

Chapter 2

Revealing Localized Electrochemical Transition of Sulfur in Sub-nanometer Confinement

2.1 Research Background

Current concerns of the pressing environmental pollution issues and limited fossil energy resources have increased the R&D interest and investment in clean energy technologies. LIBs, as commonly used clean energy storage devices, have transformed portable electronic devices and electric transportation greatly, but have limitations of high cost and relatively low specific energy [1]. Due to advantages such as high capacity, extremely low cost, and nontoxicity, sulfur has received considerable attention as a positive electrode material in Li–S batteries. Li–S batteries can deliver a very high theoretical specific energy of 2567 Wh kg^{-1} or 2199 Wh L^{-1} and dramatically outperform current LIBs [1, 2]. However, the low electronic/ionic conductivity of sulfur and the discharge products, large volume change ($\sim 80\%$) of sulfur during the lithiation/delithiation processes, and the shuttling of dissolved lithium polysulfides (Li_2S_x , $3 \leq x \leq 8$) between the sulfur cathode and the lithium–metal anode during cycling severely impede the practical applications of Li–S batteries [3, 4]. These problems not only lead to poor cycling stability, inferior rate capability, and low Coulombic efficiency, but also cause the deposition of insulating $\text{Li}_2\text{S}/\text{Li}_2\text{S}_2$ on both electrodes, resulting in low sulfur utilization and even triggering a series of safety problems [5–7].

Most current research has focused on solving the problems of polysulfide dissolution by reducing polysulfide solubility and/or adsorbing dissolved polysulfides in the cathode. The use of polymer-based or ionic liquid-based electrolytes eliminates the need for organic solvents in which polysulfides have high solubility [8–11], however the increased electrolyte viscosity and resistivity are detrimental to rate performance. Metal oxides, polymers, and silica can chemically or physically

adsorb polysulfide anions [12–15], but their semiconducting or insulating nature unavoidably slows down cathode reaction kinetics.

Porous carbon combines high adsorption capacity with good conductivity and is regarded as the best cathode sorbent. Various carbon–sulfur composite electrodes, such as carbon nanotubes/nanofibers [16–19], graphene [20, 21], mesoporous carbon [2, 22, 23], microporous carbon, and hierarchical porous carbon [24, 25] have been used in Li–S batteries. It is worth stressing, however, that these advances are partially due to the use of a non-carbonate solvent-based electrolyte and the additive LiNO_3 salt, in which the solubility of polysulfides is reduced or the polysulfide shuttle is passivated [26, 27]. Although the development of Li–S batteries requires advances in both the cathode and the electrolyte, the advantage of carbon materials that they can stabilize the sulfur cathode can be more clearly highlighted using the carbonate electrolyte that generates the most aggressive electrochemical environment attacking polysulfides. It has been found that the carbonate solvent trapped in a gel polymer electrolyte is less aggressive due to the physical shielding role of the polymer layer and allows the carbon–sulfur cathode to reversibly operate for 90 cycles [28]. Much longer cycling life of sulfur in a mixed carbonate electrolyte can be achieved by a micropore-confined cathode, which can operate stably over 500 cycles [24]. Therefore it is suggested that microporous carbon is the best candidate for Li–S cathodes using any solvent regarding merely the stability. Nonetheless the final lithium sulfide discharge product can only be formed at 1.0 V versus Li^+/Li^0 in this micropore-confined cathode [24]. The large lithiation overpotential represents the slow cathode reaction kinetics that possibly arises from retarded lithium ion migration in micropores. Unfortunately, little attention has been paid to develop a kinetically favorable micropore-confined sulfur cathode.

Based on the above analysis, it is not clear whether carbonate-based electrolyte can be used in Li–S batteries and immobilization of sulfur in pores has shown quite different cathode behavior depending on the pore size. The challenge of stable high-rate capacity remains unmet due to either the weak adsorption potential of mesopores or the blocking of porous networks after the sulfur filling. Understanding the confinement effect for different pore size and the suitable situation for employing carbonate-based electrolyte is a crucial step towards achieving high reversible capacity and long cycle life in Li–S batteries. In this work, we report the use of a microporous-mesoporous carbon with graphitic structure as the sulfur immobilizer for a high-rate stable Li–S cathode in a carbonate electrolyte. The sulfur was confined in micropores and its stability was tested over 800 cycles in an aggressive carbonate electrolyte. The high-rate capability of this cathode is excellent allowing a fast charge/discharge operation. This high-rate performance is due to the graphitic structure and mesoporous framework which facilitate the transport of both electrons and ions.

2.2 Design, Fabrication, and Characterization of Carbon–Sulfur Composite Cathode

2.2.1 Synthesis of Hierarchical Porous Carbon (HPC)

The HPC carbon matrix with microporous-mesoporous texture and graphitic structure was synthesized by mixing phenolic resin solution (100 mL, 20 wt%) with nickel hydroxide suspension. The nickel hydroxide was prepared in advance by adding nickel nitrate (5 g) into sodium hydroxide (100 mL, 10 wt%) solution. Subsequently, 25 g of 20 wt% ethanol solution of phenolic resin was added under intense stirring. The hybrid system was evaporated for 24 h in a glass utensil at 90 °C under ambient pressure to obtain the composite of inorganics and resin. The composite was carbonized in a tubular furnace under argon atmosphere via heating ramps of 10 °C min⁻¹ from room temperature to 200 °C and keeping at 200 °C for 2 h, then heating to 600 °C and keeping at 600 °C for 4 h. After carbonization, the inorganic species were etched with 3 M HCl solution and filtrated to wash the samples. The final product was obtained by subsequent drying at 90 °C in a vacuum oven for 24 h. The transmission electron microscopy (TEM) image in Fig. 2.1a reveals the mesoporous texture of the carbon matrix. The graphitic nanoribbons in the carbon matrix can be seen from the high-resolution TEM image in Fig. 2.1b. Micropores are embedded in the amorphous area surrounding the graphitic regions but are hardly visible owing to the small dimensions. The mesoporous texture favors the fast migration of solvated lithium ions, and the graphitic nanoribbons facilitate electron conduction [29].

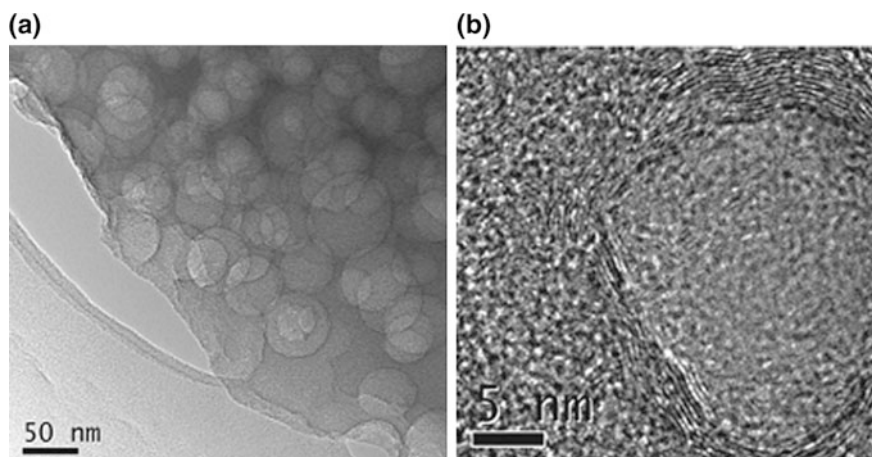


Fig. 2.1 **a** Low-magnification and **b** high-resolution TEM images of the hierarchical porous carbon

2.2.2 Synthesis of Carbon–Sulfur Composite

In order to investigate the pore-dependent confinement mechanism, sulfur was infused into different pore sizes, the detailed synthesis process is as follows: HPC and sulfur powders at a mass ratio of 1:1 were ground together and heated at 155 °C for 12 h in argon gas. At this stage, the sulfur is stored in macro/meso/micropores of HPC and sample is labeled CS-Ad. The selective extraction of sulfur from CS-Ad was carried out using carbon disulfide washing. The as-obtained CS-Ad powder was immersed in 30 mL of carbon disulfide and stirred for 10 min at room temperature. The carbon disulfide containing dissolved sulfur was quickly filtered, and the sample was washed again with clean carbon disulfide. The remaining sample, labeled CS-Ex with sulfur mainly confined in the micropores, was dried in a vacuum oven at 50 °C for 8 h (Fig. 2.2).

2.2.3 Structure Characterization of the Carbon–Sulfur Composite

The existence of sulfur in both CS-Ad and CS-Ex was confirmed by X-ray photoelectron spectroscopy (XPS) (Fig. 2.3). The peaks located at 163.6 eV, 228.3 eV,

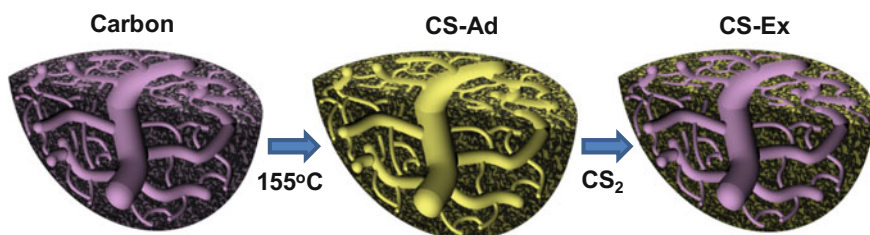
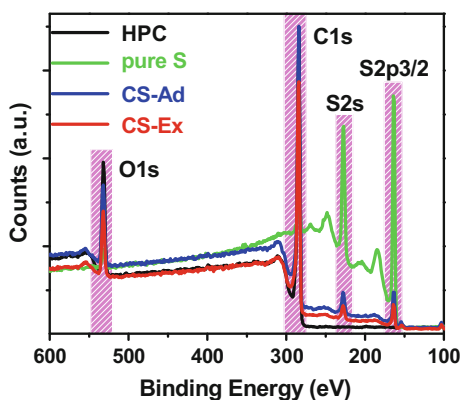


Fig. 2.2 Schematic of the preparation of CS-Ad and CS-Ex through the adsorption and extraction strategy

Fig. 2.3 XPS spectra of the hierarchical porous carbon, sulfur, CS-Ad and CS-Ex



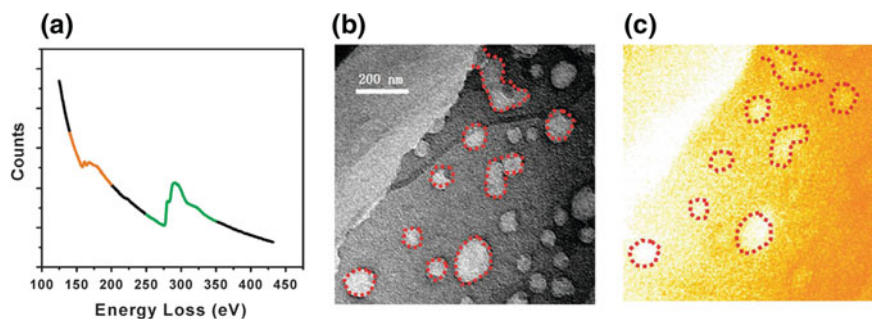


Fig. 2.4 **a** EELS spectrum of sulfur (165 eV) and carbon (284 eV) edges with an energy window of 20 eV. **b** Zero-loss low-magnification image of the carbon of CS-Ex and **c** EELS elemental mapping image of sulfur in the porous texture of CS-Ex

284.6 eV, and 532.2 eV are attributed to the $S2p_{3/2}$, $S2s$, $C1s$, and $O1s$, which are in agreement with the $S2p_{3/2}$ and $S2s$ peaks in pure sulfur and $C1s/O1s$ peaks in the HPC, indicating the successful immobilization of sulfur in the pores of HPC. The distribution of sulfur was tracked using electron energy loss spectroscopy (EELS) and EELS mapping methods (Fig. 2.4). In CS-Ex, only carbon (284 eV) and sulfur (165 eV) signal peaks can be detected from the EELS, and sulfur is preferentially confined in micropores, which are located around the mesopores highlighted by dotted red lines (Fig. 2.4b and c). The contrasting difference between the micropores and some mesopores suggests significant molecular-level confinement of sulfur in micropores, with only a small amount retained in the mesopores.

The selective immobilization of sulfur in pores with different sizes is evident from the nitrogen adsorption isotherms in Fig. 2.5a and the pore size distributions are shown in Fig. 2.5b. The molten sulfur was embedded in the voids of the carbon matrix by capillary forces, where it solidified causing a significant loss of pore volume (Fig. 2.5a). The pore volume of the carbon matrix is $0.44 \text{ cm}^3 \text{ g}^{-1}$.

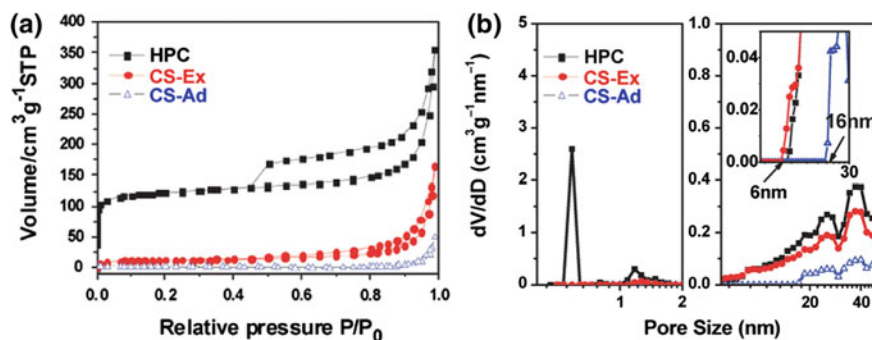


Fig. 2.5 **a** Liquid nitrogen adsorption–desorption isotherms and **b** pore size distribution of HPC, CS-Ad and CS-Ex composites

The CS-Ad sample has a pore volume less than $0.1 \text{ cm}^3 \text{ g}^{-1}$ compared to the $0.24 \text{ cm}^3 \text{ g}^{-1}$ of the CS-Ex sample. Meanwhile, the specific surface area of the carbon matrix is $413 \text{ m}^2 \text{ g}^{-1}$, while that for CS-Ad and CS-Ex are 8 and $43 \text{ m}^2 \text{ g}^{-1}$, respectively. The infiltration resulted in the disappearance of 6–16 nm mesopores in the carbon matrix as shown in Fig. 2.5b. Additionally, the pore volume in the range above 16 nm also decreased sharply due to the presence of sulfur. After CS_2 extraction, sulfur was removed substantially from mesopores, as was clear from the fact that the pore volume distribution was similar to that of the original carbon matrix, but micropores were still occupied by sulfur in the extracted sample. It is noted that no mesopores in the range between 2 and 6 nm were measured for the carbon matrix based on liquid nitrogen cryosorption analysis. It is clear that CS_2 extraction cannot remove sulfur from micropores (0.6–0.7 nm, with a peak value of 0.65 nm), but can effectively extract sulfur from the mesopores with partial sulfur removal from 1 to 1.6 nm pores, named hereafter “super-micropores”. Sulfur in super-micropores is in trace amounts. The sulfur residue after CS_2 extraction is likely to be surface adsorbed by the mesopores in the carbon scaffold. These results are consistent with the XPS analysis.

X-ray diffraction (XRD) peaks, shown in Fig. 2.6a, reveal the rhombic-monoclinic phase transition of sulfur solidified in CS-Ad from the melt, indicating the crystalline nature of sulfur in mesopores. The well-resolved peaks corresponding to monoclinic sulfur in CS-Ad disappeared completely after CS_2 extraction, indicating the amorphous nature of sulfur confined by micropores in CS-Ex [24, 30]. Raman spectroscopy confirms the crystalline nature of sulfur in mesopores and the amorphous nature of sulfur in micropores (Fig. 2.6b).

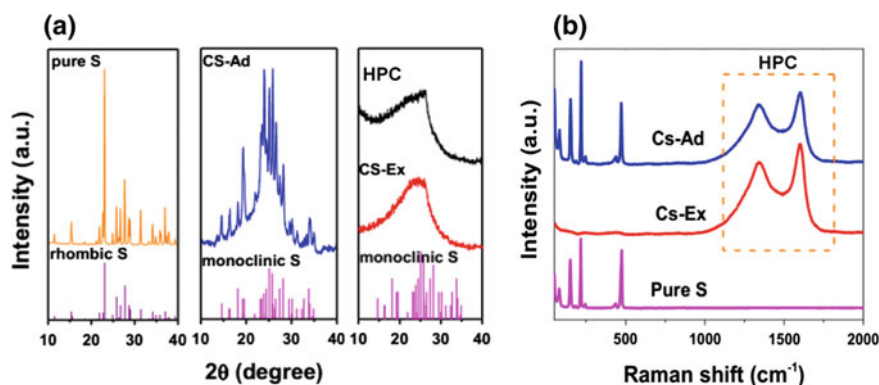


Fig. 2.6 **a** XRD patterns of HPC, pure sulfur and sulfur confined in pores with different sizes, showing the phase evolution of sulfur (rhombic-monoclinic-amorphous) corresponding to the adsorption-extraction method, and **b** Raman spectra of pure sulfur, CS-Ad and CS-Ex

2.2.4 Electrochemical Performance of the Carbon–Sulfur Composite Cathode

To understand the effect of pore size in affecting the performance, Li–S cells were assembled with a metallic lithium foil anode and a CS-Ad or CS-Ex cathode. A commercial carbonate electrolyte (LiPF_6 in EC/DMC/EMC) was used directly without any modification. Cyclic voltammetry (CV) profiles were recorded to determine the lithiation potential of sulfur confined in pores with different sizes, as given in Fig. 2.7. As seen, there are two peaks in the first reduction process of CS-Ex (Fig. 2.7a). The small peak at 2.43 V (vs. Li^+/Li^0) corresponds to the conversion from elemental sulfur (S_8) to lithium polysulfide anions (Li_2S_x , $4 \leq x \leq 8$) [2, 24]. However, this peak is not observed in the second reduction cycle (Fig. 2.7b). The small peak is most likely caused by the reduction of a trace of sulfur in pores larger than 6 nm in CS-Ex, which is weakly adsorbed and easily dissolved into the electrolyte. The tiny magnitude of this reaction with respect to the strong reduction peak at 1.62 V (vs. Li^+/Li^0) suggests the considerable confinement of sulfur in micropores. The cathodic peak at 1.62 V is in accordance with the deep

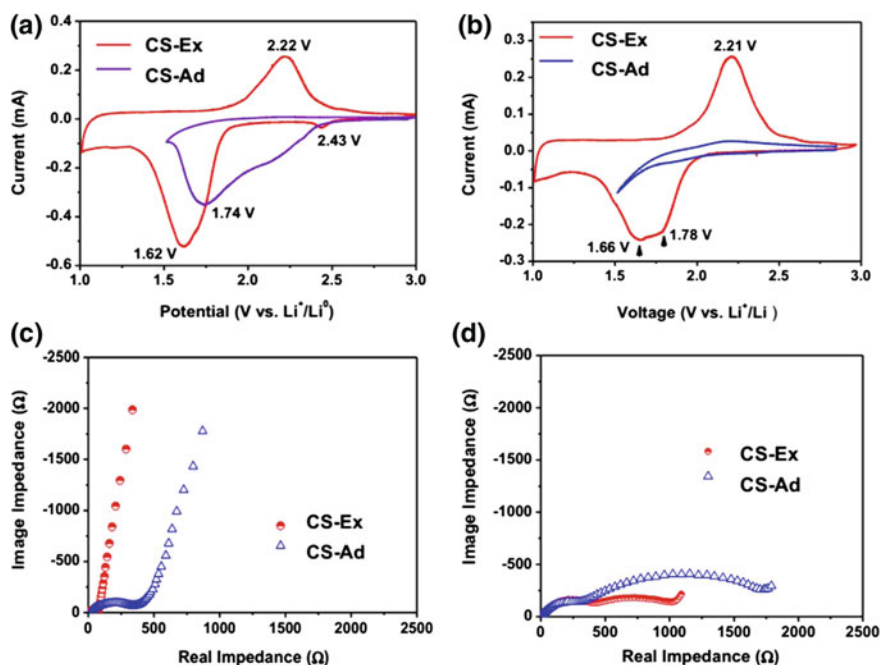


Fig. 2.7 **a** First cycle CV and **b** second cycle CV curves of CS-Ex and CS-Ad cathodes recorded at 0.5 mV s^{-1} at room temperature. EIS Nyquist profiles of CS-Ex and CS-Ad cathodes recorded from 10 kHz to 10 MHz at room temperature at cathode polarization potentials of **c** open circuit potential (2.8 V vs. Li^+/Li^0) and **d** full discharge potential (1.5 V vs. Li^+/Li^0) after discharge but before charge in the first cycle

reduction of polysulfide ions to insoluble $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$. In the CS-Ex cathode, the conversion of polysulfides to lithium sulfide occurs at around 1.8 V. The low potential reduction could be due to the extra electrode polarization required to overcome the nanoconfinement barrier of strong adsorption energy. In stark contrast, the cathodic reaction of CS-Ad initiates at 2.4 V and reaches the peak current at 1.74 V. Two slow plateaus are noticed with a transition point of about 2.2 V. The upper branch (2.4–2.2 V) indicates the formation of polysulfide ions from sulfur located in large pores. The lower oblique branch (2.2–1.74 V) originates from the slow kinetics of lithium sulfide formation on the outer surface [31]. The probable surface coverage by exterior lithium sulfide limits the full reduction of polysulfide ions and hinders the approach of electrons and ions to sulfur confined in micropores. The incomplete conversion of confined sulfur could be responsible for its higher peak potential (1.74 V, compared to 1.62 V of CS-Ex), where the reaction is actually terminated. As indicated in Fig. 2.7b, the second cycle of CS-Ad shows no current response, and clearly confirms the terminated cathode activity by exterior lithium sulfides. During the second cathodic reaction process, the major 1.62 V peak of CS-Ex was shifted to a higher potential within 1.66–1.78 V. This potential shifting is mainly attributed to the formation of complexes with lower adsorption energy after the first anodic oxidation of lithium sulfides.

The varying cathode performance is related to the pore size dependence of confinement, and is better understood by employing electrochemical impedance spectroscopy (EIS). As seen in Fig. 2.7c, the open circuit (2.8 V vs. Li^+/Li^0) EIS spectra of CS-Ad and CS-Ex both comprise a semicircle at high frequency and an inclined tail in the low-frequency region. The interfacial charge-transfer resistance recognizable from the semicircle is due to the redox formation of high-order polysulfides and low-order lithium sulfides. The monolayer adsorption of sulfur in micropores realizes a molecular-level intimate electronic contact with the carbon scaffold [32], while the bulky loading of sulfur in mesopores restricts efficient electron conduction with the carbon matrix. As a consequence, the CS-Ad cathode displays nearly four times greater resistance than the CS-Ex cathode. The mass transfer kinetics, mainly of lithium ions, inside the porous cathode can be compared qualitatively with reference to the slope of the low-frequency tail. The CS_2 extraction frees the occupied mesopores, and results in the facilitated ion transfer in the CS-Ex cathode with an increased tail slope. The combination of intimate electric connection and fast ionic transport as a result of selective confinement of sulfur in micropores is promising for developing a stable cathode with high-rate capability. EIS spectra recorded after discharge confirm the superior cathode kinetics of CS-Ex to those of CS-Ad, which is reasonably attributed to the absence of surface lithium sulfides due to the confined lithium sulfide formation in micropores (Fig. 2.7d).

The unconstrained dissolution of polysulfides in mesopores of the CS-Ad cathode caused the absolute loss of capacity in the second cycle (Fig. 2.8a). In contrast, the maximum discharge capacity of $1067 \text{ mAh g}_{\text{sulfur}}^{-1}$ was obtained from the CS-Ex cathode (Fig. 2.8b). Despite the reversible delithiation of the CS-Ex cathode, the discharge capacity in the second cycle is still higher than the charge capacity. Since the dissolution of polysulfide causes the active mass loss in the

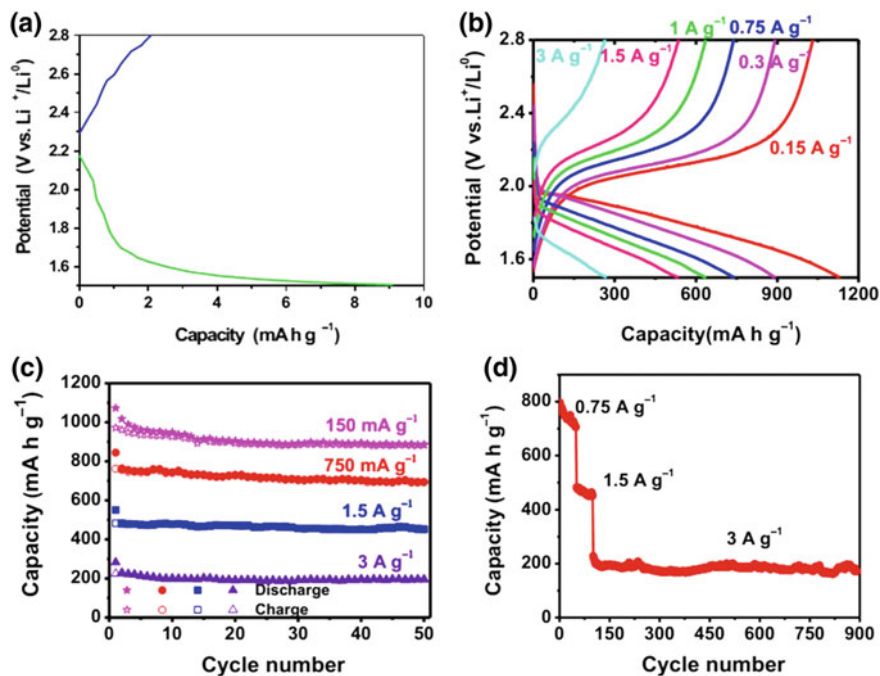


Fig. 2.8 **a** The second cycle discharge–recharge profiles of CS-Ad, **b** the second cycle charge–discharge profiles of a CS-Ex at different current densities, **c** cycle stability of the CS-Ex cathode at high rates, and **d** cycling discharge capacity tested at 0.75 A g^{-1} , 1.5 A g^{-1} and 3 A g^{-1} for 900 cycles

cathode, this phenomenon suggests the presence of residual sulfur in mesopores of CS-Ex. As seen from Fig. 2.8c, however, the discharge–charge capacity remains nearly identical after the first few cycles and retains a Coulombic efficiency close to 100%. This implies that the majority of the sulfur was removed from mesopores by CS_2 and only trace amounts remained that formed polysulfides during the very initial cycles and dissolved. It is noticeable that no potential plateau exists in the discharge–charge profiles recorded at different current densities. This is very likely due to the use of carbonate electrolyte and the micropore confinement [24]. In addition, the micropore confinement formed sub-nanometre sulfur clusters. This extreme sizing effect might alter the normal physicochemical properties of sulfur which is relevant to the anomalous lithiation–delithiation behavior. The cycling stability of sulfur cathodes is shown in Fig. 2.8c. The capacity fade at the initial cycles is most likely due to the dissolution of the sulfur residue in mesopores as described above. Most importantly, a high-rate capacity of around $200 \text{ mA h g}_{\text{sulfur}}^{-1}$ under an ultrahigh current density of 3 A g^{-1} for nearly 800 cycles was observed (Fig. 2.8d). This operation corresponds to a calculated discharge or recharge C rate of 1.8 C. It is evident that the micropores confer the stable performance of the sulfur cathode over the greatest number of cycles reported [33],

particularly in this aggressive carbonate electrolyte, while the graphitic structure and mesoporous texture contribute to the high-rate performance. We here emphasize that the micropore confinement and the combination of graphitic structure and mesoporous framework are critical to achieve such advanced performance. The micropore confinement effect is twofold. First, the micropores restrict the highly soluble polysulfides. Second, the polysulfides/lithium sulfide formed in micropores retains intimate electric contact with the mesoporous and conducting carbon matrix, and enhances reaction kinetics.

2.3 Mechanism Analysis of the Pore Size Dependence of Confinement on Electrochemical Performance in Li-S Batteries

Scanning electron microscopy (SEM) images of the CS-Ex cathode after discharge demonstrate the porous structure due to the confined lithium sulfides in micropores (Fig. 2.9a). However, the solid insulating lithium sulfide layer formed by the reduction of dissolved polysulfides covers the CS-Ad cathode surface (Fig. 2.9b). XPS analysis was used to study the surface composition of lithium sulfides confined in micropores and deposited on the outer surface. The $S2p_{3/2}$ spectra confirm the formation of lithium sulfide after the first discharge (Fig. 2.9c and d). The negative shifts of $S2p_{3/2}$ binding energy are observed for both cathodes. However, the lithium sulfides confined in micropores show a higher binding energy than the surface lithium sulfides. This difference could possibly indicate the short bond length of the lithium sulfide deposited in micropores compared to that on the outer surface without confinement.

We suggest a possible mechanism to understand the physical origin of the superior stability of micropore-confined sulfur even in the carbonate electrolyte. As generally accepted, the sulfur reduction is a solid (S)-liquid (polysulfide ions)-solid (Li_2S_2/Li_2S) process, and the mesopores stabilize sulfur through the adsorption of dissolved polysulfide ions (Fig. 2.10, left). The solvent-restricted environment and the solvent shell distortion of electrolyte ions in pores close to or less than 1 nm have recently been reported [34]. Here, we consider that micropores below 1 nm cause the desolvation of the electrolyte ions, and probably will prevent or at least slow the dissolution of polysulfide as the solvent concentration is very low or likely to be close to zero in these micropores (Fig. 2.10, right). This suggests a quasi-solid-state reaction of the sulfur under solvent-deficient conditions. Furthermore, the micropore confinement will also distort the solvation shells of polysulfide anions even if they are solvated and reduce the mobility of solvated polysulfide anions. Consequently the reduction of sulfur still produces polysulfides as intermediates, but the polysulfides remain in the pores instead of being dissolved. This inside micropore lithiation of sulfur gives rise to the micropore-confined lithium sulfides, and is the reason for the ultra-long cycling life with nearly 100% Coulombic efficiency.

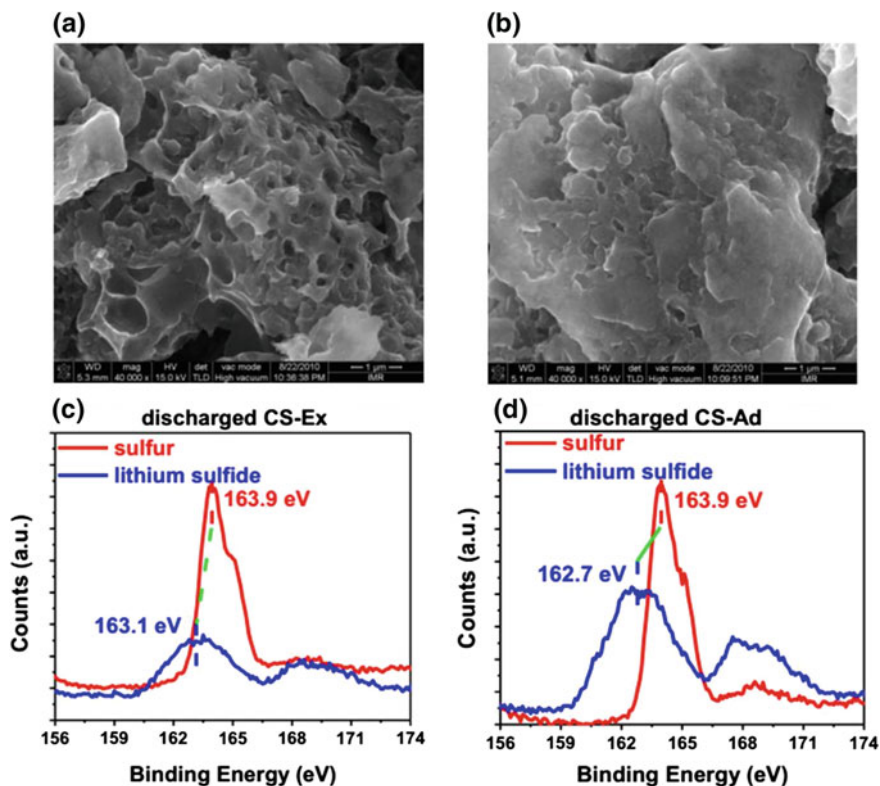


Fig. 2.9 SEM images of **a** CS-Ex and **b** CS-Ad cathodes after the first discharge, and XPS $S2p_{3/2}$ profiles of **c** CS-Ex and **d** CS-Ad cathodes compared to the raw cathodes before discharge

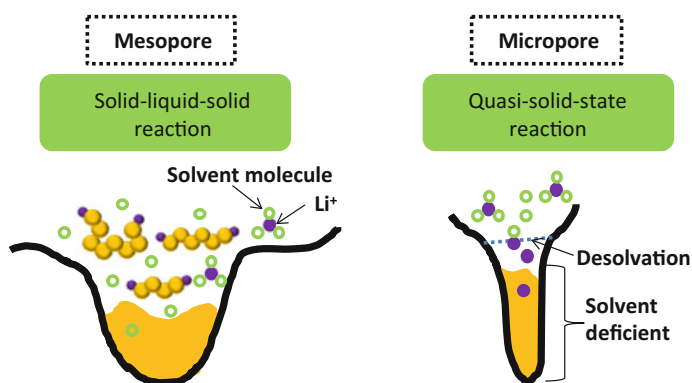


Fig. 2.10 Illustration of the different reaction process of sulfur confined in mesopores and micropores. Reprinted with permission from Ref. [35]. Copyright 2013, Royal Society of Chemistry

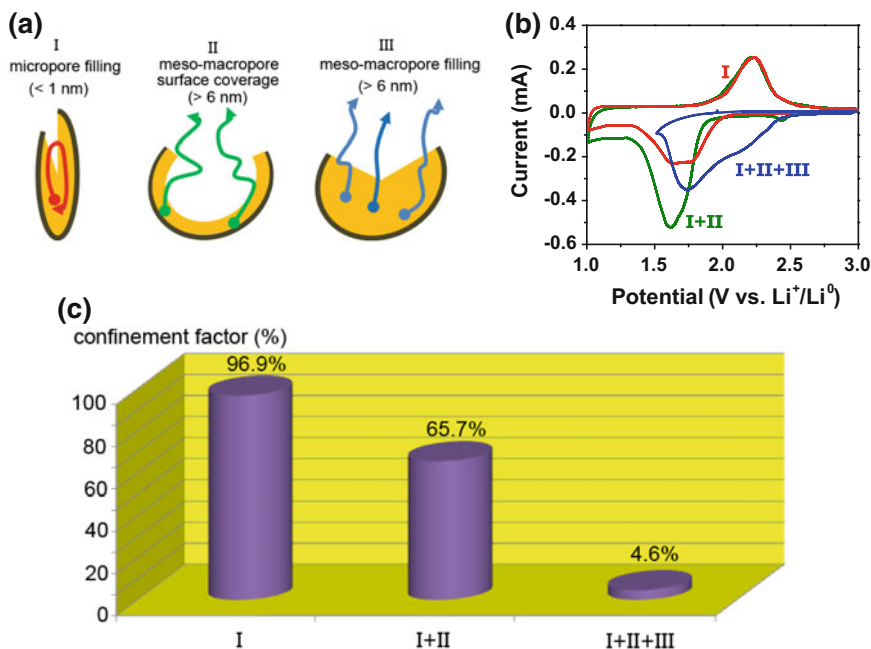


Fig. 2.11 **a** Scheme showing three different confinement systems, **b** CV curves of sulfur cathodes with three different confinement systems, **c** confinement factors for the three typical confinement systems (color figure online)

We propose three modes of confinement of sulfur occur in these systems (Fig. 2.11a): (I) the micropore filling (<1 nm), (II) the meso/macropore surface coverage (>6 nm), and (III) the meso/macropore filling (>6 nm). CS-Ex exhibits I + II, while CS-Ad is regarded as showing I + II + III. Sulfur in super-micropores is neglected here due to its occurrence only in trace amounts which can be electrochemically removed. According to Fig. 2.11b, the nearly reversible reaction is observed for sulfur confined in sub-nanometre micropores (red line), while the sulfur located in meso/macropores caused the absolute loss of reversibility due to formation of an insulating layer on the electrode surface [36] (blue line). Sulfur adsorbed on the surfaces of meso/macropores also lacks reversibility (green line). Cyclic voltammetry can determine the amount of each sulfur species participating in the reactions. The ratio of anodic peak area to cathodic peak area, representative of the population of effectively confined polysulfides that can react reversibly, is defined here as the “confinement factor” to evaluate the capability of each condition to constrain polysulfides. It is obvious that a filling system comprising solely of micropores (I) gives a near-perfect confinement level (96.9%) compared to the other confinement systems (I + II, I + II + III) (Fig. 2.11c).

2.4 Conclusion

In this chapter, we have demonstrated the immobilization of sulfur in micropores of a mesoporous carbon framework with graphitic structure and the confined electrochemical transition of sulfur-polysulfides-lithium sulfides that promises durable sulfur cathodes for Li–S batteries. The beneficial integration of the micropores for sulfur lithiation, mesopores for ion transport, and graphitic structures for electron conduction substantially improves the performance in terms of the high-rate capacity and stability. It is remarkable that stable high-rate performance was attained in a mixed carbonate electrolyte that easily dissolves polysulfides. The main conclusions are as follows:

- (1) Sulfur was selectively immobilized into the micropores of hierarchical porous carbon by a melt adsorption-solvent extraction process.
- (2) Micropores in the hierarchical porous carbon have strong adsorption potential to confine sulfur, which acts as solvent-restricted reactors for sulfur lithiation.
- (3) The localized electrochemical transition of “solid–solid” reaction instead of “sulfur-polysulfides-lithium sulfides” reaction was proposed through the desolvation effect in sub-nanometre pores.
- (4) A “confinement factor” was defined for the capability to constrain polysulfides. It is obvious that a filling system comprising solely of micropores gives a near-perfect confinement level (96.9%) compared to the meso/macropore confinement systems (4.6%). The micropores restrict the highly soluble polysulfides and improve the sulfur utilization, and the cathode is able to operate reversibly over 800 cycles with marginal capacity loss at a rate of 3 A g⁻¹.

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