impedance spectroscopy in the 100 kHz–1 Hz frequency range using a frequency response analyzer (FRA; Schlumberger Solartron model 1260) coupled with a potentiostat (EG&G Princeton Applied Research model 362). The conductivity cells were prepared by sandwiching the electrolyte membrane samples, which had an 8 mm diameter and were housed in a Teflon O ring, between two blocking stainless steel electrodes. The O ring encircled the membrane sample so as to fix thickness throughout the test duration.

The $Sn/C/CGPE/Li_2S/C$ polymer battery prototypes were assembled in 1.0 cm diameter T-cells. The charge–discharge cycling responses were run and controlled by a Maccor Series 4000 Battery Test System.

Received: December 29, 2009

Keywords: batteries · electrochemistry · lithium · sulfur · tin

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