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Recovery from self-assembly: a composite material for lithium-sulfur batteries[†]

Xiaohui Zhao,^a Dul-Sun Kim,^a James Manuel,^a Kwon-Koo Cho,^b Ki-Won Kim,^b Hyo-Jun Ahn^b and Jou-Hyeon Ahn^{*ab}

A highly ordered mesoporous carbon, AlCMK, with an assembly of carbon rods and a bimodal pore system is used for sulfur encapsulation, and the AlCMK/S composite is observed to be able to accommodate volume expansion during a discharge process and recover its original structure when recharged. It is proved that the assembly structure of AlCMK makes it "breath" during the redox reaction of lithium and sulfur. Such a novel ability greatly benefits the maintenance of electrode construction during a repeated discharge–charge process. Moreover, a long heating time (e.g. 20 h) at 300 °C in a two-step melt diffusion method is found to contribute to the uniform dispersion of sulfur in the AlCMK carbon matrix. Using this featured composite, a Li–S cell retains 627 mA h g⁻¹ after 450 cycles at 0.1 C-rate with a coulombic efficiency close to 100% and also shows good rate capability up to 5 C-rate, demonstrating a significant improvement of reversible capacity and cycle stability of Li–S cells.

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Introduction

Concerns about global petroleum supply and climate change have stimulated a resurgence of research on alternative and carbonneutral energy sources. Lithium rechargeable batteries have been considered as promising energy storage technologies for various power applications that depend on electrical energy. The state-ofthe-art lithium ion (Li-ion) batteries are able to reach a cathode capacity of \sim 250 mA h g⁻¹ and an energy density of \sim 800 W h kg^{-1} , and have demonstrated a great success in portable electronics.1 However, it is difficult for the current Li-ion batteries to satisfy the safe, low-cost, high-energy-density and long-lasting requirements for the increasing transportation market. Naturally abundant sulfur is a promising cathode material for lithium batteries due to its high theoretical specific capacity of 1675 mA h g^{-1} . The lithium-sulfur (Li-S) reaction can generate a Gibbs energy of 2600 W h kg⁻¹, that is, Li–S batteries generate three times greater energy densities than Li-ion batteries at a significantly lower cost.^{2,3} Nevertheless, they still suffer from several challenges that hinder practical applications. Conventional Li-S cells consist of a lithium metal anode, an organic liquid electrolyte and a sulfur cathode. The intimate contact between sulfur and effective conductors such as carbon is a prerequisite for electrical conductivity, and organic electrolytes have to wet the sulfur for ionic transport in that sulfur is electrically and ionically insulating. Any deficiency in either aspects would lead to low utilization of active material. Moreover, soluble lithium polysulfide intermediates (Li₂S_n, $4 \le n \le 8$) generated during cycling are easily dissolved in liquid electrolyte. The dissolved polysulfides are then oxidized or reduced on the surface of electrodes, which is often referred to as a "shuttle mechanism" that results in low coulombic efficiency and poor cycling stability.^{4,5}

To address these persistent problems, intense efforts are being made towards developing carbon-based sulfur composites with novel capacity of sulfur containment and conductivity enhancement. A breakthrough was made by Nazar's group where sulfur is housed in mesopores of CMK by a simple melt diffusion method whereby the porous carbon matrix serves as an electrochemical nano-reactor for sulfur and lithium, meanwhile avoiding the leakage of soluble polysulfides from cathodes.6 A similar strategy was also undertaken to create a diverse range of sulfur composites using nanoporous carbon, carbon fibers, carbon nanotubes, graphene or conducting polymers such as polyacrylonitrile, polyaniline, and polypyrrole.7-16 As a sulfur cathode undergoes a series of compositional and structural changes during cycling, the volume expansion of active material inevitably affects the maintenance of a rigid cathode structure.17,18 To date, a few efforts have been made to address this problem, such as the yolk-shell structured S-TiO₂ composite with TiO₂ as a shell surrounding partially etched sulfur.19 However, no carbon material has been developed for relieving or settling the volume expansion.

^aDepartment of Chemical and Biological Engineering and Research Institute for Green Energy Convergence Technology, Gyeongsang National University, 900, Gajwa-dong, Jinju 660-701, Republic of Korea. E-mail: jhahn@gnu.ac.kr; Fax: +82-55-772-1789; Tel: +82-55-772-1784

^bDepartment of Materials Engineering and Convergence Technology, Gyeongsang National University, 900, Gajwa-dong, Jinju 660-701, Republic of Korea

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In this study, a mesoporous carbon, AlCMK, comprising a highly ordered assembly of carbon rods was synthesized by a nanocasting method using aluminated SBA-15 (AlSBA-15) as a hard template and furfuryl alcohol as the carbon source. To the best of our knowledge this is the first time that Li–S cells have been assembled such that AlCMK accommodates the volume change of the electrodes during cycling. Besides, this mesoporous carbon contains a bimodal pore system which is derived from the removal of silica template and partial infiltration of the carbon source. The AlCMK/S composites were prepared by a two-step melt diffusion method at 155 °C and 300 °C, and the heating time at 300 °C was optimized for improvement of sulfur distribution which directly determines the electrochemical performance of the AlCMK/S composites.

Experimental

Synthesis of AlSBA-15 and AlCMK

SBA-15 was synthesized according to previous literature.²⁰ Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly-(ethylene glycol) (Pluronic P123, Aldrich) and tetraethyl orthosilicate (TEOS, Aldrich) were employed as surfactant and silica source, respectively. Pluronic P123 (2.0 g) was dissolved in HCl (60 mL, 2 M) at 40 °C. TEOS (4.2 g) was then added and stirred vigorously with a homogenizer. After standing still for 24 h at 40 °C, the milky solution was transferred into a Teflon jar and aged at 130 °C for 3 days in an oil bath. It was then collected by filtration without washing and dried at 60 °C. SBA-15 was obtained after calcination at 550 °C for 4 h in air atmosphere. Alumination was performed on the as-prepared SBA-15 as follows.²¹ AlCl₃·6H₂O (3.62 g) was dissolved in ethanol (200 mL) and SBA-15 (1.7 g) was then added under stirring for 1 day. The resulting solid was filtered, rinsed with ethanol and sintered at 550 °C for 5 h to obtain AlSBA-15. Furfuryl alcohol in trimethylbenzene (TMB) (50/50, v/v) was used as carbon source and it was impregnated into the pores of AlSBA-15 by the incipient wetness method. The polymerization of furfuryl alcohol was carried out by heating at 80 °C for 12 h and continuously at 150 °C for 6 h under vacuum. The carbonization process was performed by heating the composite to 300 °C at a rate of 1 °C min⁻¹, then increasing to 850 °C at a rate of 5 °C min⁻¹ and maintained for 4 h. The product was soaked in HF solution (25 wt%) for 24 h to remove the template. The final AlCMK was obtained after rinsing with water and drying at 80 °C under vacuum.

Synthesis of AlCMK/S composites

Sulfur and AlCMK in a 70 : 30 weight ratio were homogeneously mixed by ball milling for 15 min. The composites were then subjected to a two-step thermal treatment under N₂ protection at 155 °C for 20 h and 300 °C for 0, 1, 3 and 20 h. The AlCMK/S composites thus obtained were designated as AlCMK/S-20-*n*, in which *n* represents the heating time at 300 °C. For example, AlCMK/S-20-20 was synthesized at 155 °C for 20 h and 300 °C for 20 h. AlCMK/S and Super-P/S composites were also synthesized for comparison by simple ball milling instead of the melt diffusion method and designated as AlCMK/S-0-0 and SP/S-0-0, respectively.

Structural characterizations

Field emission scanning electron microscopy (FESEM, Philips XL30S FEG), field emission transmission electron microscopy (TEM, TF30ST-300 kV), high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) and energy dispersive X-ray spectroscopy (EDS) were used to observe the morphology and elemental distribution of samples. The specific surface area and the pore volume of AlCMK and AlCMK/S composites were measured with Brunauer-Emmett-Teller analysis (BET, ASAP 2010). X-ray diffraction (XRD) patterns of samples were recorded by an X-ray diffractometer (D2 Phaser Bruker AXS). Sulfur content of AlCMK/S composites was determined with thermogravimetric analysis (TGA, Q50, TA Instruments) by heating to 600 °C at 10 °C min⁻¹ under N₂ flow. X-ray photoelectron spectroscopy (XPS, ESCALAB250 VG Scientific) was carried out using a monochromatic Al Ka (1486.6 eV) X-ray source. Auger electron spectroscopy (AES, ULVAC PHI700) sputter depth profiling at a rate of 17.8 nm min⁻¹ was used to detect sulfur distribution.

Electrochemical measurements

AlCMK/S cathodes were prepared by mixing AlCMK/S composite, Super-P carbon and polyvinylidene difluoride (PVdF) in a weight ratio of 8:1:1 in N-methyl-2-pyrrolidone (NMP) and the slurry was cast on an aluminum foil. The sulfur loading in cathodes is around 0.6–1.0 mg cm⁻² (Table S1†). Li–S cells were assembled in a stainless steel (SS) Swagelok® cell by stacking AlCMK/S cathode, Celgard® 2400 separator and Li anode in an argon-filled glove box. 1 M bis(trifluoromethane) sulfonimide lithium salt (LiTFSI) in a mixed solvent of 1,3dioxolane (DOL) and dimethyl ether (DME) at a volume ratio of 1:4 was used as the electrolyte. Electrochemical impedance spectra (EIS) of cells were measured with an IM6 impedance analyzer over a frequency range of 100 mHz to 2 MHz at an amplitude of 20 mV. Cyclic voltammetry (CV) was performed at a scan rate of 0.1 mV s⁻¹ between 1.5 and 2.8 V. Cycle performances were tested with a WBCS3000 battery cycler (WonA Tech. Co.) with cut-off voltages between 1.5 and 2.8 V at different C-rates.

Results and discussion

The as-obtained AlCMK was subject to FESEM (Fig. 1a). It shows a barrel-like morphology with a vertical length of 400–1000 nm and a lateral diameter of 250–400 nm. The highly ordered mesoporous structure of AlCMK was clearly observed by TEM (Fig. 1b and c). It is compactly assembled with many carbon rods in parallel and such a highly ordered structure also creates interconnection between the carbon rods, which is expected to offer a pathway for fast lithium ion transport.^{21,22} N₂ adsorption–desorption isothermal analysis was performed to determine the porosity of AlCMK (Fig. 1d). It exhibits typical type IV sorption isotherms of mesoporous structure with two hysteresis



Fig. 1 (a) FE-SEM image, (b and c) TEM images and (d) nitrogen sorption isotherms with pore size distribution (inset) of AlCMK.

loops at relative pressures (P/P_0) of 0.45–0.7 and 0.7–1.0, indicating a bimodal pore size distribution of AlCMK.²³ According to the Barrett–Joyner–Halenda (BJH) method, the mesopores are peaked at 4 nm and 12 nm (Fig. 1d, inset), in which the voids left by the removal of silica walls contribute to the smaller pores whereas the partial carbon impregnation leads to the formation of the larger pores. BET calculation indicates that AlCMK possesses a high specific surface area of 1812 m² g⁻¹ and pore volume of 2.91 cm³ g⁻¹. Therefore, AlCMK is able to load sufficient sulfur and retain high conductivity, and the bimodal pore size distribution will favor the confinement of sulfur and polysulfides.^{7,24,25}

To prepare the AlCMK/S composite, the melt diffusion method is used to encapsulate sulfur into the mesoporous AlCMK. As shown in Fig. 2, molten sulfur with the lowest viscosity is infiltrated into the pores of carbon by capillary force at 155 °C for a fixed time interval of 20 h, which can suffice for the loading of sulfur and afford an intimate contact between insulting sulfur and conductive carbon.²⁶ The non-infiltrated sulfur is vaporized at 300 °C for a certain time, which should be sufficient to eliminate the excess loading but not impair much the active mass. The effect of heating time on sulfur–carbon composite construction was also investigated. AlCMK/S-0-0 was also synthesized for comparison by ball milling instead of the



Fig. 2 Schematic diagram of the synthesis process of the AICMK/S composite.

melt diffusion method. The significant reduction in surface area and pore volume as a result of the melt diffusion method indicates successful sulfur encapsulation into the AlCMK carbon matrix (Table S1†).

TGA is often used to determine sulfur content and sulfur location in a carbon matrix.²⁷ The analysis shows that sulfur content is decreased with heating time at 300 °C (Fig. 3, upper). One-step heating at 155 °C allows sulfur loading of 60.8 wt% in AlCMK/S-20-0. Additional 1 h heating at 300 °C significantly reduces sulfur content to 49.8 wt% in AlCMK/S-20-1, but its pore volume is still comparable to that of AlCMK/S-20-0 (Table S1⁺). These results suggest that sulfur on the external surface can be quickly vaporized within 1 h, which was also corroborated by XRD (Fig. S1[†]) since no discernable peaks corresponding to crystalline sulfur are observed in XRD patterns of AlCMK/S composites with heating at 300 °C. However, further extension of the heating time to 3 h or 20 h leads to a marginal reduction of sulfur to 47.2 wt% in AlCMK/S-20-3 and 43.8 wt% in AlCMK/S-20-20, which suggests that a longer vaporization time does not result in a more severe sulfur loss. It is likely due to the fact that sulfur can be vaporized in a closed space until the vapor pressure reaches its threshold. Derivative weight loss vs. time plots index the distribution of sulfur in AlCMK/S composites as shown in Fig. 3 (lower). Both AlCMK/S-0-0 and AlCMK/S-20-0 showed two peaks at around 275 °C and 320 °C, corresponding to sulfur on the external surface and in the interior pore space of AlCMK, whereas there is only one peak at around 330 °C in AlCMK/S-20-1, AlCMK/S-20-3 and AlCMK/S-20-20. These data once again confirmed the effect of 300 °C thermal treatment on removal of excess sulfur. It is also noted that all AlCMK/S composites have much more moderate peak slopes than



Fig. 3 TGA plots (upper) and derivative weight loss vs. time curves (lower) of elemental sulfur, AlCMK/S composites with ball milling or different heating time at 300 $^{\circ}$ C.

crystalline sulfur, suggesting a high capability of AlCMK in confining sulfur.

The morphology of AlCMK/S composites and sulfur distribution in the composites were further investigated by FESEM and TEM. The AlCMK/S-20-20 composite retains the original AlCMK morphology and highly ordered pore structure without the presence of any bulk sulfur (Fig. S2[†]). Notably, the TEM image of AlCMK/S-20-20 composite in Fig. 4a displays homogeneous distribution of sulfur in the framework of AlCMK carbon while a trace of sulfur can be observed to cover the surface or to be not uniformly dispersed in the AlCMK matrix for AlCMK/S-20-0, AlCMK/S-20-1 and AlCMK/S-20-3 composites (Fig. S3[†]). This is also evident from HAADF STEM image with uniform EDS mapping of sulfur and carbon (Fig. 4b-d). Auger electron spectroscopy was also performed to investigate the sulfur distribution as a function of depth in the AlCMK/S-20-20 composite. Stable atomic concentration of sulfur and carbon represents their uniform distribution along with sputtering time (Fig. S4[†]). Elemental analysis provides another proof that similar sulfur content was detected at different points of AlCMK/S-20-20 (Fig. S5[†]). Together, sulfur can be well dispersed within the interior of the pores of AlCMK by a long heat treatment time (e.g. 20 h) at 300 °C. It was considered that a sufficient equilibrium time and a steady pressure are required to disperse sulfur in a homogenous manner after sulfur impregnation. The long heating time (e.g. 20 h) fairly guarantees the occurrence of this equilibrium. Interestingly, the extension of heating time at 300 °C also increases the electrical conductivity of AlCMK/S which remains of the same order as that of pristine AlCMK (Table S1[†]).

XPS was carried out to detect the change of sulfur orbital state in AlCMK/S composites with different heating times at 300 °C. Distinct signals of O 1s (531.2 eV), C 1s (284.6 eV), S 2s (228 eV) and S 2p (163.9 eV) are detected in the XPS spectra for AlCMK/S-20-0, AlCMK/S-20-3 and AlCMK/S-20-20 composites (Fig. 5a). Signals of carbon and sulfur are derived from AlCMK



Fig. 4 (a) TEM image of AlCMK/S-20-20 composite, (b) HAADF STEM image of the area selected from (a) and EDS mapping of (c) carbon and (d) sulfur.



Fig. 5 (a) XPS spectra of AlCMK/S-20-0, AlCMK/S-20-3 and AlCMK/S-20-20; (b) XPS spectra of S 2p in AlCMK/S-20-20 composite.

and sulfur while the oxygen signal results from the acid group generated in the synthesis process of AlCMK. N 1s signal is only found in the spectra of AlCMK/S-20-3 and AlCMK/S-20-20 composites, which probably originates from chemisorbed N₂ species in the melt diffusion process.28 Peaks at 286 eV and 402 eV in the fitted spectra of C 1s and N 1s from the AlCMK/S-20-20 composite confirmed the interaction of nitrogen with carbon (Fig. S6a and b⁺).^{29,30} It is revealed that nitrogen is doped into the composite and its amount increases with longer heating time, which may contribute to the increase in electrical conductivity of AlCMK/S composites.³¹ The S 2p spectrum of AlCMK/S-20-20 is deconvoluted into three individual component peaks at 164 eV, 165.2 eV and 168.9 eV that are associated with S $2p_{3/2}$, S $2p_{1/2}$ and sulfate species, respectively (Fig. 5b). The fitted peaks shift to higher binding energy (0.2 eV) compared to the AlCMK/S-20-0 composite (Fig. S6c[†]), which suggests some interactions occur between sulfur and carbon with heating at 300 °C. The AlCMK/S-20-3 composite has the same fitted peaks yet at lower intensity than the AlCMK/S-20-20 composite (Fig. S6d[†]), indicating that an increase heating time strengthens the interaction and further improves the integrity of the composite.

Cycle performances of Li–S cells with AlCMK/S composites are shown in Fig. 6a. Sulfur is ball milled with AlCMK or Super-P

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Fig. 6 (a) Cycle performance of cells with SP/S-0-0 and AlCMK/S composites prepared with ball milling or different heating time. (b) Long-term cycle performance and coulombic efficiency of cells with AlCMK/S-20-3 and AlCMK/S-20-20 composites.

carbon black without heat treatment and the samples thus obtained are designated as AlCMK/S-0-0 and SP/S-0-0, respectively. Cells with AlCMK/S composites outperformed the SP/S-0-0 counterpart with greatly improved discharge capacities at a rate of 0.1 C (1 C = 1675 mA g^{-1}), which is attributed to the above-mentioned unique features of AlCMK mesoporous carbon. In addition, the melt diffusion method is superior to ball milling for the improvement of both capacity and cyclability when AlCMK/S-20-0 is compared to AlCMK/S-0-0. The capacity retention is correlated to the heat treatment time at 300 °C. The cell with AlCMK/S-20-20 delivers a reversible capacity of 821 mA h g⁻¹, representing 72% of capacity retention and equivalent to an initial capacity of the SP/S-0-0 cell after 100 cycles of discharge-charge. These results reveal that the uniform sulfur dispersion and the intimate contact with AlCMK play a key role in improving the electrochemical performance of cells, which is in accord with characterizations of AlCMK/S composites. Long-term stability of cells is an essential prerequisite for the practical use of Li-S batteries. The long-term cycle (>400 cycles) performance is explored in cells with AlCMK/S-20-3 and AlCMK/S-20-20 composites at 0.1 C-rate as shown in Fig. 6b. The cell with AlCMK/S-20-20 still retains a capacity of 627 mA h g^{-1} at the end of 450 cycles and a coulombic efficiency of up to 98%. This is only a 17% reduction over 350 cycles (101-450 cycles), corresponding to a low decay rate of 0.048% per cycle. In contrast, the cell with AlCMK/S-20-3 exhibits a

significant capacity decrease (27% of its initial capacity) with a relatively rapid decay rate of 0.089% per cycle over 300 cycles (101-400 cycles). Importantly, the decay rate is lowered with cycling in the cell with AlCMK/S-20-20. For example, the decay rate of the fourth group of 100 cycles (301-400 cycles) is decreased to 0.027% per cycle, which is just 38% of the second group of 100 cycles. These results are superior to those of other works with CMK or porous carbons with a hierarchical pore system.⁶⁻⁹ The cell with AlCMK/S-20-20 cycled 450 times before it was cut off, which is equivalent to a life span of around 200 days and is longer than that reported in many other works for which testing was done at higher current densities,13,16,17,19 indicating an outstanding stability of the internal electrochemical environment and good capacity reversibility. It is concluded that a longer heating time at 300 °C is critical for sulfur distribution in the AlCMK carbon matrix and the contact between sulfur and carbon matrix, thus contributing to the enhancement of cycle stability.

To determine a possible mechanism for the good performance of the AlCMK/S-20-20 composite, the morphologies of cathodes were visualized by FESEM and TEM after cycling (Fig. 7). As a result, fresh AlCMK/S-20-20 composite in Fig. 7a displays a quite similar morphology to pristine AlCMK in Fig. 1a. Surprisingly, the compactly assembled structure was loosened, and numerous small rods with size of *ca.* 30–40 nm were clearly distinguishable after discharge (Fig. 7b). When the cell was re-charged, the scattered carbon rods self-assembled



Fig. 7 FESEM images of the AlCMK/S-20-20 cathode (a) fresh, (b) after the 1st discharge and (c) after the 1st cycle; (d) TEM image of the AlCMK/S-20-20 cathode after the 1st discharge and its (e and f) EDS mapping; (g) TEM image of the AlCMK/S-20-20 cathode after the 1st cycle and its (h and i) EDS mapping; (j) TEM image of the AlCMK/S-20-20 cathode after the 450th cycle and its (k and l) EDS mapping. All cycles were performed at 0.1 C.

again to recover the original compact morphology (Fig. 7c). Thus, the AlCMK/S-20-20 cathode completes a "breath" to accommodate volume expansion of lithiated sulfur during the discharge-charge process. The "breath" was confirmed by EDS mapping where sulfur and carbon are dispersed in a more significant way after the cathode is discharged than after it is recharged (Fig. 7d-i). Additionally, the "breath" in several repeat cycles does not result in the structural collapse of the AlCMK/S-20-20 cathode, which is evident in the FESEM and TEM images and EDS mappings of this cathode after 450 cycles (Fig. S7[†] and 7j-l). Therefore, the unique featured AlCMK matrix and the uniform sulfur dispersion by melt diffusion with longer heating time lead to the superior performance of the AlCMK/S-20-20 cathode. AlCMK is an assembly of numerous carbon rods with adjacent channels and a bimodal pore system, which differs from other rigid carbons with a single construction and is flexible for accommodation of the volume change. Slight shift and swing of hexagonal array rods are compromised with sulfur expansion whereby the carbon rods appear scattered or separated. Moreover, the AlCMK framework bears the same pressure of sulfur expansion from each orientation due to the uniform sulfur dispersion in AlCMK, so that AlCMK is able to recover its framework after sulfur shrinkage.

The CV plot presented a typical oxidation peak at ~2.5 V and two shape reduction peaks at 2.3 V and 2.0 V (Fig. S8a†), which are related to the transformation from lithium polysulfides Li_2S_8 to Li_2S_4 and finally to Li_2S_2 and Li_2S , respectively.³² The discharge–charge capacity *vs.* voltage profiles also showed typical two voltage plateaus, corresponding to the CV plot (Fig. S8b†). The capacity of AlCMK-20-20 was also evaluated at higher C-rates. The initial capacities were 1355, 1251 and 721 mA h g⁻¹ at 1 C, 2 C and 5 C, respectively (Fig. 8), showing high active material utilization and fast reaction kinetics. The coulombic efficiency over 450 cycles was calculated to be 98% (Fig. 6b), suggesting little shuttle effect due to low dissolution of polysulfides. Accordingly, the interfacial resistance only decreased within the first few cycles and then stabilized at *ca.* 20 ohm even after 200 cycles (Fig. S9†). These results indicate



Fig. 8 Cycle performance of the cell with AICMK/S-20-20 composite at high C-rates.

that the cell with AlCMK/S-20-20 is highly reversible under a well-established internal electrochemical environment.

Conclusions

A well-designed mesoporous carbon, AlCMK, from the CMK family was used for encapsulating sulfur as a cathode material for Li-S batteries. AlCMK/S composites exhibited enhanced cycle stability and longer life span. The improved performance of AlCMK/S composites could be attributed to: (i) AlCMK with high specific surface area, high pore volume and bimodal pore distribution, which provide enough room for confining active materials and serve as a highway for the transport of both lithium ions and electrons; (ii) uniform distribution of sulfur in the AlCMK carbon matrix by the melt diffusion method, where the heating time at 300 °C is extended to 20 h to improve sulfur dispersion, guaranteeing a composite with high electrical conductivity and (iii) the unique "breath" capability, a selfassembly process of carbon rods of AlCMK, which can accommodate the volume expansion and preserve the electrode construction from collapse. We believe this AlCMK with a novel structure would favor the development of Li-S batteries and also shed light on the fabrication of other composite materials related to the issues of volume expansion.

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