In Situ Formed Lithium Sulfide/Microporous Carbon Cathodes for Lithium-Ion Batteries

Shiyou Zheng,†‡ Yvonne Chen,§ Yunhua Xu,† Feng Yi,‡ Yujie Zhu,‡ Yihang Liu,‡ Junhe Yang,†,* and Chunsheng Wang†,*

†School of Materials Science and Engineering, University of Shanghai for Science & Technology, Shanghai 200093, China, ‡Department of Chemical and Biomolecular Engineering, University of Maryland, College Park, Maryland 20742, United States, §Space and Defense Division, Saft America Inc., Cockeysville, Maryland 21030, United States, and ‡Material Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, United States

ABSTRACT Highly stable sulfur/microporous carbon (S/MC) composites are prepared by vacuum infusion of sulfur vapor into microporous carbon at 600 °C, and lithium sulfide/microporous carbon (Li2S/MC) cathodes are fabricated via a novel and facile in situ lithiation strategy, i.e., spraying commercial stabilized lithium metal powder (SLMP) onto a prepared S/MC film cathode prior to the routine compressing process in cell assembly. The in situ formed Li2S/MC film cathode shows high Coulombic efficiency and long cycling stability in a conventional commercial Li-ion battery electrolyte (1.0 M LiPF6 + EC/DEC (1:1 v/v)). The reversible capacities of Li2S/MC cathodes remain around 650 mAh/g even after 900 charge/discharge cycles, and the Coulombic efficiency is close to 100% at a current density of 0.1C, which demonstrates the best electrochemical performance of Li2S/MC cathodes reported to date. Furthermore, this Li2S/MC film cathode fabricated via our in situ lithiation strategy can be coupled with a Li-free anode, such as graphite, carbon/tin alloys, or Si nanowires to form a rechargeable Li-ion cell. As the Li2S/MC cathode is paired with a commercial graphite anode, the full cell of Li2S/MC-graphite (Li2S-G) shows a stable capacity of around 600 mAh/g in 150 cycles. The Li2S/MC cathodes prepared by high-temperature sulfur infusion and SLMP prelithiation before cell assembly are ready to fit into current Li-ion batteries manufacturing processes and will pave the way to commercialize low-cost Li2S-G Li-ion batteries.

KEYWORDS: Li-ion battery - lithium - sulfur - Li2S - microporous carbon

Lithium–sulfur (Li–S) batteries are considered to be a promising candidate for next-generation lithium batteries owing to their high theoretical specific capacity (1675 mAh/g) and high energy density (2600 Wh/kg).

Li–S batteries utilize elemental sulfur as the active cathode material to reversibly react with metal lithium as

$$S_8 + 16Li^+ + 16e^- \leftrightarrow 8Li_2S$$

(1)

Sulfur is naturally abundant, low-cost, and environmentally friendly. However, the commercialization of Li–S batteries faces the following challenges: (i) low active material utilization due to the insulating nature of sulfur and solubility of lithium polysulfide intermediates (Li2Sx, 4 ≤ x ≤ 8) in liquid electrolytes,4,5 (ii) poor cycle life and low Coulombic efficiency arising from the dissolved lithium polysulfide shuttle and large volume change of the sulfur cathode during lithiation/delithiation,6,7 and (iii) the use of a metal lithium anode creates known safety issues with liquid electrolytes.8,9

A variety of strategies have been pursued to circumvent the sulfur cathode problems. The most effective methods are optimization of organic electrolytes10–14 and fabrication of sulfur-conductive polymer composites15–17 and sulfur–carbon-based composites.18–22 Among them, sulfur–porous carbon nanocomposites are more attractive because porous carbon can (1) improve the electronic conductivity, (2) accommodate volume change, and (3) suppress the dissolution of polysulfides.23–25 Nazar et al.26 reported that a nanostructured sulfur–mesoporous carbon cathode showed stable and reversible capacity. Manipulation of the pore size27–29 and structure of carbon materials (nanotubes,30–32 graphene,33–35 and carbon hybrids36) can further improve the electrochemical performance of Li–S batteries. We developed a highly stable S/C cathode by infusing short-chain S2 into
microporous carbon at a high temperature, which effectively prevented the formation of high-order polysulfides during lithiation, thus significantly improving the Coulombic efficiency and cycling stability of the S cathode. In addition, the absence of high-order polysulfides will allow using low-cost carbonate-based electrolytes since the side reaction between the carbonate solvent and polysulfide anions is avoided.

Although great advances have been made in stabilizing the S cathode, the cycling stability and Coulombic efficiency of these S cathodes are still lower than current ceramic ones. Moreover, all of these superior S-based composite cathodes do not contain Li and still require metal lithium or lithiated anodes for the redox couple. Today, metal lithium anodes are not used in liquid electrolyte secondary batteries due to the inevitable formation of lithium dendrites during cycling. The formation of lithium dendrites will lead to poor cyclic performance and increase the probability of internal short circuit, thus resulting in safety issues. To mitigate the safety problem of Li–S batteries, a few researchers have explored the possibility of preparing Li2S–C composites as cathodes. Currently, Li2S–C composites are synthesized using complex wetting chemistry, high-energy dry ball milling and carbonization of polyaniline–Li2S. Since Li2S is thermodynamically unstable in air due to moisture, Li2S–C materials have to be synthesized in a protected atmosphere. Due to the high humidity sensitivity of Li2S materials, the Li2S–C composite cathodes fabricated using the above methods showed poor cycling stability during prolonged cycling, which limited the practical applications of Li2S–C cathodes for Li-ion batteries.

In the present work, a superior stable sulfur/microporous carbon (MC) cathode in a low-cost carbonate-based electrolyte was synthesized by infusing small sulfur molecule (S2) vapor into MC under vacuum at 600 °C. The fabricated S/MC composite cathode was then prelithiated by spraying stabilized lithium metal powder (SLMP) onto the S/MC cathode film followed by compressing (i.e., a routine step in the cell manufacturing process) prior to cell assembly, which is a novel and facile in situ technique. The SLMP has a Li content of 98% and is air stable and safe to be handled in ambient conditions. Once the outer protective shell of the SLMP is broken by applying mechanical force on the SLMP/S/MC electrode, the Li can be released and the activated Li can quickly transport through a 3D carbon matrix and uniformly react with S in porous carbon to form Li2S in situ (Scheme 1), as evidenced by the uniform distribution of potentials with 1 V (vs Li/Li+) in different locations of the as-prepared Li2S/MC film electrodes when they are tested in half-cells. The extra SLMP can be added to a Li2S/MC cathode to compensate for the first irreversible capacity of anode, which is very important for coupling with high-capacity Si and Sn anodes. Surprisingly, the Li2S/MC cathode shows stable, high capacities together with good rate and long cycling stability in a conventional commercial Li-ion battery electrolyte (1.0 M LiPF6 in a mixture of ethylene carbonate/diethyl carbonate (EC/DEC, 1:1 by volume)). Furthermore, this Li2S/MC film cathode prepared via an in situ strategy can be coupled with a Li-free anode, such as graphite, carbon/tin alloys, or Si nanowires to form a “true” rechargeable Li-ion cell. A commercial graphite was chosen as a model anode to pair with the Li2S/MC cathode, forming a Li2S–graphite (Li2S–G) full cell, which shows high capacity and long cycling stability. The technology reported will play a significant role in the commercialization of Li2S cathodes for low-cost and high-energy Li-ion batteries.

**RESULTS AND DISCUSSION**

**Structure Analysis.** The phase structure of the S/MC composite powders was characterized by X-ray diffraction (XRD). To index the sulfur and microporous carbon in the S/MC composite, the XRD of a physical mixture of S and MC (denoted as mixed S–MC hereafter) with the same composition as the S/MC, pure S, and MC was also tested as control. XRD patterns of the samples for S, MC, mixed S–MC, and S/MC are compared in Figure 1a. As expected, the peaks belonging to S8 crystalline phases are not observed in the S/MC composite (curve b), whose pattern is almost identical to that of the MC (curve a), showing only two broad peaks within the range of 20–50° from the amorphous carbon. This result suggests that XRD cannot detect the short-chain phase (S2) in the S/MC composite,

![Scheme 1. Schematic illustration of in situ fabrication process of a Li2S/MC composite electrode.](image)
in the case of mixed S–MC, the sharp and intense peaks from the S8 crystal are clearly visible. It was reported that at 600 °C 99% of S8 will break into S2, and these S2 would strongly interact with the surface and fill the first micropores and then form a mono- or few-layered coverage of the matrix particle surface.41 When the temperature is cooled to room temperature, the S phases inside the micropores remain as the state of S2.42 The XRD fails to detect S2 peaks in MC either because S2 in the pores of carbon is an ultrathin layer or because S is amorphous. The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of the resulting S/MC composite and the corresponding energy-dispersive X-ray spectrometry (EDS) C and S maps are displayed in Figure 1b–f. The S/MC composite powder has a spherical shape with a particle size of about 600 nm. The elemental mapping images of C and S in Figure 1e and f show that the S map covers the C map. This clearly indicates that the sulfur is well dispersed in the S/MC composite.

The morphologies of the S/MC, SLMP-sprinkled S/MC (SLMP/S/MC), and compressed SLMP/S/MC electrode films are presented in Figure 2a–c. For the pristine S/MC electrode film, the S/MC particles were uniformly coated on the Al current collector to form a porous structure, as shown in Figure 2a. After sprinkling SLMP, the SLMP spheres spread onto the surface of the S/MC electrode film and remain intact with the S/MC electrode due to the inert coating layer on the Li metal (Figure 2b). The particle size of the SLMP spheres is around 50 μm. Undergoing mechanical compression, these SLMP spheres are pressed down evenly and imbedded into the S/MC composite electrode; see Figure 2c. That is, the active Li can be released by breaking the outer protective shell of the SLMP and react with the active material sulfur. The variation of phase components for the S/MC electrode film before and after the introduction of SLMP was also determined by XRD. The XRD patterns of the pristine S/MC film, SLMP/S/MC film, compressed SLMP/S/MC film, and the compressed SLMP/S/MC film with a drop of electrolyte are shown in Figure 2d. As compared to the pristine S/MC electrode film, a metal Li peak at around 36 degrees is clearly visible in the SLMP/S/MC film sample because of the load of SLMP (curve (ii) in Figure 2d). After mechanical compression, the peak belonging to the Li phase became weak and an new peak at 26.8 degrees (marked by a heart in curve (iii) of Figure 2d) appeared; the new peak can be indexed as (111) of Li2S. The coexistence of Li and Li2S phases implies that the Li is activated and Li2S can be in situ formed by solid phase reaction but not completely. After a very small amount of electrolyte is dropped on the compressing SLMP/S/MC film, the Li peak becomes invisible and an new peak at 26.8 degrees (marked by a heart in curve (iii) of Figure 2d) appeared; the new peak can be indexed as (111) of Li2S. The coexistence of Li and Li2S phases implies that the Li is activated and Li2S can be in situ formed by solid phase reaction but not completely. After a very small amount of electrolyte is dropped on the compressing SLMP/S/MC film, the Li peak becomes invisible and the intensity of the Li2S peak increases, suggesting that the active Li reacts with the S in the S/MC composite and completely transforms to Li2S in the electrolyte environment. The XRD results verify the feasibility of in situ fabrication of Li2S in the sulfur-containing electrodes. Therefore, the Li in SLMP will completely react with S in MC to form a Li2S/MC cathode after cell assembly.

**Electrochemical Properties.** The electrochemical performances of the Li2S/MC electrode were characterized in a coin cell using Li metal foil as the counter and reference electrode and 1.0 M LiPF6 in EC/DEC (1:1 v/v) as the electrolyte. The initial three-cycle lithiation/delithiation behaviors of the pristine S/MC and as-prepared Li2S/S/MC electrodes were characterized using cyclic voltammetry (CV), shown in Figure 3. For the pristine S/MC electrode, the open-circuit potential of the cell is around 3.0 V (vs Li/Li+); during the cathodic scan (lithiation), the cell exhibits two cathodic peaks at about 2.4 and 1.1 V (vs Li/Li+) in the first cycle, as shown in Figure 3a. The small peak at high voltage of 2.4 V (vs Li/Li+) is associated with the formation of soluble high-order polysulfides through lithiation of the minor resident S8 on the outside surface of porous carbon based on eqs 2–4:

$$S_8 + 2e^- \rightarrow S_{8}^{2-}$$  \hspace{1cm} (2)
The small cathodic peak at 2.4 V (vs Li/Li⁺) vanishes in the flowing cycles, which may be attributed to dissolution of a small amount of high-order polysulfides into the electrolyte and potential side reaction between polysulfide anions and carbonate solvent. The low-voltage peak at 1.1 V (starting at 1.8 V (vs Li/Li⁺)) is related to formation of insoluble low-order polysulfides as

\[ 3S_8^{2-} + 2e^- \rightarrow 4S_6^{2-} \]  
\[ 2S_6^{2-} + 2e^- \rightarrow 3S_4^{2-} \]  

The second peak is broad and appears at a low voltage, which is probably due to the physical or chemical interaction between S₂ and porous carbon. The S₂ in porous carbon was formed by the breakage of S₈ at 600 °C, and then these S₂ were infused into the micropores of the porous carbon and were stabilized at room temperature due to the restriction of pore size and interaction between S₂ and carbon, but the S₂ absorbed on the outside of carbon changed back to S₈ when the temperature cooled to room temperature. After the first cycle, the low-voltage peak current near 1.1 V (vs Li/Li⁺) was significantly reduced and shifted toward a more positive direction due to volume change. A positive voltage shift was also observed for other Li₂S/MC cathodes with large volume changes. The low voltage in the first lithiation scan is attributed to large strain/stress since a large volume change requires a large overpotential, while the strain/stress was reduced in the second lithiation due to the introduction of large defects in the electrode and pore size expansion of carbon in the first lithiation, thus reducing the overpotential and shifting the voltage to high voltage in the second lithiation. For the anodic scan, only one peak, at 2.0 V (vs Li/Li⁺), associated with oxidation of Li₂S back to S₄ or S₂, can be observed. However, for the as-prepared Li₂S/MC, the cell shows a open-circuit potential of 1.0 V (vs Li/Li⁺) (Figure 3b), further confirming the formation of Li₂S in MC. Contrary to the S/MC electrodes, the Li₂S/MC cathode has to be delithiated first. As the Li₂S/MC cathode was scanned from an open-circuit of 1.0 toward 3.0 V (vs Li/Li⁺), only one anodic peak, at 2.0 V (vs Li/Li⁺), and one cathodic peak, at 1.6 V (vs Li/Li⁺), were observed. The current and potential of both the cathodic and the anodic peaks are very stable except that the current of the cathodic peak in the initial cycle is slightly higher than that in the following delithiation scans. This suggests that the in situ formed Li₂S/MC do not have an activation process reported in the ball-milled Li₂S–C cathode and observed in pristine S/MC (Figure 3a). The stable cathodic current peaks in the first and following cathodic scans also demonstrate that the large irreversible capacity in the S/MC cathode has been compensated by the SLMP in the Li₂S/MC cathode during the prelithiation process.
The first three charge/discharge cycles at 0.1C (1C = 1675 mA/g) of the S/MC and as-prepared Li2S/MC electrodes are also compared in Figure 3. The discharge/charge curves of the S/MC electrode show a very short plateau at 2.4–2.5 V (vs Li/Li⁺) and a long plateau at 1.7 V (vs Li/Li⁺) in the first discharge and only one plateau at 2.0 V (vs Li/Li⁺) in the charge (Figure 3c). The short plateau at 2.4–2.5 V (vs Li/Li⁺) disappeared in the second discharge due to dissolution of a small amount of high-order polysulfides. The lithiation capacity is around 1200 mAh/g in the first cycle, 510 mAh/g in the second cycle, and approximately 508 mAh/g in the third cycle for the pristine S/MC cathode. The large irreversible capacity in the first charge/discharge cycle is due to dissolution of high-order polysulfide intermediates and the side reaction between dissolved polysulfide anions and carbonate solvent, which agrees with the CV scans. This large irreversible capacity in the first cycle was also reported in other S/C composite cathodes.42 The irreversible capacity of Li-free S/MC in the first cycle requires an extra Li-containing anode, which will reduce the overall capacity of the full cell. The large irreversible capacity of 690 mAh/g (lithiation capacity minus delithiation capacity in the first cycles) observed in the pristine S/MC (Figure 3c) was completely compensated in the Li2S/MC cathode. The Li2S/MC even provides extra delithiation capacity of 100 mAh/g in the first charge/discharge cycle for the compensation of the irreversible capacity of anode couples. The amount of extra capacity of the Li2S/MC cathode can be manipulated by adjusting the SLMP loading to match different anodes with a variety of irreversible capacities. As high-capacity anodes (such as Si and Sn) normally have large irreversible capacities, the degree of prelithiation can easily be estimated from the open-circuit potentials of prelithiated electrodes. For the as-prepared Li2S/MC sample, the open-circuit voltage is around 1.0 V (vs Li/Li⁺). Although the charge and discharge sequences for the Li2S/MC are opposite those of the pristine S/MC cathodes, its potential plateaus are almost identical to those of the pristine S/MC after the first cycle (Figure 3c and d). Therefore, the Li2S/MC cathodes synthesized via the in situ strategy can effectively preactivate the electrodes mainly because Li2S/MC is in an expanded state. Here, it is worth noting that the discharge capacities of the Li2S/MC electrode are higher than those of the pristine S/MC after the initial cycle and achieve more than 650 mAh/g in the second and third cycles. This indicates that in situ fabrication of Li2S/MC can also improve the utilization of sulfur.

The cycling stability of the pristine and in situ lithiated S/MC electrodes is displayed in Figure 4, showing high Coulombic efficiency and long cycling stability for both the pristine S/MC and in situ lithiated Li2S/MC electrodes. Figure 4a presents the charge and discharge voltage profiles of the S/MC electrode in the first, 10th, 200th, and 500th cycle. The S/MC maintains a capacity of 500–550 mAh/g except for the first cycle. Capacity evolution with the cycles for S/MC shown in Figure 4b demonstrates exceptional stable capacity during 800 charge/discharge cycles, which is rarely
reported in the literature. The Coulombic efficiency is close to 100%. The long cycling stability and high Coulombic efficiency of S/MC in carbonate-based electrolytes are attributed to the elimination of high-order polysulfide intermediates, which avoids the shuttle reaction and reduces the side reaction between polysulfide anions and the carbonate solvent. The side reaction between polysulfide anions and carbonate solvent has been reported for the S8/C cathode and was confirmed using a S8/MC composite cathode. The S8/MC control sample was prepared by physically mixing MC and S8 corresponding to 30% of S in MC. The long voltage plateau at 2.4 V (vs Li/Li+) in the first discharge demonstrates the formation of high-order polysulfide intermediates (Figure S1). These high-order polysulfide intermediates will be dissolved into electrolyte to form polysulfide anions and react with carbonate solvent, resulting in disappearance of the 2.4–2.5 V (vs Li/Li+) plateau in the second discharge and a reduced capacity from 610 mAh/g in the first discharge to 200 mAh/g in the second one.

The superior cycling stability and Coulombic efficiency of S/MC are inherited by in situ lithiated Li2S/MC electrodes (Figure 4c and d), and Li2S/MC cathodes can provide even higher capacity (650 mAh/g) than that (550 mAh/g) of S/MC (Figure 4a–d). Unlike the chemically lithiated Li2S–C cathodes, for which a large overpotential is needed to activate the Li2S in the first delithiation,37,39 the delithiation potential profile of in situ SLMP lithiated Li2S–C in the first cycle is similar to the behavior in the following cycles. Therefore, the Li2S–C formed by in situ lithiation using SLMP is in an active state. The Li2S/MC cathode shows minor capacity fade and around 100% Coulombic efficiency with progressive cycling for 900 times. Such electrochemical performance has not been reported for Li2S/C cathodes to date.

The rate capabilities of the S/MC and Li2S/MC electrodes are shown in Figure 5. The S/MC cathode provides 510 mAh/g at 0.1C (1C = 1675 mAh/g) and 100 mAh/g at a high current of 10C, demonstrating a high rate performance. The prelithiated cathode of in situ formed Li2S/MC shows even better rate capability than the S/MC electrode. For instance, it can provide a reversible capacity of 650 mAh/g at a current density of 0.1C and 150 mAh/g at 10C, which is around 30–50% higher than that of S/MC cathodes. Overall, the in situ formed Li2S/MC electrode has a high and stable capacity together with a high rate capability.

The Li2S/MC cathodes prepared by sulfur vapor infusion at 600 °C and in situ SLMP lithiation have demonstrated one of the best cycling stabilities and one of the highest Coulombic efficiencies reported in the literature. Therefore, we should expect the full cell with a Li2S/MC cathode and Li-free anode to have a high cycling stability. A full cell using graphite as a model anode and Li2S/MC as a cathode was assembled, and the electrochemical performance was investigated. The graphite anodes were first tested in a Li/G half-cell configuration using the same electrolyte that was utilized in the Li2S/MC-Li half-cells. The capacity of graphite is around 270 mAh/g with a stable cycling capacity (see Figures S2 and S3). The Li2S/MC-graphite (Li2S-G) full cell has a capacity ratio of Li2S/MC to G of 0.98 (Li2S/MC is a limiting electrode).
Figure 6a shows the voltage profiles of the first, 10th, and 50th charge and discharge cycle for a Li$_2$S/MC-graphite full cell at a current density of 168 mA/g. The average discharge voltage of the Li$_2$S-G full cell is around 1.6 V. Although a slight decay in capacity occurs in the first several cycles, the Li$_2$S-G full cell retains a reversible capacity of around 600 mAh/g in 150 cycles and the Coulombic efficiency is close to 100%. The irreversible capacity of the Li$_2$S-G full cell in the first charge/discharge cycles is less than 15% due to the extra Li in the in situ formed Li$_2$S/MC cathode (Figure 3b). The irreversible capacity of the present Li$_2$S-G is much lower than that (55%) of the Li$_2$S/Si cell. The cycling test of the full cell is still under way. The electrochemical performance of the Li$_2$S/MC-graphite cell can be further improved by optimizing the electrode thickness and capacity ratio. The result confirms that the in situ fabricated Li$_2$S/MC electrode can not only provide the lithium source but also possess superior electrochemical performance.

**CONCLUSIONS**

In summary, highly stable S/MC materials were synthesized by infusing S into porous carbon at a temperature of 600 °C, and Li$_2$S/MC composite cathodes were fabricated by spraying SLMP onto a coated S/MC cathode electrode followed by compressing prior to cell assembly. The S/MC cathode in which S exists mainly as S$_2$ shows almost 100% Coulombic efficiency and provides a capacity of around 510 mAh/g without noticeable capacity decline for 800 cycles in a conventional carbonate-based electrolyte (1.0 M LiPF$_6$ + EC/DEC (1:1 v/v)). The in situ prelithiated Li$_2$S/MC cathode with an open circuit voltage of 1.0 V (vs Li/Li$^+$) shows even better electrochemical performance than that of the pristine S/MC. At a current density of 0.1C (1C = 1675 mA/g), the reversible capacities of the Li$_2$S/MC cathode demonstrate almost no capacity fade even on cycling up to more than 900 cycles, and the Coulombic efficiency is close to 100%. Moreover, the Li$_2$S/MC cathodes formed by in situ lithiation can pair with nonmetallic lithium anodes, such as graphite, carbon/Tin alloys, and Si nanowires through manipulating the first delithiation capacity. A Li$_2$S-G full cell model shows a high and stable capacity of around 600 mAh/g in 150 cycles. We believe that the results described here may substantially contribute to the progress of Li–S battery technology.

**EXPERIMENTAL SECTION**

*Synthesis of Microporous Carbon.* MC was synthesized according to a reported procedure. Sucrose was dissolved in 6.0 M sulfuric acid to form a mass fraction of 5% sucrose solution, which was placed in a round-bottom flask and refluxed at 120 °C for 10 h to yield a dark brown precursor. The precursor was filtered, washed by water, and air-dried at 100 °C overnight to form a solid. Then the solid product was calcined under argon at 1000 °C for 2 h, with a heating rate of 5 °C/min.
Preparation of S/MC Composite. Identical to the procedure described in a previous publication, the S/MC composite was prepared by infiltration of sulfur into the MC carbon fiber (CMC) matrix. In this work a mass ratio of CMC:sulfur = 5:3 was employed. The prepared MC and the sublimed sulfur (Sigma-Aldrich) were mixed by ground milling. First the mixture was sealed in an evacuated quartz tube and then heated to 600 °C at a rate of 5 °C/min and kept at this temperature for 6 h. After that, a long cooling time of 24 h was employed to ensure a complete infiltration of sulfur into the pores of MC. After cooling to room temperature, the S/MC composite was obtained. To verify the actual sulfur content in the S/MC composite, thermogravimetric analysis (TGA) was performed on a Netzsch STA 449 F1, Germany, with a heating rate of 10 °C/min, and high-purity Ar as the purge gas.

Preparation of Li2S/MC Electrode. The S/MC composite was mixed with acetylene black and sodium carboxymethyl cellulose binder in a weight ratio of 70:15:15 mixed in distilled water. The slurry was coated on an aluminum foil to obtain a film with a thickness of approximately 40 μm, then dried in a vacuum oven at 100 °C overnight. The active material loading was around 1 mg/cm². Then commercialized stabilized lithium metal powders (AMC Lithium, USA), with a metallic Li content of no less than a mass fraction of 98%, was sprinkled onto the S/MC film. The SLMP loading was determined from the sulfur loading in S/MC to ensure the formation of Li2S/MC. Due to a good stability of the SLMP, the sprinkling process was conveniently carried out in ambient conditions. The resulting film was compressed and cut into pieces with a diameter of 1 cm for assembling half-cells in a glovebox with an Ar atmosphere. For comparison, the film without the addition of SLMP was also compressed and cut into the same size for cell testing.

Structural Characterization. X-ray diffraction patterns were recorded on a Rigaku D/max 2400, Japan, with Cu Kα radiation in the 2θ range from 10° to 80°. The electrode film samples after sprinkling SLMP and compressing for XRD studies were smeared on a glass slide in an argon glovebox and then covered with Scotch tape to prevent reaction with water and/or oxygen during measurement. Additionally, a fresh Al foil covered with Scotch tape was scanned in the same conditions as background (Figure S4). Scanning electron microscopy images were obtained on a Hitachi S-4700 (Japan) operating at 10 kW. The transmission electron microscopy samples were examined in a JEOL (Japan) 2100F field emission TEM equipped with an energy-dispersive X-ray spectrometer.

Electrochemical Measurements. The cells were assembled in a glovebox filled with high-purity Ar. Lithium metal was used as the counter electrode and reference electrode in half-cells. Commercial graphite, Timrex KS Graphite (Timcal Group, Switzerland), was used as the anode material for full cells. The separator was mesoporous polypropylene Celgard3501 (Celgard, Switzerland), was used as the anode material for full cells. The lithium metal was used as the counter electrode and reference electrode in half-cells.

REFERENCES AND NOTES