

# Influence of Primary Particle Morphology and Hydrophilicity of Carbon Matrix on Electrode Coating Quality and Performance of Practical High-Energy-Density Li–S Batteries

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Li-S batteries have attracted attention as the next-generation secondary batteries. While substantial progress is made in understanding Li-S chemistry at a fundamental level, only a limited number of studies are dedicated to achieving high energy density at the practical pouch cell level. The challenge lies in attaining high-energy-density Li-S batteries under harsh conditions, which involve a minimal amount of electrolyte and a relatively high areal S-loading cathode. This discrepancy creates a substantial gap between fundamental material research and comprehensive cell-level investigations. In this study, it is investigated how the morphology and properties of two carbon materials, namely Ketjen black (KB) and mesoporous carbon nano-dendrites (MCND), influence the composite cathode architecture and determine the performance of Li-S batteries. Unlike KB, MCND allows for a higher sulfur-loading cathode without evident cracks in the composite cathode. This achievement can be attributed to the high porosity, excellent wettability, and high conductivity exhibited during an identical electrode preparation procedure. Furthermore, large-format Li-S pouch cells incorporating MCND/S cathodes are successfully fabricated. These cells demonstrate an energy density surpassing 250 Wh kg<sup>-1</sup> and an initial discharge capacity of 3.7 Ah under challenging conditions (S-loading > 5 mg cm<sup>-2</sup> and E/S <3.5 μL mg<sup>-1</sup>).

# 1. Introduction

The demand for rechargeable batteries with high energy densities, reduced costs, and long-term cycling performance is rapidly increasing. This growing demand is driven by the desire to fully harness renewable energy and facilitate the widespread adoption of electric vehicles, including unmanned aerial vehicles.<sup>[1-4]</sup> However, conventional lithium-ion batteries (LIBs) based on Li-ion intercalation chemistry, which have been widely applied in portable devices, cannot satisfy the demand for energy densities >250 Wh kg<sup>-1</sup>.<sup>[5,6]</sup> Therefore, lithium-sulfur (Li-S) batteries have attracted attention as one of next-generation rechargeable secondary batteries owing to their extremely high theoretical energy densities (2600 Wh  $kg^{-1}$ ), primarily due to the high capacity of elemental sulfur (1672 mA h  $g^{-1}$ ). Moreover, sulfur is abundant in nature and cost-effective, making it an attractive active cathode material for practical

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applications.<sup>[7,8]</sup> However, several obstacles continue to hinder the practical application of Li–S batteries, including the intrinsically low electronic conductivity of sulfur and its electrochemically reductive products (Li<sub>2</sub>S<sub>x</sub>: x = 8-1), which limits the specific capacity of Li–S batteries.<sup>[9,10]</sup> large volumetric expansion of S<sub>8</sub> by 1.8 times upon its full lithiation to Li<sub>2</sub>S, and dissolution of lithium polysulfides (Li<sub>2</sub>S<sub>x</sub>, especially for x = 8-4), which are generated as intermediates during the discharge/charge processes into electrolytes.<sup>[11-14]</sup>

Significant progress has been made in addressing these issues to improve the specific capacity, rate capability, and cycling stability of Li-S batteries.<sup>[15-17]</sup> For example, to address the issues originating from the insulating properties of  $S_8$  and  $Li_2S_x$ , to trap the dissolved polysulfides, and to alleviate their consequent shuttle effect, the most common approach is to encapsulate sulfur into carbon matrices, such as mesoporous/microporous carbons,<sup>[16,18,19]</sup> graphene,<sup>[20-23]</sup> hollow carbon black,<sup>[20-23]</sup> and hollow carbon fiber/nanotube.<sup>[24-26]</sup> Additionally, to further suppress the dissolution of polysulfides and accelerate the redox kinetics of sulfur species, some metal oxides and sulfides with moderate polarities that enhance the interaction between polysulfides and substrates have been demonstrated to work as effective chemical anchors and electrochemical catalysts for sulfur species.<sup>[27-28]</sup> Unfortunately, most of these metal compounds are obtained via complex, high-cost processes and, in most cases, cannot be produced on a large scale, making them difficult to use in practical applications. Besides, according to recent studies, the high energy density of practical Li-S batteries on an entire cell level can only be achieved under lean electrolyte conditions (E/S  $[\mu L_{-electrolyte}/mg_{-sulfur}] < 4$ ).<sup>[29]</sup> However, it is challenging and almost impossible to normally operate Li-S batteries under this lean electrolyte conditions when 1 M lithium bis(trifluoromethanesulfonyl)amide, Li[N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>] (Li[TFSA]), dissolved in a 1:1 mixture of 1,2-dimethoxyethane (DME) and 1,3dioxolane (DOL), which is the most common organic electrolyte for Li-S batteries.<sup>[30]</sup> This organic electrolyte shows extremely high solubility of Li<sub>2</sub>S<sub>x</sub> and consequently requires sufficient electrolyte amount to ensure smooth dissolution/precipitation reaction pathways for the redox reactions of sulfur. In this case, Li-S batteries with low E/S ratios result in high  $Li_2S_x$  (x = 8-4) concentrations in the electrolyte, which cause high viscosity of the electrolyte and significantly sluggish Li<sub>2</sub>S electrodeposition.<sup>[31]</sup> Therefore, severe polarization and capacity degradation occur with a reduction in E/S.<sup>[32]</sup> Considering the aforementioned issues associated with the use of polysulfide-soluble electrolytes, sparingly solvating electrolytes for polysulfides have been proposed as promising alternatives.[33-34] Thermodynamic suppression of polysulfide dissolution has been accomplished in weakly coordinating electrolyte solutions such as ionic liquidbased electrolytes.<sup>[35–37]</sup> highly concentrated electrolytes.<sup>[38–39]</sup> and fluoroether-based electrolytes.<sup>[40-43]</sup> In our previous study, we reported that highly concentrated Li[TFSA] dissolved in sulfolane (SL) and further diluted with 1,1,2,2-tetrafluoroethyl 2,2,3,3tetrafluoropropyl ether (HFE) as a localized highly concentrated electrolyte shows extremely low polysulfide solubility.<sup>[44]</sup> A Li-S pouch cell with a discharge capacity of  $> 1000~mA~h~g^{-1}$  was fabricated successfully under an extremely low E/S conditions.<sup>[45-46]</sup>

In addition to lean electrolytes, the utilization of thick cathodes with relatively high areal sulfur loading is another essential factor for achieving a high energy density of Li-S batteries at the cell level, which can be compatible with current lithium-ion technologies.<sup>[47-54]</sup> However, in this case, the actual mass transport becomes difficult compared with that in thin-film cathodes, because of the increased transport distance of ions inside the porous electrodes and inhomogeneous proceeding of sulfur discharge reactions, which accompanies volume expansion.<sup>[46]</sup> In our previous study, we reported that, especially in the case of a lean amount of Li<sub>2</sub>S<sub>x</sub>-sparingly solvating electrolyte, a weak actual mass transport capability results in an extremely low discharge capacity.<sup>[46]</sup> Therefore, to realize the utilization of thick cathodes, it is particularly important to prepare high-quality cathodes that enable smooth mass transport and homogeneous sulfur discharge reactions. Thus, herein, two carbon materials, Ketjen black (KB) and mesoporous carbon nano-dendrites (MCND), were selected as sulfur host matrices by characterizing and comparing the differences in morphology and physical properties of these two carbon materials to clarify significant factors for preparing high-quality composite cathodes with higher areal sulfur loadings. We believe that this research provides a prospective method for synthesizing and selecting related carbon materials that possess specific characteristics towards practical high energy density Li-S batteries.

### 2. Results and Discussion

#### 2.1. Characterizations of Carbon Materials

First, the KB and MCND morphologies were imaged using transmission electron microscopy (TEM) and scanning electron microscopy (SEM). As shown in **Figure 1**a,b, primary particles of KB had a relatively small aspect ratio and showed a hollow sphere-like morphology with a primary particle size of  $\approx$ 30 nm. The imaged morphologies were highly consistent with product information.<sup>[55]</sup> The primary particles of the MCND had a higher aspect ratio and particle size than KB and exhibited a branch-like morphology. Based on these differences, the primary particles of KB are easily considered to lead to a compact accumulation and thus agglomerate to form several "clusters" (Figure S1a, Supporting Information). In contrast, the branch-like primary particles of MCND are difficult to accumulate together compactly, thus leading to a relatively uniform distribution (Figure S1b Supporting Information).

Another unique physical property of the carbon materials used as sulfur hosts is their specific area and pore volume, which were investigated through nitrogen adsorption/desorption measurements. As shown in Figure S2 (Supporting Information), KB and MCND have high Brunauer–Emmett–Teller (BET) specific areas of 1380 and 1447 m<sup>2</sup> g<sup>-1</sup> and pore volumes of 2.206 and 1.344 cm<sup>3</sup> g<sup>-1</sup>, respectively.

From Figures S2b and S3 (Supporting Information), KB and MCND can be defined as micro/mesoporous carbon materials. MCND had mainly 2–8 nm mesopores, whereas KB showed a rather wide mesopore size distribution ranging from 2 to 35 nm. Notably, the significant increase in the cumulative pore volume starting from the pore size of 45 nm in Figures S2b and S3 (Supporting Information) cannot be attributed to the intrinsic mesopores in the primary particles but originated from the secondary pores, which are generally considered as the



Figure 1. Morphologies of the primary particles of carbon materials: a) KB and b) MCND observed by TEM.

internal space formed by the agglomeration of the carbon's primary particles. According to the product information and related studies,<sup>[55,56]</sup> the average particle size of KB and MCND is only  $\approx$ 30–40 nm. Therefore, the agglomeration of primary particles forms secondary pores that are supposed to be detected in the high relative pressure region, as shown in Figure S2a (Supporting Information). The increase in volume absorbed in the high relative pressure region was significant in the case of KB, whereas it was relatively slight in the case of MCND. This also indicates that the agglomeration of primary particles is suppressed in the MCND, as discussed above.

For preparing carbon/sulfur composites, KB and MCND were loaded with sulfur (75 wt%) in the presence of titanium black (TiB) (3 wt%) as cathode additive via melt-diffusion method at 155 °C for 12 h.<sup>[45]</sup> After sulfur loading, the pores of KB and MCND were filled; thus, the corresponding BET surface areas decreased considerably to 30 and 22 m<sup>2</sup> g<sup>-1</sup>, respectively, and the pore volumes decreased to 0.129 and 0.075 cm<sup>3</sup> g<sup>-1</sup>, respectively (Figure S4, Supporting Information).

#### 2.2. Comparison of Carbon/Sulfur Composite Cathodes

Nano-sized materials frequently require a large amount of polymer binder and conductive additive to construct a homogenous and efficient electrode film, which is quite unbeneficial because a cathode with a relatively high areal sulfur loading is required to achieve high-energy-density Li-S batteries.[47-54] In this study, to ensure a high sulfur content in the cathode (>70 wt%), we exploited the traditional aqueous binders, carboxymethyl cellulose (CMC) and styrene-butadiene rubber (SBR), completely at a low content of 3.5 wt% without extra conductive carbon. Figure 2 shows the different morphologies of the KB- and MCND-based cathodes. Many apparent cracks were observed in the coating of the KB-based cathode (Figure 2a,b), whereas the coating of the MCND-based cathodes was quite uniform without evident cracks, even when the areal sulfur loading was >5 mg cm<sup>-2</sup> (Figure 2c,d). A large volumetric shrinkage of nanomaterials occurs when the solvent (water) is removed from the slurry, forming numerous cracks.<sup>[57]</sup> For this reason, the no-crack coating of the MCND-based cathode benefits from the branch-like structure of the MCND primary particles as this unique structure makes compact agglomeration difficult, consequently inhibiting severe volumetric shrinkage while drying the slurry. Another reason is the dispersion of the constituent materials in the slurry. Because the rheological properties of electrode slurries are highly dependent on the dispersion state of the constituent materials and their interactions, the rheological behavior was studied to confirm the dispersion state of the constituents in the KB-based- and MCNDbased slurries. As shown in Figure S5 (Supporting Information), both slurries exhibited shear-thinning behavior, characterized by a decrease in viscosity with an increasing applied shear rate. This behavior results from the breaking of the network structures originating from attractive interactions between the dispersed solid materials in the slurries. As the ratio of the constituent materials in these two slurries is completely equivalent, in the relatively low shear rate region, the higher viscosity of the MCNDbased slurry suggests that a denser network structure was formed than that in the KB-based slurry, which can be considered evidence of the better-dispersed state achieved in the MCND-based slurry. In addition, the affinity of the constituent materials for the solvent strongly determines their dispersion state in the slurry. Carbon materials are typically hydrophobic, making them difficult to disperse well in aqueous slurries. Hence, water vapor adsorption measurements were performed to evaluate the affinity of KB and MCND for water. As shown in Figure 3, MCND showed a higher affinity to water vapor adsorption as a function of relative pressure than KB, which is undoubtedly beneficial for obtaining a better dispersion state in an aqueous slurry. We speculate that MCND possesses richer oxygen-containing functional groups according to their synthesis process,<sup>[56]</sup> in which the silver particles on the MCND are removed by washing with nitric acid. According to previous studies,[58-60] acid treatment can significantly increase the surface oxygen content of carbon materials by generating carboxyl groups and acid anhydrides. These polar functional groups could explain why the MCND exhibited a relatively higher affinity towards H<sub>2</sub>O. Besides, the electrolytes were also expected to penetrate the MCND-based

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Figure 2. Photographs and SEM images of a,b) KB- and c,d) MCND- based cathode sheets prepared with a doctor blade (300  $\mu$ m gap) resulting in the areal sulfur loading up to 5–6 mg cm<sup>-2</sup>.

electrode coating film more easily to achieve a better mass transport effect.

The porosity and pore structure of the electrode are also essential factors in determining battery performance because a proper porosity and porous structure can ensure more efficient ionic transport. Coincidentally, the KB- and MCND-based cathodes with identical sulfur loadings had almost the same thickness



Figure 3. Water vapor sorption isotherm of KB and MCND (Insert is enlarged figure at the relative pressure of 0.1–0.6).

as the coating. This indicates that the two carbon/sulfur composite electrodes should have almost equal porosity macroscopically. However, because of the severe cracks observed on the surface of the KB-based cathode (Figure 2b), sulfur, as the active material, was supposed to be concentrated and compactly packed in the crack-less region. The coating with few cracks at a relatively microscopic level (Figure 2d) suggests uniform porosity for the MCND-based cathode. To confirm the above conjecture, the KB- and MCND-based cathode coatings were scanned via Xray computed tomography (CT) technique with a spatial resolution of 2 µm, respectively. Qualitatively, as shown in Figure 4a, the interconnecting pores represented by the gray portion are distributed more homogeneously for the MCND-based cathode. In contrast, narrow voids seen in the S/KB-rich regions and large voids corresponding to the cracks were observed for the KBbased cathode. In addition to qualitative analysis, a quantitative analysis was performed. The volume ratio (Figure 4b), tortuosity (Figure 4c), and surface area/volume ratio (Figure 4d) were calculated using the segmentation data from the CT images. The void ratio of the MCND-based cathode coating (39%) was evidently higher than that of the KB-based cathode coating (33%), although the tortuosities of these two cathode coatings were comparable. Moreover, the surface area/volume ratio of the voids was smaller for the MCND-based cathode coating, suggesting that the void size in the MCND-based cathode film was larger, which is also in agreement with the high-magnification SEM images (Figure S6, Supporting Information). This is favorable for facile ionic transport and accommodates the volumetric expansion and

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Figure 4. a) ex situ 3D segmented X-ray CT images, b) volume ratio, c) tortuosity, and d) surface area/volume ratio for void, carbon, and sulfur of KBand MCND-based cathode coatings.

contraction of the sulfur active material in the cathode during the charge/discharge process.

Electronic conductivity was also studied using a four-probe method to investigate the connectivity of the carbon materials. The MCND-based cathode coating exhibited electronic conductivity of 4.16 S cm<sup>-1</sup>, which was more than two times higher than the KB-based cathode coating (2.00 S cm<sup>-1</sup>). This result indicates that a more efficient electron-conducting path was formed in the MCND-based cathode, despite the slightly lower volume ratio and higher tortuosity of conductive carbon in the analysis of the CT images (Figure 4b,c). The homogeneous and crack-less composite film of the MCND-based cathode (Figure 2) was likely responsible for its higher electronic conductivity. Considering that cracks usually spread only in the shallow region of the coating but not in the entire bulk,<sup>[61]</sup> which is unfavorable for penetration by the electrolyte, the uniform and crack-free porous structure achieved by the MCND-based cathode would also be favorable for uniform electrolyte distribution in a thick composite cathode of a high-energy-density Li-S battery under lean electrolyte conditions. Figure S7 (Supporting Information) displays photographs of a droplet of the Li<sub>2</sub>S<sub>v</sub> sparingly solvating electrolyte on the composite cathodes, taken 5 min after the electrolyte was dropped. On the surface of the KB-based cathode, the electrolyte droplet remained unpenetrated (retaining its round shape). However, on the surface of the MCND-based cathode, the droplet disappeared as it penetrated into the material.

#### 2.3. Li-S Battery Performance (Coin Cell)

In this study, all electrochemical measurements were performed using a thick cathode with a sulfur loading >5.0 mg cm<sup>-2</sup> to achieve a high energy density of Li-S batteries. The initial discharge capacity of the MCND-based cathode was 1135 mA h  $g^{-1}$ , which was much higher than that of the KB-based cathode (531 mA h g<sup>-1</sup>) (Figure 5). The MCND-based cathode exhibited a discharge capacity of  $\approx 1000$  mA h g<sup>-1</sup> during four subsequent four cycles at a relatively low discharge current (425  $\mu$ A cm<sup>-2</sup>; 0.05 C). The discharge capacity gap of the KB- and MCND-based cathodes became more significant at a higher discharge current density of 850  $\mu A~cm^{-2}$  (0.1 C, after the 6th cycle): the discharge capacity of the MCND-based cathode continuously decayed but still stabilized at a level >600 mA h  $g^{-1}$  (Figure 5c). One possible reason for the continuous capacity decay was the destruction of the cathode microstructure caused by the volumetric change in the sulfur species during the cycling test. For a fair comparison, we used the same binder content as the KB-based slurry preparation for the MCND-based slurry preparation, which may not necessarily be optimum for MCND to enhance cycling stability. In contrast, the KB-based cathode exhibited an extremely low discharge capacity of less than 100 mA h g<sup>-1</sup> at this discharge current density of 850 µA cm<sup>-2</sup>, and the second discharge plateau disappeared, as shown in Figure 5a. According to our previous study,<sup>[46]</sup> this behavior can be attributed to an inhomogeneous

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Figure 5. Discharge/charge profiles of galvanostatic test for high areal sulfur loading composite cathode: a) KB/S cathode, b) MCND/S cathode; c) discharge capacity and d) Coulombic efficiency.

reaction along the thickness of the cathode. The sulfur reduction to form  $\text{Li}_2S$  became conspicuous at the electrolyte/porous electrode interface, whereas the reduction reaction became less pronounced near the current collector side. Surface-localized reactions become more significant under conditions of relatively low mass-transport capability. This may also be a reflection of the MCND-based cathode possessing a stronger mass transport capability than the KB-based cathode.

To further investigate the electrochemical influence of KB and MCND on Li-S battery performance, a galvanostatic intermittent titration technique (GITT) combined with electrochemical impedance spectroscopy (EIS) was performed. As shown in Figure 6a, at almost all discharge depths, the cell with the KBbased cathode exhibited a larger polarization, indicating that the MCND-based cathode was kinetically more favorable than the KB cathode. From Figure 6b, until  $\approx$ 1100 mA h g<sup>-1</sup>, the polarization of the cell with MCND-based cathode increased relatively mildly while the polarization of the cell with KB-based cathode increased more dramatically. One possible reason for the continuous increase in the polarization and relatively low discharge capacity of the KB-based cell is that, according to our previous study,[46] when using a relatively high-sulfur-loading composite cathode, the weak mass transport capability of the Li ions in the KB-based cathode tends to cause the cathodic reaction to be easily concentrated on the surface of the cathode (vide supra). The closure of the porous structure in the cathode originated from the volumetric expansion of the sulfur species through lithiation, which further decreased the mass transport capability of Li ions into the

deeper region of the cathode, consequently exacerbating the inhomogeneity of the above behavior. Although the GITT measurements can be used to separate thermodynamic and kinetic factors, various kinetic factors that contribute to the polarization, such as mass transport, charge transfer resistance, and an iR drop, cannot be distinguished. Thus, EIS measurements were performed in the open circuit voltage (OCV) state with a depth of discharge of 886 mA h g<sup>-1</sup> (green star in Figure 6a) to separate the resistance components for further discussion, as shown in Figure 6c. Its magnified figure in high-frequency region is also shown in Figure S8 (Supporting Information). The Nyquist plots consist of two depressed semicircles (a lower-frequency semicircle is rather flattened) with an inclined spur. According to previous studies<sup>[62–63]</sup>, the depressed semicircles correspond to the charge transfer processes at the electrodes  $(R_{ct})$ , whereas the inclined line at 45°, referred to as the Warburg impedance, generally corresponds to the mass transport resistance inside the cathode. The variation in  $R_{e}$  (i.e., the real part of the impedance) as a function of  $\omega^{-0.5}$  (i.e., the reciprocal square root of the angular frequency) for the KB- and MCND-based cathodes are shown in Figure 6d, and the results were analyzed according to Equations (1) and (2):

$$Re = R_{\text{bulk}} + R_{\text{ct}} + \sigma \cdot \omega^{-0.5} \tag{1}$$

$$\sigma = \frac{RT}{n^2 F^2 A C} \cdot \frac{1}{\sqrt{2D_{ij}}} \tag{2}$$

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**Figure 6.** a) GITT measurement for initial discharge; b) overpotential at specific depth of discharge; c) Nyquist plot obtained from EIS measurement; d)  $R_e$  as function of  $\omega^{-0.5}$ .

where  $R_{\text{bulk}}$  is the bulk electrolyte resistance,  $\sigma$  is the Warburg coefficient, *R* is the gas constant, *T* is the absolute temperature, n is the number of transferred electrons, F is the Faraday constant, A is the area of the electrode, C is the concentration of the Li ion, and  $D_{Ii}$  is the diffusion coefficient of the Li-ion. Because we employed composite cathodes, it was impossible to obtain the absolute values of the parameters in  $\sigma$  (A, C, and  $D_{Ii}$ ); however, Figure 6d shows that the MCND-based cathode had a smaller  $\sigma$ . Here, i) the better current collection of the MCND-based cathode, as discussed previously, possibly ensured a wider electrochemically active area, ii) higher affinity of MCND toward the electrolyte, relatively higher porosity, and more uniform void space distribution of the MCND-based cathode, as confirmed by X-ray CT measurement, guaranteed the facile ionic transport, and iii) more homogeneous cathodic reaction in the MCND-based cathode could avoid the closure of the porous structure and ensure the continuous facile ionic transport during the entire discharge process. Hence, we considered that the above factors contribute to the lower mass transport resistance of the MCND-based cathode.

#### 2.4. Li-S Battery Performance (Pouch Cell)

Pouch-type cells with a low dead volume inside the cells were fabricated to evaluate the Li–S battery performance under extremely lean electrolyte conditions (low E/S). The structure of pouch cells is shown in Figure S9 (Supporting Information). For the areal sulfur loading, 4.7 mg cm<sup>-2</sup> was for the KB-based cathode, and 4.9, 6.0, and 8.7 mg cm<sup>-2</sup> were for the MCND-based cathodes, respectively. All four pouch-type cells were controlled to have an equal E/S value of 5.0  $\mu$ L mg<sup>-1</sup>. The charge/discharge curves are shown in Figure S10 (Supporting Information), and the cycling performance is shown in Figure 7. Consistent with the coin cell results, pouch-type cells with the MCND-based cathodes exhibited initial discharge capacity >1300 mA h  $g^{-1}$ , whereas for the KB-based cathode it was 1015 mA h g<sup>-1</sup> with much lower areal loading (i.e.,  $4.7 \text{ mg cm}^{-2}$ ). In the subsequent cycles under a relatively high current density, the areal sulfur loading was increased up to 8.7 mg cm<sup>-2</sup>, and pouch-type cells with the MCND-based cathodes exhibited discharge capacities 900–1100 mA h g<sup>-1</sup>, whereas it was <500 mA h g<sup>-1</sup> for the KB based cathode. Unfortunately, as shown in Figure 7a, the discharge capacity of the MCND-based cathode decayed faster as the areal sulfur loading increased. This may be caused by the destruction of the cathode structure, as discussed previously. The behavior becomes much more significant as the coating becomes thicker because the current collection from the Al current collector becomes more difficult, which will be the focus of our future study. In short, these results strongly demonstrate that MCND are more favorable sulfur host materials than KB for practical Li-S batteries.

Finally, we fabricated a large-format pouch-type Li–S cell, the structure of which is shown in Figure 8a. As shown in Figure 8c,d, a high initial discharge capacity of 1129 mA h  $g^{-1}$  was



Figure 7. Cycling performance (140  $\mu$ A cm<sup>-2</sup> for initial discharge and 700  $\mu$ A cm<sup>-2</sup> for subsequent cycles) of Li–S pouch-type cells under the lean electrolyte conditions with E/S = 5.0  $\mu$ L mg<sup>-1</sup>: a) discharge capacity and b) Coulombic efficiency.

obtained even under extremely lean electrolyte conditions (E/S =  $3.5 \ \mu L \ mg^{-1}$ ) and a relatively high sulfur loading (5.5 mg cm<sup>-2</sup>), consequently the pouch-type cell delivered a high capacity of  $3.7 \ Ah$  (Figure 8b). As a result, a high energy density of 255 W h kg<sup>-1</sup> was successfully achieved (calculated based on the theoretical amount of lithium, and the weights of the Al-laminated film and tabs were not included). In addition, stable cycling with only a slight capacity decay was achieved as the capacity was still >3.0 Ah, whereas the energy density was still >210 Wh kg<sup>-1</sup>.

# 3. Conclusion

In this study, we selected two carbon materials, KB and MCND, as sulfur host matrices to investigate the properties of carbon ma-

terials for preparing carbon–sulfur composite cathodes towards practical high-energy density Li–S batteries. A series of measurements and analyses were performed to understand the differences between KB and MCND. As porous carbon materials, although KB and MCND show comparably high BET surface areas and porous volumes, the relatively high-quality coating and, thus, better Li–S battery performance achieved by MCND indicates that other important factors play pivotal roles. Through detailed investigation, the unique microsized secondary structure due to the branch-like interconnected primary particles with a relatively high aspect ratio could prohibit the shrinkage of carbon during the evaporation of the solvent from composite electrode slurries; thus, the cracks and pinholes on the coating were effectively suppressed. Therefore, the MCND-based cathode has a better current collection effect, and simultaneously, higher and uniform

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Figure 8. Large format Li–S pouch-type cell: a) Schematic representation of the internal structure; b) Discharge capacity and energy density; c) Discharge and charge profile; d) Cycling performance. Charge/discharge current density: 460  $\mu$ A cm<sup>-2</sup>.



porosity ensures smoother ionic transport capability. Additionally, the higher affinity of MCND to polar molecules, as demonstrated by water sorption, is considered to enhance further the wettability of the electrode towards the electrolyte, which is beneficial to battery performance, particularly with a lean amount of electrolyte. These facts confirmed that the MCND-based cathode exhibited a better Li-S battery rate performance and higher discharge capacity, even with a higher areal sulfur loading of 8.7 mg cm<sup>-2</sup>. Finally, a large-format Li–S pouch-type cell that exhibited a 3.7 Ah initial discharge capacity and thus achieved a high energy density of 255 Wh kg<sup>-1</sup> was successfully fabricated under harsh conditions with a relatively high areal sulfur loading (5.5 mg cm<sup>-2</sup>) and a lean amount of electrolyte (E/S =  $3.5 \mu$ L mg<sup>-1</sup>). Therefore, we believe that this study clarifies the properties of carbon materials that they should have as a good sulfur host matrix and thus provides guidance on the significance of the selection of carbon to achieve high-energy-density Li-S batteries.

# 4. Experimental Section

Preparation of the Carbon/Sulfur Composite Cathodes: A carbon/sulfur (C/S) composite combined with titanium black (TiB, Mitsubishi Material, Japan) as a multifunctional cathode additive<sup>[45]</sup> was prepared by the meltdiffusion method using a mixture of elemental sulfur (S<sub>8</sub>, Wako Chemical, Japan, 75 wt%), either KB (ECP600JD, Lion Corporation, Japan, 22 wt%) or MCND (Nippon Steel & Sumikin Materials, 22 wt%) and TiB (3wt%). S<sub>8</sub> and TiB were mixed using an agitating mortar, to which weighed amount of either KB or MCND was added, and the mixtures were transferred to a sealable vial, and maintained at 155 °C for 12 h to allow the diffusion of molten sulfur into the pores of the KB or MCND. Aqueous slurries for electrode coating were prepared by mixing the C/S composite with TiB and CMC (CMC2200, Daicel Fine Chem, Japan) with SBR (JSR Corporation, Japan) in a weight ratio of 96.5:1.5:2. The obtained slurries were then coated onto carbon-coated aluminum foils as current collectors and dried in an oven at 60 °C for 12 h to obtain the cathode materials. The sulfur content of the cathode was 72.4 wt%. Subsequently, the cathodes were cut into discs (for coin cells) or rectangles (for pouch cells) and dried in an oven under vacuum at 40 °C for 12 h prior to use.

Preparation of the Electrolytes: The electrolytes were prepared according to the method reported in the previous study.<sup>[44]</sup> More specifically, battery-grade LiFSA (Kishida Chemical, Japan) and LiTFSA (Kishida Chemical, Japan) in an Ar-filled glove box at appropriate molar ratios to prepare [Li(SL)<sub>2</sub>][FSA<sub>0.1</sub>TFSA<sub>0.9</sub>]. The binary mixture of LiFSA and LiTFSA was used in order to enhance the metallic lithium anode reversibility.<sup>[64]</sup> Subsequently, [Li (SL)<sub>2</sub>][FSA<sub>0.1</sub>TFSA<sub>0.9</sub>] was diluted with HFE (Daikin Industries, Japan) to obtain [Li (SL)<sub>2</sub>][FSA<sub>0.1</sub>TFSA<sub>0.9</sub>] + 2HFE as the Li<sub>2</sub>S<sub>x</sub> sparingly solvating electrolyte for cell fabrication. The water content of the electrolyte was <30 ppm, as determined by Karl Fisher titration (CA-07, Mitsubishi Chemical, Japan).

*Cell Assembly*: A 2032-type coin cell was assembled in an Ar-filled glove box using either a KB-based cathode or an MCND-based cathode (13.8 mm in diameter), a Li metal anode (Honjo Metal, 16 mm in diameter), one piece of polyolefine-based separator, and electrolyte as the volume of 120  $\mu$ L. For small pouch-type cells (Figure S9, Supporting Information), two pieces of single-side-coated cathodes (45 × 37 mm), two pieces of aramid-coated separators (50 × 43 mm), and one piece of anode (50 × 40 mm) were included. For the large-format pouch-type cell (Figure 8a), two single-side-coated cathodes, five dual-side-coated cathodes (70 × 70 mm), two aramid-coated separators (73 × 72 mm), and six anodes (72 × 72 mm) were included. Li metal coated on both sides of a Cu foil (Li thickness = 90  $\mu$ m, Honjo Metal, Japan) was used as the anode. Charge/discharge measurements were performed using a charge-discharge tester (HJ1001SD8, Hokuto Denko, Japan) at 30 °C and cut-

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off potentials of 1.4 and 3.3 V for the discharge and charge steps, respectively. Galvanostatic intermittent titration technique (GITT) measurements (VMP3, Bio-Logic, France) were performed with constant discharge currents of 600  $\mu$ A cm<sup>-2</sup> (1/15 C for 5.4 mg cm<sup>-2</sup>). The discharge time was set to 1 h for each pulse, and the relaxation time between pulses was set to reach the time dependence of the cell voltage <15.0 mV h<sup>-1</sup>. After the GITT measurements that were carried out to a certain depth of discharge and subsequent relaxing of the cell potential to the equilibrium state (potential variation <15.0 mV h<sup>-1</sup>), electrochemical impedance spectroscopy (EIS) measurements were performed on a VMP3 instrument (Bio-Logic, France) in the frequency range of 500 kHz to 10 mHz with a sinusoidal voltage amplitude of 10 mV.

Characterization: Scanning electron microscopy (SEM) was performed using a Hitachi FE-SEM SU8000 (Japan) instrument at 1.5 kV for the carbon materials and 5.0 kV for the composite cathodes. Transmission electron microscopy (TEM) was performed using a JEM-2100F instrument (Tokyo, Japan) at 200 kV. Nitrogen and water vapor adsorption/desorption isotherm and BET surface area measurements were performed on an Autosorb-iQ instrument with preheating treatment at 60 °C for 3 h. A rheometer (Physica MCR301, Anton Paar) was used to measure the viscosity of the slurry as a function of the shear rate under dry air conditions at 30 °C using a cone and plate with a diameter of 50 mm and a cone angle of 1°. X-ray computed tomography (X-ray CT) was performed using a BL20XU at SPring-8 (Japan). The composite cathode samples were fixed on a stage to be vertical to the ground as well as to the X-ray beam to take CT shots, then the samples were irradiated with 30 keV synchrotron radiation, and transmission images were acquired by rotating the samples for  $180^{\circ}$  with an exposure time of 50 ms for every  $0.1^{\circ}$  with a resolution of 2  $\mu m.$  Afterward, the obtained information was analyzed and calculated with CT analyzing software Dragonfly to get the segmented images, volume ratio, tortuosity, and surface area/volume ratio of the composite cathodes.

# **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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# **Conflict of Interest**

The authors declare no conflict of interest.

# **Data Availability Statement**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

# **Keywords**

composite sulfur cathode, high-energy-density battery, lithium–sulfur battery, mesoporous carbon, pouch cell

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