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Lithium/sulfur batteries with high specific energy: old challenges and new opportunities

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In this review, we begin with a brief discussion of the operating principles and scientific/technical challenges faced by the development of lithium/sulfur cells. We then introduce some recent progress in exploring cathodes, anodes, and electrolytes for lithium/sulfur cells. In particular, several effective strategies used to enhance energy/power density, obtain good efficiencies, and prolong cycle life will be highlighted. We also discuss recent advancements in techniques for investigating electrode reactions in real time and monitoring structural/morphological changes of electrode materials under cell operating conditions to gain a better understanding of the mechanistic details of electrode processes. Finally, the opportunities and perspective for future research directions will be discussed.

1 Introduction

Electrical energy storage systems play an important role in the efficient use of electricity in micro-grids or smart-grids to compensate for the mismatch between demand and supply, especially for renewable energy sources of intermittent and cyclic nature (*e.g.*, solar- or wind-based electrical generation).[1] In the transportation sector, the transition from the current hybrid electric vehicles (HEVs) to all-electric vehicles (EVs) hinges critically on the development of electrical energy storage systems with dramatically improved specific energy (gravimetric energy density), specific power (gravimetric power density), durability, and reduced cost.[2] Among available electrical energy storage systems, rechargeable lithium-ion batteries represent the state-of-the-art technology and remain the best solutions for many applications.[3–5] Notably, lithium-ion batteries play an important role as the primary power source in portable electronics such as smart-phones and laptops, thus greatly influencing the performance, portability, and reliability of these devices. The energy and power characteristics of energy storage systems will critically impact the commercial viability of emerging advanced technologies.

However, the performance of current lithium-ion batteries is not capable of meeting tomorrow's energy storage requirements for advanced transportation, portable, and residential applications.[6] For instance, new energy storage systems with substantially higher specific energy and excellent cycle life must be developed if electric vehicles are to be widely adopted as replacements for gasoline-powered vehicles.[2] The obtainable specific capacities of current positive electrode materials remain insufficient to meet the ever-increasing requirements of the rapidly progressing emerging technologies.[7,8] Therefore, explorations of new materials and new chemistries are urgently needed to go beyond incremental improvements in the specific energy of existing batteries.

When the heavy positive electrode material (typically oxides or phosphates) in a lithium-ion cell is replaced by a light-weight sulfur (usually porous carbon–sulfur nanocomposites) electrode, we have a lithium/sulfur cell with dramatically higher specific energy. Since their first introduction in 1962, lithium/sulfur cells were first investigated as high-temperature cells with a molten salt electrolyte in the late 1960s.[9,10] With its high theoretical specific capacity (1675 mA h g^{-1}), sulfur has been considered to be one of the most promising alternatives to replace existing positive electrode materials used in lithium cells. The theoretical specific energy and volumetric energy density of a lithium/sulfur cell is often stated as $\sim$2600 W h kg^{-1} and $\sim$2800 W h L^{-1}, respectively, under the assumption of complete Li_2S formation, which is far greater than that of current lithium-ion cells as shown in Fig. 1 and Table 1.[2,11,12]

In addition to its high theoretical specific capacity, sulfur is inexpensive, abundant on earth, and environmentally benign. With these appealing features, lithium/sulfur cells are considered to be the next-generation power source in emerging advanced technologies such as electric vehicles where weight is a critical factor. However, in order to realize this potential, numerous scientific and technical challenges

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are yet to be overcome; there is still a long way to go for the development of lithium/sulfur cells with high specific energy.

In this review, we begin with a brief discussion on the operating principles and scientific/technical challenges faced by the development of lithium/sulfur cells. We then introduce some recent progress in exploring positive electrodes, negative electrodes, and electrolytes for lithium/sulfur cells. In particular, several effective strategies used to enhance energy/power density, obtain good efficiencies, and prolong cycle life will be highlighted. We also discuss recent advancements in techniques for investigating electrode reactions in real time and monitoring structural/morphological changes of electrode materials under cell operating conditions to gain a better understanding of the mechanistic details of electrode processes. Finally, the opportunities and perspectives for future research directions will be discussed.

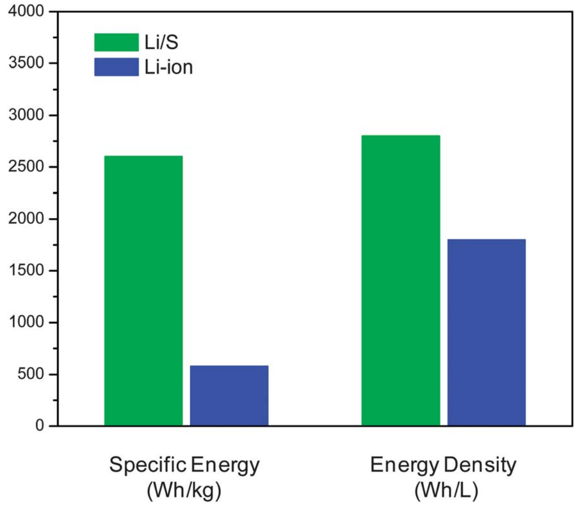

Fig. 1 Comparison of theoretical specific energy and energy density of the lithium/sulfur cell with those of current lithium-ion cells.

Table 1 Comparison of characteristics of lithium-ion cells and lithium/sulfur cells

Characteristic	Lithium-ion cells	Lithium/sulfur cells
Cell voltage	3.4–4.0 V	2.15 V
Cathode specific capacity	140–200 mA h g^{-1}	1675 mA h g^{-1}
Theoretical specific energy	500–600 W h kg^{-1}	~2600 W h kg^{-1}
Practical (obtainable) specific energy	150–200 W h kg^{-1}	200–700 W h kg^{-1} (estimated)
Theoretical energy density	~1800 W h L^{-1}	~2800 W h L^{-1}
Cycle life (current status)	300–1000 deep cycles	<200 cycles

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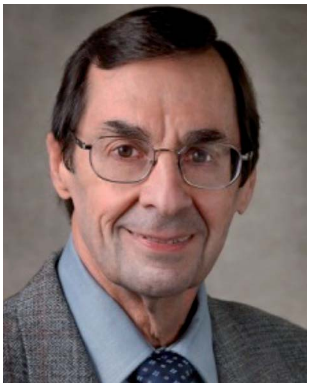

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Yuegang Zhang received his B.S. and M.S. degrees in Physics from Tsinghua University and Ph.D. degree in Materials Science from the University of Tokyo. He conducted research on nanotubes and nanowires at NEC Fundamental Research Labs and Stanford University before he joined Intel Corporation in 2002 where he led the Intel Carbon Nanotube Research Project and chaired Intel Memory Strategic Research Sector. During his tenure at Lawrence Berkeley National Laboratory, he conducted research on a graphene based electronic device and electrochemical energy storage. He is currently a Professor at the Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences.

2 Fundamentals of lithium/sulfur cells

2.1 Operating principles

To date, two different configurations of lithium/sulfur cells have been investigated, depending on where lithium sources are located, as schematically shown in Fig. 2. Both cell configurations can employ either liquid electrolytes or solid electrolytes. In the most common configuration investigated thus far, lithium metal serves as the negative electrode and is electrochemically coupled with sulfur as the positive electrode. During discharge, lithium ions move spontaneously through the electrolyte from the negative electrode to the positive electrode while electrons flow through the external circuit, delivering electrical energy. During charge, both lithium ions and electrons are forced back in the opposite direction by applying an external voltage, storing electrical energy as chemical energy in the cell. When pre-lithiated sulfur (*e.g.* Li_2S) is used as the positive electrode, other high-capacity electrode materials (*e.g.* silicon or tin-based compounds which can form alloys with lithium) are often used as the negative electrode with improved safety.[13,14] As the positive electrode is in the fully discharged state (Li_2S), the cell needs to be charged first. After the first charge, the cell behaves in the same manner as cells with sulfur as the starting material.

In both configurations, the electrochemistry occurring at the positive electrode is far more complex than intercalation chemistry of conventional lithium-ion cells because of the phase transformations of sulfur that occur during cell operation.[15] Overall, the electrochemical reaction can be described as below, assuming the formation of Li_2S from elemental sulfur during discharge and *vice versa*.

$$S_8 + 16Li \leftrightarrow 8Li_2S;\ E^0 = 2.15\ V$$

Although solid sulfur (S_8 is the most stable form at standard temperature and pressure) is employed in most cases as the electrode material, the solid sulfur is reduced to form polysulfides at the beginning of discharge. These polysulfides are soluble in many organic solvent based electrolytes. In fact, lithium/sulfur cells were explored as electrochemical power sources employing a liquid polysulfide positive electrode,[16] although the fully oxidized state (S_8) and the fully reduced state (Li_2S) are solid.

When the elemental sulfur octet, S_8, is subjected to discharge (electrochemical reduction), in general, two or three plateaus appear in the discharge curve, depending on the choice of electrolytes.[9,17,18] Typical cyclic voltammograms and charge–discharge profiles of lithium/sulfur cells are shown in Fig. 3. During the cathodic scan of Fig. 3a, three main reduction peaks at around 2.4, 2.1 and 1.8 V appear. The peak at about 2.4 V can be assigned to the reduction of elemental sulfur to higher-order polysulfides (Li_2S_n, $n \geq 4$). The peaks at about 2.1 and 1.8 V correspond to the further reduction of high-order polysulfides to low-order polysulfides (Li_2S_n, $1 < n < 4$) and Li_2S. Similarly, during the constant-current discharge of Fig. 3b, in general, two or three plateaus are observed. The high-voltage plateau (2.4–2.1 V) is related to the reduction of elemental sulfur to the higher-order lithium polysulfides (Li_2S_n, $n \geq 4$).

$$S_8 + 2Li \leftrightarrow Li_2S_8$$

$$Li_2S_8 + 2Li \leftrightarrow 2Li_2S_4$$

Li_2S_8 is unstable in many aprotic electrolytes and undergoes disproportionation to form Li_2S_n, which can also experience electrochemical reduction.

$$Li_2S_8 \leftrightarrow 2Li_2S_n + (8 - n)S$$

Further reduction of high-order polysulfides (Li_2S_n, $n \geq 4$) to low-order polysulfides (Li_2S_n, $n < 4$) and lithium sulfide occurs at the low-voltage plateau (<2.1 V).

$$Li_2S_4 + 2Li \leftrightarrow 2Li_2S_2$$

$$Li_2S_2 + 2Li \leftrightarrow 2Li_2S$$

Because of the low solubility and the slow kinetics of Li_2S_2 in typical electrolytes, further reduction to Li_2S may not be completed; contradicting results on this issue were reported in the literature.[19,20] The mechanistic details of the electrochemical reduction process of lithium polysulfides are very complex and need deeper understanding. Reaction pathways may be also quite different depending on the composition of the electrolyte.

2.2 Factors influencing cell performance

(1) Formation/dissolution of lithium polysulfides and their high mobility in typical electrolytes. The solubility and transport properties (such as diffusivity) of lithium polysulfides in the electrolyte can significantly influence the electrochemical utilization of sulfur (*i.e.*, discharge capacity), rate capability and cycle life of lithium/sulfur cells. The main impediment originates from the dissolution of high-order lithium polysulfides, Li_2S_x ($4 \leq x \leq 8$), formed in the early stages of the discharge process. Dissolved polysulfide anions (S_n^{2-}) can diffuse through

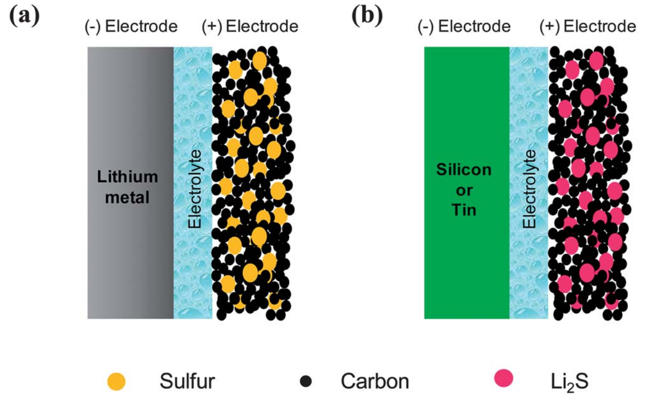

Fig. 2 Schematic diagrams of two starting configurations of lithium/sulfur cells.

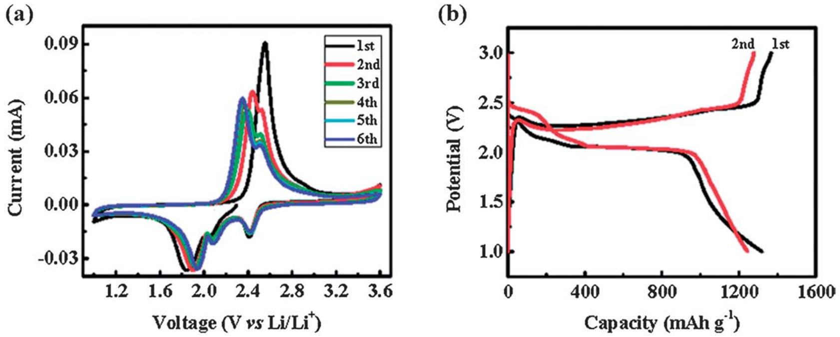

Fig. 3 Typical (a) cyclic voltammetry curves and (b) constant-current discharge and charge profiles of a lithium/sulfur cell employing graphene oxide–sulfur composite electrodes.[17] Reprinted with permission. Copyright 2011 American Chemical Society.

the separator to the negative electrode and undergo chemical reactions with the lithium metal, leading to the loss of sulfur from the positive electrode, corrosion of the lithium metal, and self-discharge.[21,22] These influences make optimization of the electrode and electrolyte very important for high-performance lithium/sulfur cells.

(2) **Insulating nature of sulfur and Li_2S.** The poor intrinsic conductivity (5×10^{-30} S cm^{-1} at 25 °C) of sulfur often leads to low electrochemical utilization and limited rate capability, which necessitates intimate contact with conductors (*e.g.*, porous carbons).[23,24] Moreover, polysulfides that are not lost from sulfur electrodes during cycling are further reduced to insulating Li_2S_2 and/or Li_2S. Therefore, to enhance the electrode kinetics, improve the cyclability, and reduce the energy loss associated with the discharge–charge overpotentials, porous carbons with high surface area are often introduced to the positive electrodes. It should be noted that both porous carbons and other current-collecting additives are important for achieving high specific energy and specific power with reasonable service life.

(3) **Volume/morphology change of the sulfur electrode during cycling.** The performance of lithium/sulfur cells is often limited by the deterioration of microstructure or architecture of the electrodes associated with the volume expansion/contraction (~76%) and morphology change of the active electrode material during cycling. Avoiding the agglomeration of sulfur particles during cycling is difficult regardless of the initial morphology of the composite electrodes. When charging, dissolved polysulfides in the electrolyte can be oxidized to sulfur on the surface of the positive electrode, which might be no longer in the intimate contact with electrically conductive carbon.[25] The migration of sulfur (as polysulfides) from the positive electrode accounts for the loss of active material and can even lead to structural failure of the electrode.

(4) **Polysulfide shuttle between negative and positive electrodes during cycling.** When discharging a lithium/sulfur cell, the elemental sulfur is reduced to form soluble high-order polysulfides (or the low-order polysulfides are oxidized to high-order polysulfides during charge) at the sulfur electrode and create a concentration gradient inside the cell. Due to the higher concentration of high-order polysulfides at the positive electrode than that at the negative electrode, these high-order polysulfides can diffuse to the negative electrode and undergo chemical reactions with lithium to form low-order polysulfides and even insoluble Li_2S or Li_2S_2 if the lithium metal electrode is not protected. As a result of diffusion and chemical reaction, the lithium electrode may have a relatively high concentration of low-order polysulfides. These lower-order polysulfides can diffuse back to the sulfur electrode and can be oxidized to higher-order polysulfides. This phenomenon, the diffusion back and forth of polysulfides between the two electrodes is known as the "polysulfide shuttle," which is unique to lithium/sulfur cells.[21] These issues appear to be a significant cause for capacity fading and we should understand the mechanistic details of these complex, interrelated processes in order to dramatically extend the cycle life of lithium/sulfur cells.

(5) **Interrelated causes for capacity loss.** We should be aware that the polysulfide shuttle is related not only to the sulfur electrode but also to the lithium electrode and the electrolyte. Both discharge and charge capacities are significantly affected by this phenomenon. For example, once insulating Li_2S forms on the lithium surface by chemical reaction of polysulfide anions with lithium metal, this passivation layer can make the cycling efficiency of the lithium electrode worse and increase the cell resistance. The polysulfide shuttle, if it takes place, can result in fast capacity fading. It also reduces the charge/discharge efficiency of lithium/sulfur cells especially at the high voltage plateau and can cause fast self-discharge. The rapid decrease of the high voltage plateau capacity is ascribed to the high chemical reactivity of high-order polysulfide anions with lithium metal. Capacity decay at the low-voltage plateau is associated with degradation of the electrode structure and the precipitation of insoluble Li_2S on the surface of both negative and positive electrodes. When insulating Li_2S is formed on the surface of the sulfur electrode, it can passivate the electrode and increase the cell resistance, leading to capacity loss and poor rate capability. Even when the cell is fully charged, Li_2S may remain on the sulfur electrode.[26]

The strategy for improving a single component may not be able to address all of the issues that are interlinked. More comprehensive approaches are required to remedy this complicated situation in order to dramatically improve the cycling stability of lithium/sulfur cells.

2.3 Key challenges facing the development of lithium/sulfur cells

Lithium/sulfur cells have not yet been commercialized due to the following issues which need to be fully addressed before the full potential of lithium/sulfur cells can be realized:

(1) The obtainable specific energy (or discharge capacity) is lower than the theoretical value and decreases with the increasing rate of discharge. The cycle life of lithium/sulfur cells is less than that of current lithium-ion cells.

(2) The power density is not yet sufficient for the intended applications such as electric vehicles due to the low intrinsic conductivity of elemental sulfur and the slow kinetics of reduction of low-order polysulfides.

(3) Soluble long-chain polysulfide species lead to chemical shorting of the cell by the diffusion of polysulfides during cycling. Once the polysulfide shuttle occurs, the active mass of sulfur is decreased, coulombic efficiency is lowered, and the deposition of insoluble layers (Li_2S and/or Li_2S_2) on both positive and negative electrodes can interfere with mass transport, leading to a loss of capacity.

(4) When lithium metal serves as the negative electrode, dendrite formation must be effectively mitigated to avoid cell shorting and safety concerns. The poor cycling efficiency of lithium metal should also be improved. When a solid electrolyte is used, unwanted reaction between the lithium metal and the solid electrolyte should be avoided.

(5) Finding a good electrolyte with high conductivity and electrochemical/chemical stability has been a grand challenge even for conventional lithium-ion cells. In lithium/sulfur cells, minimizing the liquid phase diffusion of polysulfides while achieving good utilization of sulfur (*i.e.*, high capacity) remains an additional hurdle.

In the following section, we will discuss some recent progress in exploring positive electrodes, negative electrodes, and electrolytes to mitigate these challenges facing the development of high specific energy lithium/sulfur cells.

3 The latest developments and new opportunities

In this section, we discuss recent technical approaches and provide specific examples in order to highlight the important progress recently made to improve specific energy/power, obtain good efficiencies and improve cycling stability as steps toward high-performance lithium/sulfur cells.

3.1 Recent progress in sulfur electrodes

The positive electrode in high-capacity lithium/sulfur cells has been intensively studied.[27–52] As discussed earlier, the main challenge results from the formation/dissolution of lithium polysulfides and their high mobility in typical electrolytes.[21,30,53] During cycling, sulfur undergoes a solid-to-solid phase transformation through liquid intermediates and this poses a grand challenge for the cyclability of sulfur electrodes. The ideal sulfur electrode must maintain its structural integrity during cell operation. When dissolved polysulfides are reduced to solid Li_2S and/or Li_2S_2, these solid phases should be uniformly deposited inside the sulfur electrode in order to allow for complete reaction of all of the sulfur. Additionally, the ideal electrode has to maintain a porous structure to provide pathways for lithium ions while retaining good electrical connectivity to facilitate electron transport. Once the polysulfide shuttle occurs, high-order polysulfides can migrate to the lithium electrode. Ideally, when these mobile polysulfide species shuttle back to the positive electrode, solid sulfur deposits should be formed inside the porous electrode to maintain close contact with the conductive carbon.

Recent advances in nanoscience and nanotechnology have offered exciting opportunities for the development of advanced lithium-ion cells.[4] In lithium/sulfur cells as well, the capability to synthesize nanostructured sulfur electrodes with tailored, high surface area architectures holds a great potential to maximize sulfur loading and constrain dissolved polysulfides within the positive electrodes, thereby dramatically improving specific energy and cycling performance. Porous electrodes with a wide variety of nanostructures or nano-architectures have been investigated to help alleviate the difficulties facing the development of electrodes for high-performance lithium/sulfur cells. Their advantages are briefly summarized as follows:

(1) Large surface area can increase the number of active sites for electrode reactions by enlarging the contact area between the electrode and the electrolyte, thereby reducing electrode polarization loss and improving high-rate capability and energy efficiency.

(2) Porous electrodes offer more possibilities for surface modification to obtain multi-functionality in order to enhance surface reactivity and to constrain liquid polysulfides inside the positive electrode.

(3) For electrode materials with very low electronic conductivity (*e.g.*, Li_2S_x after discharge), a large surface to volume ratio can increase the contact area between the active material and the distributed current collectors to provide for efficient utilization of the active materials, which in turn increases usable specific energy and reduces electrode polarization.

(4) Short diffusion lengths associated with the nanoscale dimensions of nanostructured electrodes can effectively reduce the distance that lithium and electrons must travel in the solid state through electrode materials during operation.

(5) Ionic and electronic conductivity can also be enhanced by the formation of nanocomposites, in which the extended interfaces between the phases ensure fast transport of ionic and electronic species.

Cell performance is often limited by the performance of the constituent materials of electrodes such as conductive additives and binders. It is very important to understand that these constituent materials play significant roles in providing for maximum performance. It is often expected that sophisticated nanoscale control of electrode parameters such as pore size, morphology, and architecture can lead to a significant improvement in electrochemical performance, but this can only be realized with a proper choice of optimized binders and conductive additives. In the following section, the latest advancements in design, synthesis, and optimization of various nanostructured sulfur electrodes will be discussed.

3.1.1 Design of carbon–sulfur nanocomposites.

Since elemental sulfur has inadequate electronic conductivity (5×10^{-30} S cm^{-1} at 25 °C), the use of conductive carbons with high surface area and porosity is essential to achieve good utilization of sulfur in positive electrodes, especially at high rates. Various sulfur–carbon composites have been investigated and some improvements were reported.[22,27,32,38,54–60] However, inhomogeneous contact between sulfur and carbon materials leads to capacity fading upon cycling and low efficiency. Recently, Nazar and coworkers reported that positive electrodes based on highly ordered composites of sulfur and mesoporous carbon (CMK-3), prepared by a simple "melt-diffusion strategy" at 155 °C where the viscosity of liquid sulfur is the lowest, can exhibit high reversible capacity with good cycling performance and efficiency.[33] The use of a conductive mesoporous carbon framework constrained sulfur within its pores/channels and produced intimate electrical contact. After heat treatment, the electrical conductivity of carbon–sulfur composites remained the same because sulfur occupied the channels of the mesoporous carbon and did not coat the external surface. The inhibition of polysulfide diffusion due to the adsorption properties of mesoporous carbon effectively reduced the polysulfide shuttle. To further constrain polysulfides, the surface properties of the C/S composite were modified by coating with polyethylene glycol (PEG) after sulfur infiltration. The PEG-modified material could effectively trap highly polar polysulfide species by providing a hydrophilic chemical gradient on the surface, thus limiting the concentration of polysulfide anions in the electrolyte. As shown in Fig. 4, deposition of solid Li_2S on the positive electrode surface was successfully inhibited, indicating the importance of "polymer protection" to obtain good cyclability of sulfur electrodes. However, the authors reported cycling performance up to only 20 cycles, still insufficient for lithium/sulfur cells to be considered as a practically viable option. Additional strategies to trap or immobilize lithium polysulfides during cycling are needed.

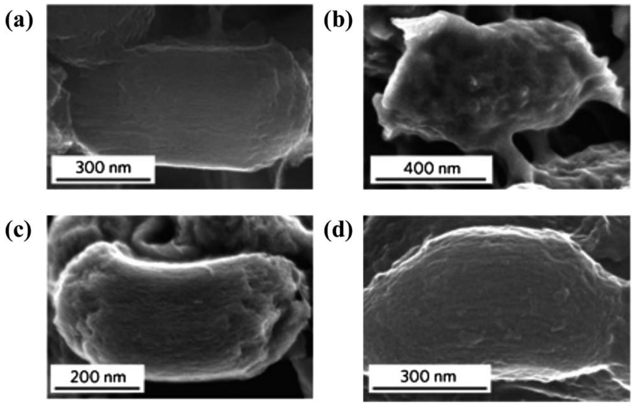

Fig. 4 SEM images of carbon–sulfur composites (a) before and (b) after cycling showing the precipitation of insoluble products on the surface. SEM images of PEG-modified carbon–sulfur composites before (c) and after cycling (d) showing very little changes in morphology.[33] Adapted by permission from Macmillan Publishers Ltd.: *Nat. Mater.*, copyright 2009.

Recently, a low-cost and environmentally benign chemical reaction–deposition strategy to immobilize sulfur on quasi-two dimensional graphene oxide (GO) was reported.[17] This chemical reaction–deposition approach reliably provides intimate contact between sulfur and carbon, which would not necessarily be the case for ball milling and thermal treatment (melt-diffusion). After a nanoscale sulfur coating was deposited onto GO sheets by chemical reaction in a micro-emulsion system, the as-prepared samples were heat-treated in order to remove some bulk sulfur which is not in direct contact with the GO layers. When GO–S nanocomposites are heat treated, the bulk sulfur melts and can diffuse into the pores of GO due to strong adsorption effects derived from both the high surface area and the functional groups on the surface of the GO. At the same time, this mild heat treatment process can partially remove and/or chemically modify some of the functional groups on the GO surface, thereby improving the conductivity of the as-synthesized GO–S nanocomposite. The unique structure of the GO–S nanocomposite can significantly improve the overall electrochemical performance. First, it can accommodate the significant volume changes of sulfur when it is converted to Li_2S and back to sulfur. Additionally, partially reduced GO with its large surface area along with ubiquitous cavities can create more intimate electronic contact with the sulfur and avoid agglomeration and the loss of electrical contact from the current collector during operation. Further, the low-temperature heat-treated GO still contains various kinds of functional groups, which can have strong adsorption to anchor sulfur atoms and effectively prevent the subsequently formed lithium polysulfides from dissolving into the electrolyte during cycling, which was confirmed by *ab initio* calculations and soft X-ray absorption spectroscopy (XAS) measurement as shown in Fig. 5. Hydroxyl and epoxy groups can enhance the binding of S to the C atoms due to the induced ripples by functional groups, showing the important roles of functional groups in extending the cycle life of sulfur electrodes. Indeed, novel GO–S nanocomposite electrodes displayed good reversibility and excellent cycling stability up to 50 cycles. It is expected that the electrochemical performance of GO–S nanocomposite electrodes will be further improved when coupled with the optimized electrolyte and protected lithium metal electrodes. Although GO–S composite electrodes exhibited an acceptable reversible capacity of ~370 mA h g^{-1} at 2 C, their rate capability would be insufficient to be used for high-power applications such as electric vehicles or power tools.

In general, to obtain high power density or rate capability, the electrode must have proper architecture and nano-structure to enhance fast charge transfer across interfaces and rapid transport of lithium ions to active sites for electrode reactions. Thus, the design of electrode materials with proper morphology, microstructure, and architecture is crucial to the development of lithium/sulfur cells with far better high-rate capability. The poor electronic conductivity of sulfur is a major factor limiting the effective utilization of the active material at high rates. Recently, porous hollow carbon–sulfur composites were shown to have excellent rate capability.[9] In this work, mesoporous hollow carbon capsules were synthesized using a

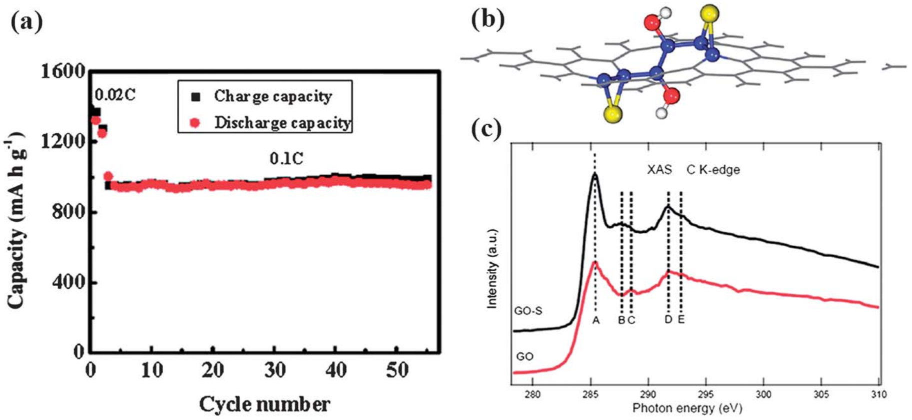

Fig. 5 (a) Cycling performance of GO–S electrodes. (b) Representative drawing of GO immobilizing sulfur. Yellow, red and white balls represent S, O, and H atoms while others are C atoms. (c) C K-edge XAS spectra of GO and GO–S nanocomposites after heat-treatment.[17] Reprinted with permission. Copyright 2011 American Chemical Society.

template-based method, and sulfur was encapsulated inside a porous shell by a vapor-phase infusion method. When employed as positive electrodes, these nano-capsules exhibited a discharge capacity of 1071 mA h g^{-1} at 0.5 C and showed 91% capacity retention after 100 cycles. More importantly, these nanocomposites showed excellent rate capability of over 600 mA h g^{-1} at 2 C and 450 mA h g^{-1} at 3 C with relatively large sulfur loading (70% S in the composite and ~65% S in the total electrode), as shown in Fig. 6. It was claimed that the pores in the porous carbon framework are large enough to allow fast access of lithium ions and that the partially graphitic character of the carbon framework could provide fast transport of electrons to (and from) the insulating sulfur.

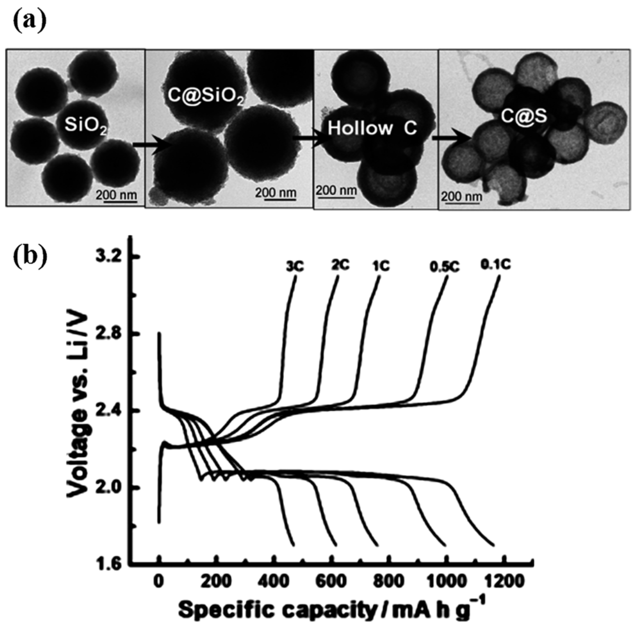

Fig. 6 (a) TEM images of hollow carbon spheres (left) and carbon–sulfur nanocomposites (right).(b) Typical charge–discharge curves of hollow carbon–sulfur composites recorded at different rates, showing excellent rate capability.[9] Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

Interestingly, the effect of a graphitized carbon layer on the electrochemical performance of sulfur electrodes was also discussed in another recent report but with a slightly different view.[61] As shown in Fig. 7, disordered carbon nanotubes (DCNTs) were synthesized by a template wetting method using anodic aluminum oxide (AAO) membranes. After removing the AAO template, sulfur impregnation was performed by putting sublimed sulfur powders on top of DCNTs and dropping CS_2 to dissolve and infuse the sulfur. Then, as-synthesized samples were sealed in quartz tubes under vacuum and heat-treated at three different temperatures (160, 300 and 500 °C), forming sulfur-impregnated DCNTs (S-DCNTs). DCNTs possess graphitic clusters and amorphous carbon structures.

It was claimed that vaporized sulfur at elevated temperature under vacuum could be intercalated into graphitized carbon layers and smaller voids/defects in the amorphous carbon structure that the liquid electrolyte cannot reach directly, preventing the polysulfide shuttle. Heat-treatment conditions had a significant effect on the electrochemical performance. Among three different samples, S-DCNTs treated at the highest temperature, 500 °C, showed the best cycling stability with capacity retention of 72.9% after 100 cycles. However, the sulfur content of the S-DCNTS treated at 500 °C was only 40%, which is significantly lower than the 60% of S-DCNTs treated at 160 °C which showed the fastest capacity decay during cycling. As sulfur content also has a strong influence on cycling performance, further studies may be necessary to confirm whether the observed improvement in cycling performance was attributed to the incorporation of vaporized sulfur into the carbon structure (Table 2).

3.1.2 Adsorption additives.

As described above, many different approaches have been used in the literature with some successfully mitigating the polysulfide shuttle. However, the cyclability of sulfur electrodes is yet to be improved further and it is still critical to find additional and more effective methods. A new strategy, "on-site adsorption" using additional adsorbents, has been employed with some success in improving the cyclability and coulombic efficiency of positive electrodes during cell operation.[62,63] In addition to conventional conductive additives

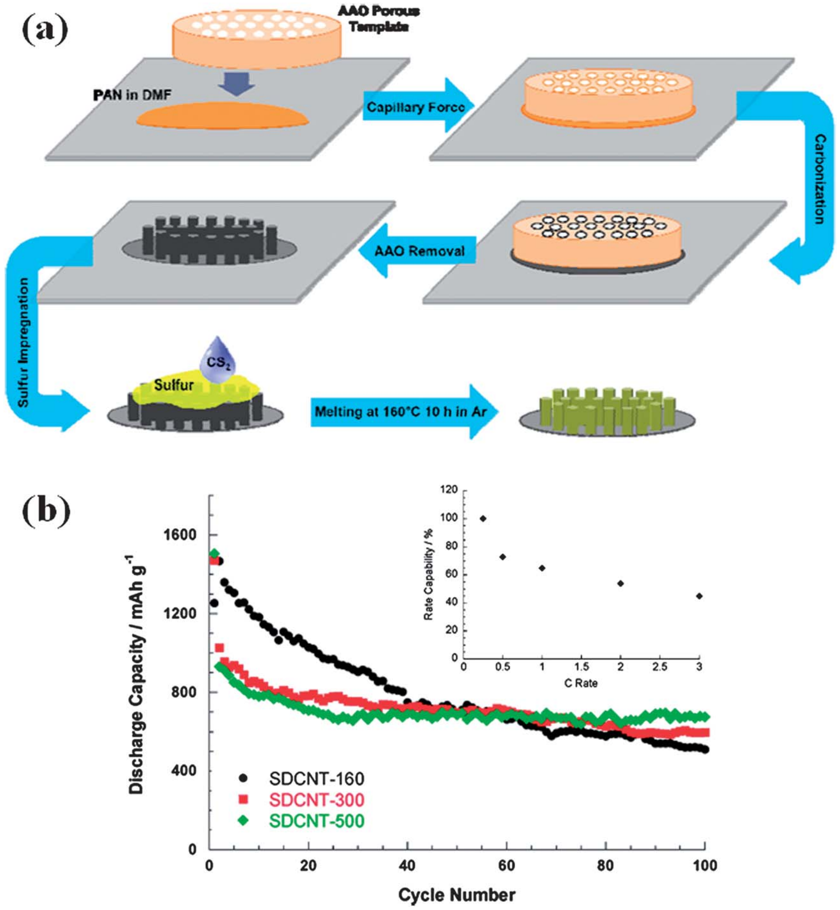

Fig. 7 (a) Synthesis process for sulfur impregnated disordered carbon nanotubes and (b) their cycling stability as positive electrodes of lithium/sulfur cells. The numbers (150, 300, and 500) represent the heat-treatment temperature.[61] Reprinted with permission. Copyright 2011 American Chemical Society.

(typically carbon blacks) for effective current collection, high surface area, micro-porous materials are added to the electrodes in order to help trap or immobilize the intermediate liquid polysulfides. An optimal adsorbent should be inert to electrochemical reactions occurring during cycling, show strong adsorption capacity, and also permit facile desorption/release of polysulfide anions.

Recently, a small fraction of porous silica particles (SBA-15, 10 wt%) were embedded within carbon–sulfur nanocomposites (90 wt%) and acted as an internal polysulfide reservoir.[63] SBA-15 has a high surface area, large pore volume, and highly hydrophilic surface properties. The cavities inside porous silica help adsorb the polysulfides by weak binding *via* the positively charged silica surface, but also allow fast desorption and release. As shown in Fig. 8, with the addition of SBA-15, the cycling performance of sulfur electrodes with adsorbent additives was better than that of electrodes without additives, although the cell experienced initial capacity fading. This concept showed some promise, but the demonstrated cycle life was less than 50 cycles and requires much longer cycling tests to confirm how stable internal polysulfide reservoirs can be; they may also lose their capability upon cycling. More importantly, the key to success of this approach is to obtain reversible adsorption/desorption behavior, but it is still not clear whether the release rate of polysulfide species from SBA-15 is constant or not. High-rate capability should be also evaluated using this approach.

3.1.3 Important role of a binder. The binder plays a vital role in improving cell performance, especially in prolonging the cycle life of lithium/sulfur cells.[24,54,64–70] The uniform mixing of the active material (sulfur) and conductive carbon is very important in developing a high performance sulfur electrode. The important requirements of a good binder include good adhesion with electrode materials and the ability to create a good electric network structure between sulfur and conductive carbon and maintain the integrity of the electrode during cycling. In the literature, polyethylene oxide (PEO) and polyvinylidene fluoride (PVDF) are the most commonly used binders, but both still pose some problems. For example, the PEO binder has poor adhesion properties[66] and the PVDF binder is often dissolved in *N*-methyl-2-pyrrolidone (NMP), which is toxic and difficult to vaporize due to its high boiling point. To address this issue, gelatin has recently been investigated as a water-soluble binder for sulfur electrodes.[66–68] Sulfur electrodes using gelatin as the binder exhibited higher initial capacity and better cycling performance than those with the PEO binder.[66] The improvement was attributed to gelatin's good adhesion property and effective dispersion of active materials during the fabrication of electrodes.

Table 2 Electrochemical performance of carbon–sulfur nanocomposite electrodes discussed in Section 3.1.1

Carbon substrate	Sulfur loading in the electrode (wt%)	Binder	Composition (C–S : additive : binder)	Electrolyte	Discharge rate	Voltage range	Discharge capacity (mA h g^{-1} S^{-1})		Reference
							Initial	After n^{th} cycle	
Porous hollow carbon	64.5	PVDF	92.5 : 0 : 7.5	1 M LiTFSI in TEGDME	0.5 C	1.7–3.1 V	1075	850 (100th)	9
Graphene oxides	46.2	PVDF	70 : 20 : 10	1 M LiTFSI in PEGDME + PYR$_{14}$TFSI	0.1 C	1.0–3.0 V	1000 (3rd)	954 (50th)	17
Mesoporous CMK-3	58.8	PVDF	84 : 8 : 8	1.2 M LiPF$_6$ in ethyl methyl sulphone	0.1 C	1.5–2.8 V	1320	1100 (20th)	33
Disordered carbon nanotubes	40	None	100 : 0 : 0	1 M LiTFSI in TEGDME	0.25 C	1.5–3.0 V	1500	700 (100th)	61

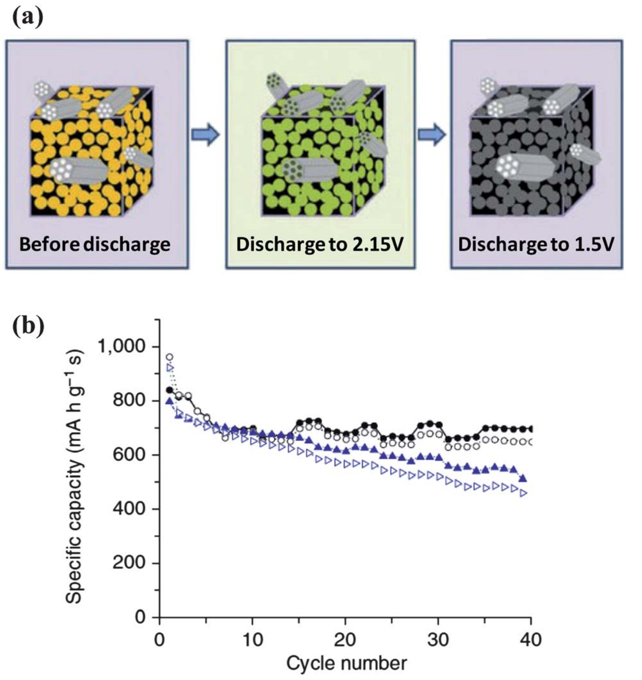

Fig. 8 (a) Schematic diagram of the concept of using a polysulfide reservoir (SBA-15) embedded in sulfur–carbon nanocomposites. The black area, grey particles, and green area represent porous carbon, SBA-15, and polysulfide species, respectively. (b) Comparison of the cycling performance of C–S composites with (black circle) and without (blue triangle) adsorption additives.[63] Adapted by permission from Macmillan Publishers Ltd.: *Nat. Commun.*, copyright 2011.

Volume change (~76%) is inevitable in the sulfur electrode during cycling and can lead to gradual capacity fading due to electrical isolation of active materials (*e.g.* elemental sulfur and/or lithium polysulfides) from current collectors, which can increase the resistance to the transport of electrons to (or from) active sites. Furthermore, the volume expansion (or contraction) of sulfur electrodes associated with solid-to-solid phase transformation from elemental sulfur to Li_2S and/or Li_2S_2 through liquid intermediates (and *vice versa*) may induce stress and strain in the positive electrodes, eventually resulting in collapse or mechanical degradation of electrodes. Therefore, elastomeric binders would be essential to maintain the integrity of the positive electrode structure during cycling. Indeed, when an elastomeric styrene butadiene rubber (SBR) binder was used with carboxy methyl cellulose (CMC) as a thickening agent, sulfur electrodes exhibited significantly improved cycling performance than those with PEO and PVDF binders.[71] The electrode with the SBR + CMC binder showed the smallest charge-transfer resistance after 30 cycles due to the improved structural integrity as shown in Fig. 9, indicating the importance of intimate contact between the sulfur and carbon during cycling. In addition to the elastomeric behavior of the SBR binder, He *et al.* found that the SBR–CMC mixture has good adhesion and dispersion capabilities, resulting in enhanced cycling performance of sulfur electrodes.[72]

3.1.4 Conductive additives. As discussed previously, to make effective utilization of carbon–sulfur composite electrodes, porous carbon and sulfur must be in intimate contact. At the same time, some conductive additives (usually carbon black or acetylene black, *etc.*) are introduced to facilitate electron transport while allowing fast ingress of lithium ions. These carbon additives must maintain good electrical connectivity to the current collector (usually metal foam/foil) to efficiently collect (or inject) electrons from (or to) active electrode materials during cell operation. Deterioration of electrode performance often results from adverse changes in the electrode microstructure during cycling. For example, reduced connectivity between carbon additives and active electrode materials may lead to electrical isolation of active electrode materials, and increased resistance to charge transport, which can result in capacity fading and poor rate capability.

In lithium/sulfur cells, it is expected that the optimization of the electrode structure *via* formation of conductive network structures would lead to improved electrochemical performance of sulfur electrodes. In this regard, the use of carbon nanofibers or nanotubes would be very helpful. Indeed, the cycling performance and rate capability of sulfur electrodes were improved when multi-walled carbon nanotubes (MWCNTs) were introduced as conductive agents.[56] The long and thin MWCNTs formed three-dimensionally porous, electronically conducting network structures, resulting in the better retention of soluble polysulfides, increased sulfur utilization, and lower charge transfer resistance measured by electrochemical impedance spectroscopy. Recently, the performance of C–S composites with

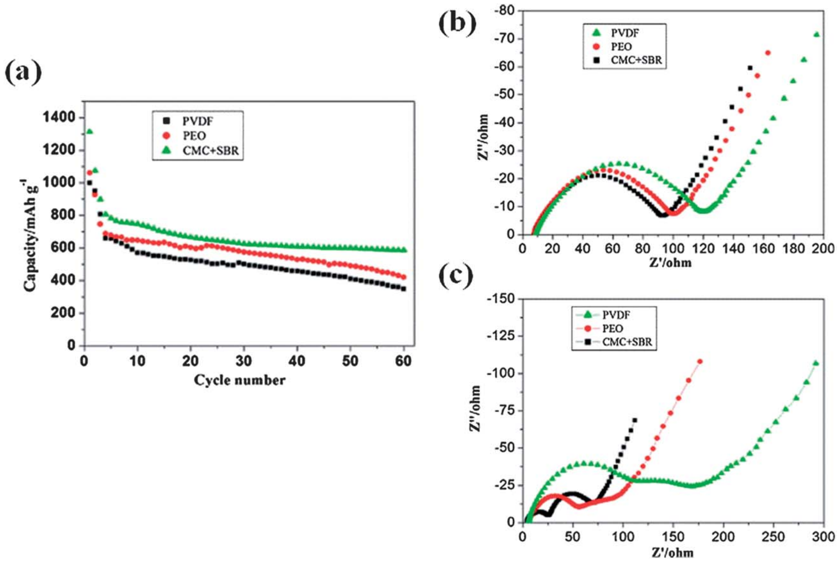

Fig. 9 (a) Cycle performance of sulfur electrodes fabricated with different binders. (b) Impedance plots of cells before cycling and (c) after the 30th discharge.[71] Copyright 2012, with permission from Elsevier.

carbon particles and carbon nanofibers was compared.[73] It was found that C–S composite electrodes with carbon nanofibers showed improvement in both discharge capacity and cycling stability, which was also attributed to the formation of a three-dimensional network structure, effectively suppressing the agglomeration of sulfur or Li_2S during cycling as shown in Fig. 10.

3.2 Recent progress in lithium metal negative electrodes

Besides the problems associated with the sulfur electrode discussed above, highly reactive lithium metal electrodes pose challenges to the development of practical lithium/sulfur cells. While lithium metal has the highest capacity (3860 mA h g^{-1}) of all solid electrodes,[74–76] the use of lithium metal as a negative electrode material in rechargeable batteries has been avoided due primarily to safety concerns arising from the high reactivity toward conventional electrolytes.[77] Also, dendrite growth during cycling can eventually result in shorting between the two electrodes and a catastrophic thermal runaway of the cell.[78] Surface modification of lithium metal electrodes to minimize or eliminate dendrite formation represents a challenge to the utilization of lithium metal electrodes in rechargeable cells. In lithium/sulfur cells, the challenges are even greater. Due to the polysulfide shuttle phenomenon, soluble polysulfides can corrode the lithium electrode. The insoluble Li_2S_2 and/or Li_2S deposited on the lithium electrode surface can passivate the lithium electrode. The passivation layer can gradually grow during cell operation, leading to capacity fading and high cell resistance. To address these issues, protected lithium metal electrodes have been developed to mitigate the parasitic chemical reactions with the soluble polysulfides. However, finding a suitable material for protecting the lithium metal electrode while maintaining high capacity and sufficient rate capability is not an easy task. While the protective layer can prevent unwanted chemical reactions of polysulfides with lithium metal electrodes, thus improving the cyclability of lithium/sulfur cells, it often exhibits a low ionic conductivity, which needs further optimization.

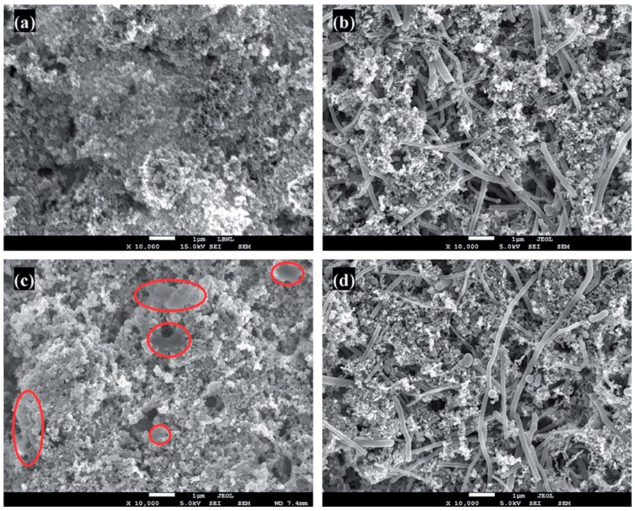

Fig. 10 SEM images of C–S composite electrodes with (a) carbon particles and (b) carbon nanofibers before discharge; (c) carbon particles and (d) carbon nanofibers after 50 cycles. Red circles show the aggregation of solid sulfur or lithium sulfide after cycling.[73] Copyright 2012, with permission from Elsevier.

Recently, the effect of $LiNO_3$ in the electrolyte on the surface of Li electrodes has been investigated.[79–82] Aurbach *et al.* demonstrated that $LiNO_3$ can prevent polysulfide shuttling by the effective passivation of the lithium metal surface, which can prevent chemical reactions of polysulfide species in the electrolyte with the reactive lithium electrodes.[79] Due to the formation of Li_xNO_y film on the lithium metal surface, polysulfides in the electrolyte were prevented from directly contacting the lithium metal. Cui and coworkers also demonstrated that the coulombic efficiency and cyclability were dramatically improved when they added 0.1 M of $LiNO_3$ into the electrolyte as shown in Fig. 11.[83] In this study, hollow carbon nanofiber arrays were synthesized using anodic aluminum oxide (AAO) membranes as templates. This AAO template allowed sulfur to infuse into the hollow fibers, but not on the exterior carbon surface. The benefits of this unique design include a structure for efficient polysulfide containment, limited surface area for direct contact of sulfur with the electrolyte, sufficient space to accommodate the volume change of sulfur, and a short pathway for transport of both electrons and lithium ions. Indeed, sulfur electrodes showed a capacity of $\sim$730 mA h g^{-1} at 0.2 C even after 150 cycles. In this report, 0.1 mol L^{-1} of $LiNO_3$ was added to the electrolyte in order to passivate the lithium metal surface, thus inhibiting the polysulfide shuttle. Very interestingly, while the initial discharge capacity was similar to that without an additive, the coulombic efficiency increased significantly from 84% (without $LiNO_3$ additive) to over 99% (with $LiNO_3$ additive) at 0.2 C, implying the additive plays an important role in protecting the lithium metal electrode in order to achieve a stable cycling performance with high coulombic efficiency.

The effect of varying amounts (1–10 wt%) of lithium bis(oxalato) borate (LiBOB) as the additive in the electrolyte was also investigated.[84] The addition of LiBOB increased mass transfer resistance, but the lithium/sulfur cells with 4 wt% LiBOB showed higher discharge capacity and improved cycling performance, which was attributed to the formation of a smoother and denser surface layer on the lithium electrode than without additives.

In fact, some problems with lithium metal electrodes can be mitigated by techniques developed for aqueous lithium/air cells where lithium metal should be perfectly protected from water. Aqueous Li–air cells, first introduced in the late 1970s,[85] have not been widely accepted[86] due to safety concerns and corrosion issues with lithium electrodes. Recently, Visco *et al.* introduced the concept of protected lithium electrodes,[87,88] where they proposed a water-stable NACISON-type Li-conducting ceramic electrolyte with an interlayer blocking reactions between the lithium electrode and solid electrolytes. It would be reasonable to expect that the cycle life of lithium/sulfur cells would be enhanced with this protected lithium electrode.

3.3 Recent progress in electrolytes

The primary role of electrolytes is to provide fast transport of lithium ions between negative and positive electrodes. Due to their relatively low operating potential, lithium/sulfur cells do not suffer from decomposition of their liquid electrolytes. On the other hand, lithium/sulfur cells have a significant problem with capacity fading during cycling primarily resulting from the high solubility of polysulfides in many liquid electrolytes. This can lead to polysulfide shuttling, corrosion of the lithium metal, and deposition of an insulating film of Li_2S_2 and/or Li_2S. In lithium/sulfur cells, electrolyte problems are linked not only to the lithium metal electrode but also to the sulfur electrode. Liquid electrolytes, if used, must meet the following requirements: (1) high lithium ion conductivity to deliver energy at reasonable rates, (2) low viscosity to fill the small pores of electrodes, (3) minimal solubility of polysulfides, (4) good electrochemical stability in the operating range of potentials, and (5) good chemical stability with lithium metal electrodes.

Carbonate solvents, which are commonly used in current lithium-ion cells, are generally considered a poor choice for

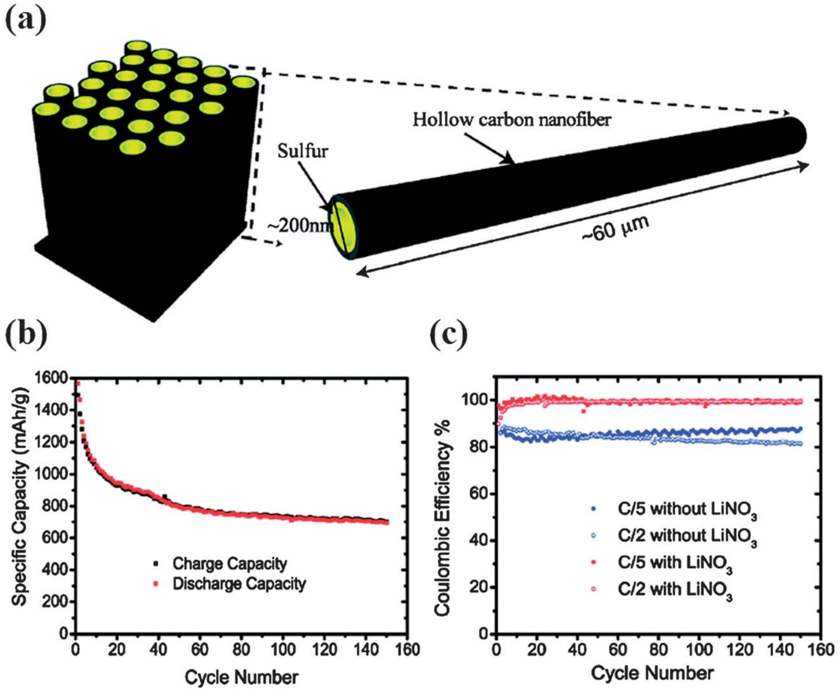

Fig. 11 (a) Schematic of the hollow carbon nanofiber–sulfur electrode. (b) Cycling performance obtained at 0.2 C rate in the electrolyte with the $LiNO_3$ additive. (c) Comparison of coulombic efficiencies with and without the $LiNO_3$ additive in the electrolyte.[83] Reprinted with permission. Copyright 2011 American Chemical Society.

lithium/sulfur cells because polysulfides are soluble in these solvents, resulting in the loss of active material and fast capacity fading. To address this issue, many electrolyte systems with different lithium salts have been investigated. The liquid electrolytes explored thus far include 1,3-dioxolane (DOL),[89] dimethoxyethane (DME),[90] tetraethylene glycol dimethyl ether (TEGDME),[91] polyethylene glycol dimethyl ether (PEGDME),[54] and tetrahydrofuran (THF).[16,92,93] However, single electrolyte systems often exhibited limited cycle life with low utilization of sulfur. For example, cells assembled with pure ionic liquids showed low capacities and poor cycling performance.[94] However, ionic liquid electrolytes mixed with a low molecular weight polymer such as PEGDME or TEGDME have shown promise for improved cycling performance with the help from the reduced dissolution of polysulfides.[95,96] Also, the mixture of DOL and DME exhibited promising results with good cycling life.[83]

A different approach was taken recently by Liang and coworkers.[97] In this report, phosphorous pentasulfide (P_2S_5) was introduced into the electrolyte in order to promote the dissolution of Li_2S, thus decreasing the capacity loss from the deposition of insulating Li_2S on the surfaces of the electrodes. P_2S_5 can also passivate lithium metal surfaces to inhibit the polysulfide shuttle by forming Li_3PS_4. As shown in Fig. 12, the solubility of various mixtures of lithium polysulfides with/without P_2S_5 in the TEGDME electrolyte was investigated. While Li_2S is insoluble in TEGDME, the 1 : 1 molar ratio Li_2S_x–P_2S_5 mixture was completely dissolved in TEGDME. The improved solubility of Li_2S and Li_2S_2 in TEGDME was attributed to the nature of P_2S_5 forming complexes with Li_2S_x. Indeed, a lithium/sulfur cell with the P_2S_5 additive in the electrolyte showed better cycling stability and higher coulombic efficiency.

The cyclability of lithium/sulfur cells can be significantly improved by replacing liquid electrolytes with polymer electrolytes or gel electrolytes, which slows down polysulfide shuttling and protects the lithium metal electrode.[38,98–101] Solid electrolytes may also function as separators in the cell, isolating the negative and positive electrodes. Because the diffusion of polysulfides in polymer electrolytes is much slower than in liquid electrolytes, the polysulfides are held near the positive electrode during cell operation. The migration of sulfur to the lithium electrode region is largely avoided. Thus, the loss of active materials through diffusion is minimized in lithium/sulfur cells that employ polymer electrolytes. However, the ionic conductivity of polymer electrolytes is low at room temperature. Lithium/sulfur cells with polymer electrolytes require a high operating temperature to achieve a reasonable ionic conductivity. Thus, polymer electrolytes should be optimized further to achieve higher discharge capacity and better rate capability at room temperature. Also, it should be noted that a high overpotential is often observed with solid electrolytes, leading to low energy efficiency. All-solid-state lithium/sulfur cells have a significantly lower discharge potential than those of liquid-based lithium/sulfur cells.[14] The high interfacial resistance in all-solid-state lithium/sulfur cells needs to be reduced further. The reactivity of lithium metal with polymer or ceramic membranes at elevated temperatures and the low ionic conductivity at ambient temperature hinder the utilization of solid electrolytes in lithium/sulfur cells. For lithium/sulfur cells involving a solid electrolyte, one of the key technical challenges is to find a solid electrolyte that has sufficient Li ion conductivity and adequate stability against lithium metal. A breakthrough in electrolytes could provide the most practical solution to the challenges that current lithium/sulfur cells face.

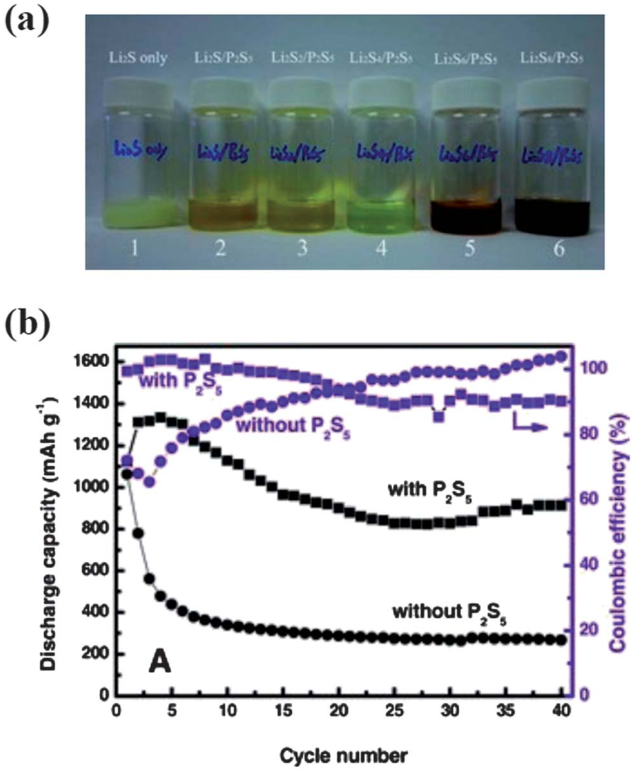

Fig. 12 (a) Solubility test of Li_2S and the Li_2S_x–P_2S_5 mixture in the TEGDME electrolyte. (b) Cycling performance and coulombic efficiency of lithium/sulfur cells with and without the P_2S_5 additive.[97] Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

3.4 Recent progress in characterization of reaction mechanisms

The development of lithium/sulfur cells with high specific energy, excellent cycle life and good rate capability will require a more profound understanding of charge transfer and transport processes of polysulfides and lithium ions during the electrochemical energy storage process. The interfaces between electrodes (both sulfur and lithium electrodes) and electrolytes are very complex and even less well-understood when liquid polysulfides are present in the electrolyte. To understand the change of composition and the structure at the interface during charge transport and transfer processes, it is necessary to use more powerful characterization tools than have been previously applied. With this fundamental knowledge, completely novel electrode materials/architectures can be designed and new insights into the physical and chemical phenomena that underlie the operation of lithium/sulfur cells can be gained.

Synchrotron-based spectroscopic and scattering techniques are very powerful tools capable of helping to unravel the complex electrode processes occurring in lithium/sulfur cells. In particular, *in situ* characterization of the electrolyte–electrode interface with microscopic imaging capabilities is very important for understanding the fundamental processes of chemical energy storage in lithium/sulfur cells without being misled by any artifacts from post-treatments of electrodes after cycling. This approach will require the combination of various electrochemical characterization techniques and advanced characterization tools, so that chemical information can be obtained in real time with high spatial resolution. This *in situ* analysis is very important to understand reaction mechanisms and the optimal design of novel materials/architectures that can exhibit exceptionally high performance. Additionally, the information obtained through such tools will help identify the principal causes of failure and suggest remedies for them.

Recently, Nelson *et al.* monitored the structural and morphological changes during operation of a sulfur electrode in real time using transmission X-ray microscopy combined with synchrotron-based X-ray diffraction.[20] During the discharge, the intensity of the X-ray diffraction peaks from crystalline sulfur decreased and entirely disappeared at the end of the first plateau, where molecules of elemental sulfur were reduced to high-order lithium polysulfides, and reappeared at the end of the charge curve. It was also found that the majority of morphological changes occurred during the first plateau of the discharge curve. As shown in Fig. 13, the green outline around the particle in (a) is redrawn in (c) to show the slight decrease in particle size and increased porosity after the first discharge plateau. Nelson *et al.* also demonstrated that recrystallization of sulfur at the end of the discharge–charge cycle depends on the method of preparing the sulfur electrodes. Furthermore, the formation of Li_2S was not found at the end of discharge among all sulfur electrodes they studied, which is contradictory to previous *ex situ* studies on sulfur electrodes. Interestingly, most soluble polysulfides were found to be trapped within the positive electrode during cycling; but even very small amounts of dissolved polysulfides led to capacity decay. This excellent study highlights the importance of the *in situ* characterization approach to acquire a fundamental understanding of the reaction mechanisms and calls for more efforts along this direction to gain critical insights into rational design of better electrodes.

Aurbach and coworkers investigated the degradation of sulfur electrodes using *ex situ* atomic force microscopy (AFM), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HR-TEM) equipped with energy dispersive spectroscopy (EDS), and Raman spectroscopy.[19] In this study, pronounced structural and morphological changes of sulfur electrodes were observed during the operation of cells. In particular, significant morphological changes were found due to irreversible electrode reactions with distinct changes in surface electrical conductivity, which were closely analyzed by AFM, as shown in Fig. 14. The pristine electrode (before cycling) had a disordered topography due to the nature of the composite structure. An interphase layer was formed on the surface at the

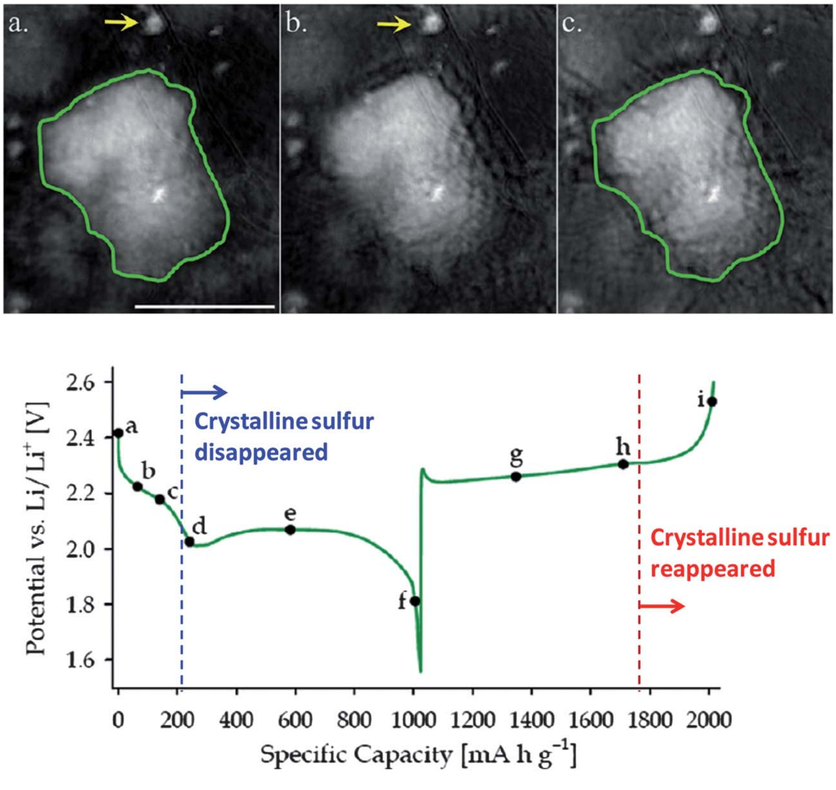

Fig. 13 *In situ* transmission X-ray microscopy images (above) of a sulfur–carbon composite during cell operation, where the letters correspond to points along the cycle labeled in the curve (below).[20] Reprinted with permission. Copyright 2012 American Chemical Society.

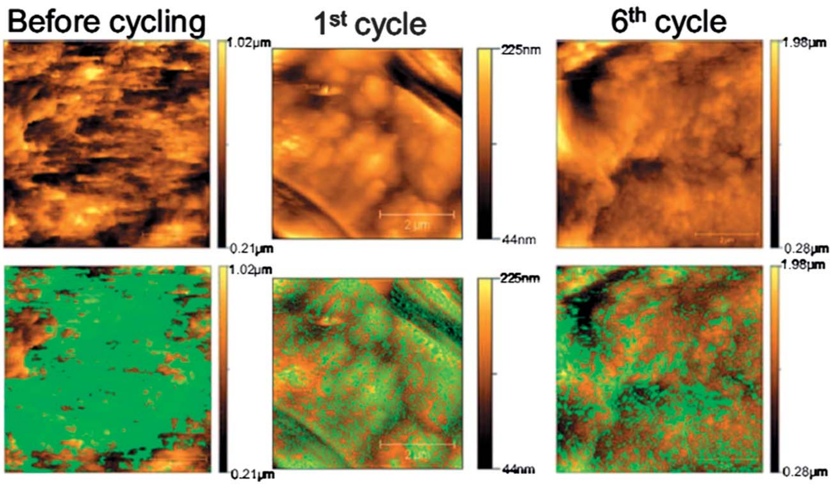

Fig. 14 AFM topography images (top row) and conductivity images (bottom row) of sulfur electrodes before and after 1st and 6th cycles.[19] Reproduced by permission of The Electrochemical Society.

end of each discharge, which made the surface look smoother, but decreased the electrically conductive area on the surface. Upon cycling, the bulk sulfur powder in the pristine sulfur electrode (before cycling) was dissolved, leaving holes in the electrodes and the collapse of the carbon structure was also observed by electron microscopy. Interestingly, electron diffraction analysis showed the electrodes still contained elemental sulfur after the very first discharge. But after 10 cycles, the main discharge product was Li_2S with some Li_2S_x species deposited on the surface. Significant morphological changes were observed and even led to the formation of some cracks within the first 10 cycles. After 10 cycles, the cycling performance of the sulfur electrode became stable and exhibited better capacity retention.

3.5 Other configurations: Li_2S electrodes with high-capacity negative electrodes

While very attractive in terms of its high specific capacity (3860 mA h g^{-1}), the use of lithium metal as the negative electrode also brings some safety concerns mainly arising from the formation of lithium dendrites during operation, which can lead to the short-circuiting of cells and catastrophic failure. Recently, effective ways to avoid this safety issue were proposed, *e.g.*; replacing a lithium metal by a high-capacity negative electrode material together with pre-lithiated sulfur: *i.e.*, lithium sulfide (Li_2S) as the positive electrode, instead of elemental sulfur.[13,14,102–106]

Scrosati and Hassoun used Li_2S–C composites as positive electrodes to fabricate lithium metal-free sulfur cells using Sn–C composites as negative electrodes instead of lithium metal.[14] As shown in Fig. 15, they also replaced a separator soaked in the liquid electrolyte by a lithium-ion conducting polymer gel membrane to prevent dendrite growth from the lithium metal electrode and control the dissolution of polysulfides. The Sn/Li_2S cell was successfully activated by initially converting lithium sulfide to sulfur ($8Li_2S \rightarrow 16Li + S_8$) and exhibited good cycling performance.

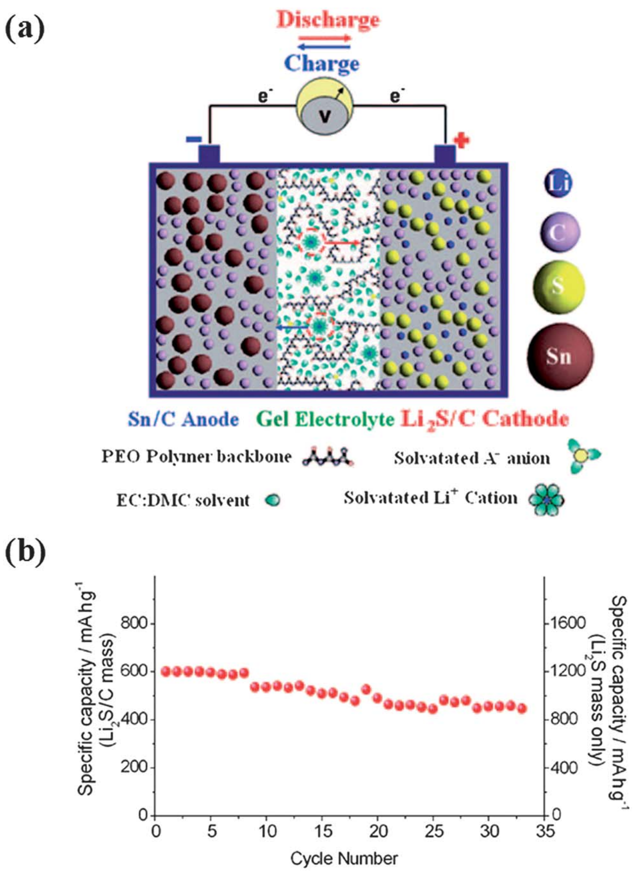

Fig. 15 (a) Schematic diagram of novel configuration of cell containing Li_2S–C composites and Sn–C composites as positive and negative electrodes, respectively. A PEO-based polymer gel was used as the electrolyte. (b) Cycling performance of the Sn/Li_2S cell cycled at C/20 in the range of 0.2–4 V.[14] Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

Similarly, Cui's group demonstrated a lithium metal-free cell consisting of Li_2S–mesoporous carbon composites as positive electrodes combined with silicon nanowires as negative electrodes.[13] Due to its very high specific capacity, silicon would be

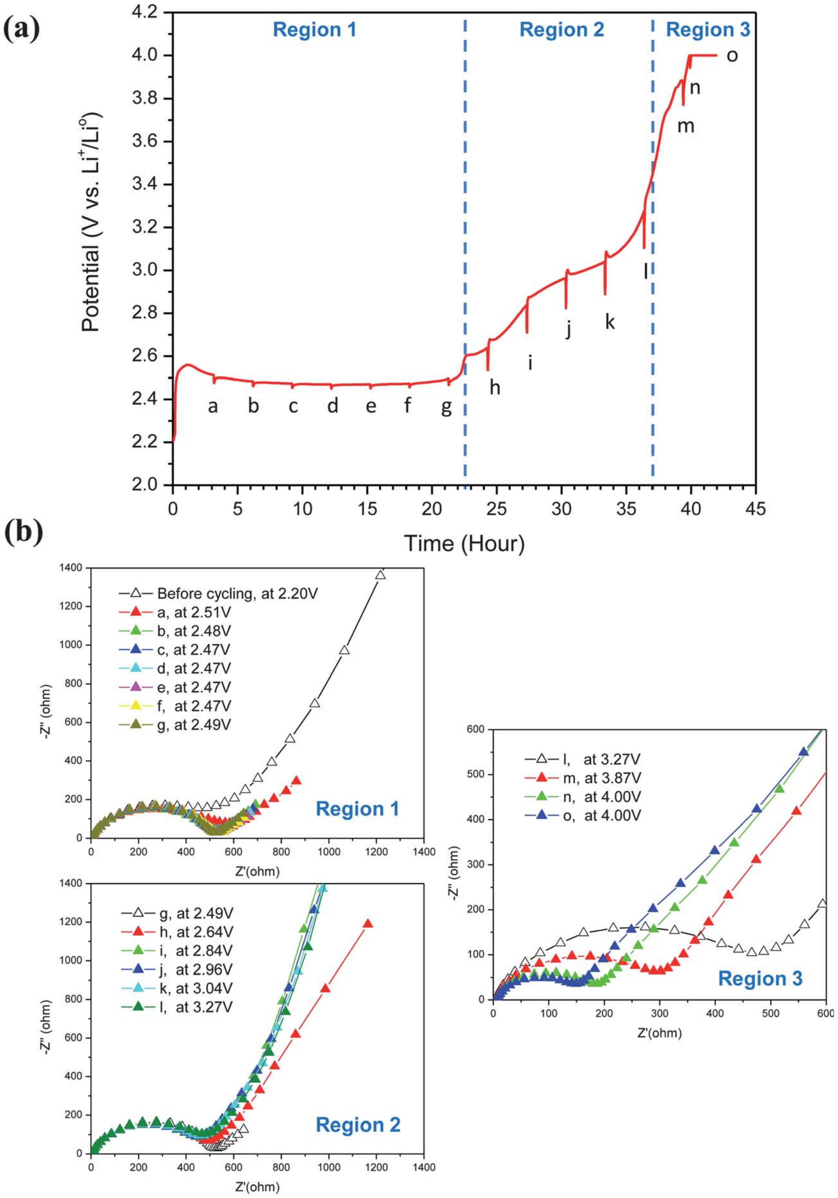

Fig. 16 Electrochemical impedance spectra collected during constant current charging of Li_2S–C nanocomposite cathodes up to 4 V. (a) The first charge profile with a constant current of 33.5 mA g^{-1} of Li_2S. (b) Impedance spectra collected at every 3 hours.[106] Reprinted with permission. Copyright 2012 American Chemical Society.

an ideal choice for this novel configuration. Indeed, the fabricated cells showed high capacity (482 mA h g^{-1}) at the first discharge, which resulted in the specific energy of 630 W h kg^{-1} for the full cell when considering active materials only. However, the capacity continuously decayed during operation up to 20 cycles. Further optimization of size and morphologies of Li_2S particles would be necessary to make this novel configuration more attractive in the near future.

Recently, a simple but effective electrochemical activation process was investigated to allow nearly full conversion of Li_2S to sulfur, thus dramatically improving the utilization of Li_2S electrodes, by initial charging of the Li_2S cell up to 4 V.[105,106] This activation process was confirmed by electrochemical impedance spectroscopy as shown in Fig. 16.[106] The diameter of the semicircle (corresponding to the charge transfer resistance at the interface) decreases dramatically above 3.7 V, indicating that the sulfur electrode becomes noticeably more active. Below 3.7 V, however, only the long linear tail (corresponding to the mass transfer resistance) changed, indicating that the microstructure of the Li_2S electrode changed significantly. With further improvement in capacity retention, Li_2S–C nanocomposite electrodes may provide a noteworthy opportunity to go beyond traditional lithium-ion cells toward the development of rechargeable cells with much higher specific energy.

4 Concluding remarks and outlook

Lithium/sulfur cells have shown much promise with their high theoretical specific energy. Although lithium/sulfur cells have been studied for many years and gained intense attention

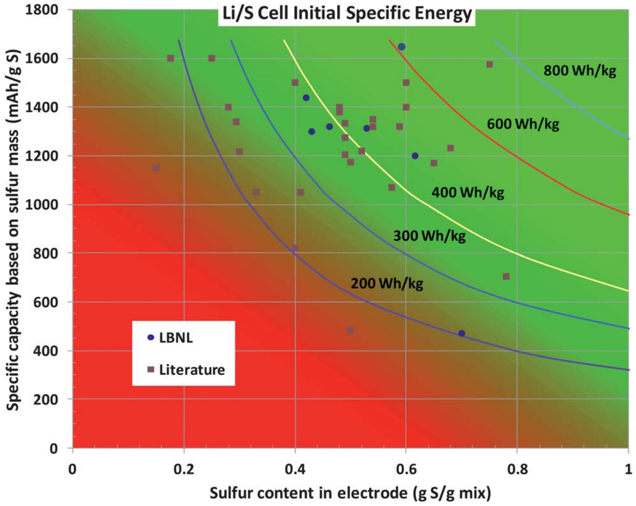

Fig. 17 Estimated cell specific energy plot (including all components except the cell housing) as a function of the sulfur content of the electrode and the specific capacity based on sulfur mass.

recently, transforming the advantages of these new cell chemistries into a real product remains a grand challenge. Major problems of sulfur electrodes are associated with the formation/diffusion of soluble polysulfides within cells and the deposition of insulating products (of Li_2S) on both negative and positive electrodes. These deposits can passivate the electrode surfaces, thus physically blocking the reaction sites for electrode reactions. It is vital to understand that the polysulfide shuttling affects not only sulfur electrodes, but also lithium electrodes and electrolytes. Other significant problems include the large volume change that accompanies the conversion of S to Li_2S. More comprehensive research is urgently needed to unravel the principles that underlie these complex, interrelated processes in order to dramatically prolong the service life of lithium/sulfur cells.

The cell safety and impact on the environment should not be compromised by performance. In the literature, performance improvement often came at the cost of synthesis processes that involve low yield, complex procedures and processing with toxic precursors, rendering them useful only under limited circumstances. The use of materials with potentially high cost or in limited supply, and processes that are not scalable should be avoided. From a practical point of view, lithium/sulfur cells will need to compete with current lithium-ion cells and other energy technologies such as lithium/air cells or fuel cells for many applications. Therefore, more effort should be applied to the development of practical systems. The development of large-scale, low-cost fabrication strategies for electrode materials with desirable performance represents an important challenge in the development of cost-effective lithium/sulfur cells.

Also, sulfur loading should be significantly increased to improve overall specific energy while maintaining good cycle life and utilization in order for these cells to be considered as practical power sources for emerging advanced technologies. The specific energy values estimated from recent publications are shown in Fig. 17 for comparison purposes. It is clear that high cell specific energy can be obtained only when the loading of sulfur is high, and good utilization is obtained. The estimated cell specific energy values are often below 400 W h kg^{-1} in spite of their high specific capacities normalized by the sulfur mass, which is insufficient to meet the ever-increasing requirements of emerging energy storage applications.

In Fig. 18, the specific capacities based on total electrode mass and their demonstrated cycle life are adapted from recent publications and shown in order to illustrate the current status of lithium/sulfur cells and future development directions. It is clearly shown that, to go beyond traditional lithium-ion cells, we need to not only dramatically increase the loading of sulfur (thus high cell specific energy), but also achieve long cycle life.

To meet these rigorous goals, however, more fundamental studies are required at the material, component, and system levels. In addition to the efforts aiming to understand how to manipulate each material's functionalities at the most fundamental level possible, we need to develop the scientific foundations for ways of effectively linking these constituent materials together to form systems that function collectively on much larger scales. For example, extensive studies on the optimization of pore structures of carbon electrodes are needed. It is important to obtain a better understanding of the mechanistic details of enhanced cycling performance by nanostructured carbons so that we can obtain critical insights into the practical design of electrode structures such as dimensions, morphology, and pore size/distribution. In particular, there are many fundamental gaps in understanding the atomic- and molecular-level processes governing the operation and limitations of this novel chemistry. Theoretical approaches such as multi-scale modeling and simulations can be helpful for optimization of electrode structures and cell design. For example, information on the morphology and location of insulating products would be helpful in designing optimal pore structures for high-performance electrodes with excellent cycle life. New continuum, molecular, and quantum mechanical models are needed to analyze new material chemistries and architectures, and to discover new phenomena at both the nanoscale interfaces of electrode–electrolyte and the system level. To date, little is known about how dissolved lithium polysulfides behave in nanoscale pores and channels. More powerful *in situ* characterization techniques for probing and mapping electrode reactions are required to gain critical insights into the dynamic phenomena at electrode surfaces during cell cycling. In addition, more exploration into novel electrode architectures would be very useful because the same materials with different geometries can exhibit totally different behavior. Properly designed and controlled electrode architectures or innovative cell design may lead to the transformative availability of lithium/sulfur cells.

In the literature, many interesting approaches have been explored to develop high specific energy lithium/sulfur cells with some success. It is still not clear, however, how to achieve the optimal design of electrode structures, electrolytes and their interfaces to obtain the best performance. We believe that significant difficulties lie in the lack of fundamental understanding of the mechanistic details governing the operation and limitations of lithium/sulfur cells. However, in authors' view, good opportunities remain in research and some examples are briefly described as follows:

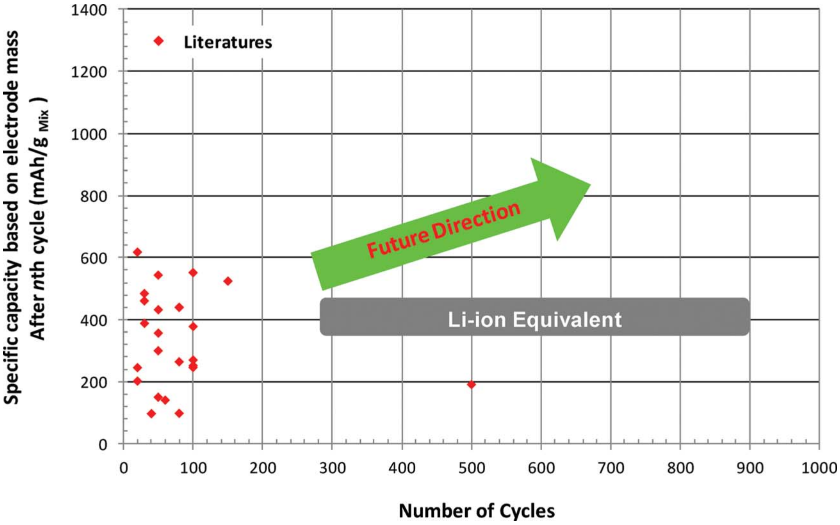

Fig. 18 Current status and future development direction of lithium/sulfur cells.

(1) design and tune the geometry of porous carbon materials further to maximize sulfur loading (thus specific energy) while improving energy density and increasing the utilization of sulfur by maintaining intimate contact of sulfur with carbon;

(2) improve the cycle life of lithium/sulfur cells by retaining polysulfides inside the positive electrode structure using lightweight adsorbent additives;

(3) explore nanoscale coatings (such as a solid Li-conducting electrolyte or adsorbents) on sulfur electrodes to retain polysulfides inside the electrode while still providing good pathways for electrons and lithium ions;

(4) develop effective coatings on the lithium electrode to suppress dendrite growth, promote stable SEI formation and effectively prevent the polysulfide shuttle phenomenon while still allowing good ionic conductivity;

(5) identify novel electrolyte compositions or find good additives in order to improve the utilization, enhance rate capability, improve safety, create stable SEI formation on lithium metal, and avoid the polysulfide shuttle;

(6) investigate the failure mechanisms of positive and negative electrodes using *in situ* characterization tools with microscopic imaging capability to gain new insights into rational design of better electrodes.

With high theoretical specific energy and abundant, environmentally benign sulfur, the future of lithium/sulfur cells is still bright, but it will emerge as an important future energy storage option only with advances in fundamental science.

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