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# Mesoporous carbon spheres with tunable porosity prepared by a templatefree method for advanced lithium–sulfur batteries



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## ABSTRACT

Mesoporous carbon spheres (MCS) with tunable porosity are prepared by a mass-producible spray-drying process using chitosan as carbon precursor with ethanol as porosity tuning agent. By this template-free method, MCSs with different porosity are deduced by manipulating the volume ratio of ethanol in the solvent for chitosan. The resulted MCSs show controllable surface areas, pore volumes and bimodal pore size distribution. They are employed as substrates for the preparation of sulfur/carbon composite cathode. Electrochemical performance of the MCSs with 50 wt% sulfur loading is investigated. One of the S/MCS composite cathodes displays initial discharge capacity of 1163 mAhg<sup>-1</sup>, excellent rate capability of 510 mAhg<sup>-1</sup> at 2 C and good cycling stability of 715 mAhg<sup>-1</sup> after 100 cycles at 0.2 C. The sulfur loading content could reach as high as 60%, while it still could deliver a capacity of 642 mAhg<sup>-1</sup> after 100 cycles at 0.2 C.

## 1. Introduction

Lithium-ion batteries have received great attention in recent years because of their potential applications to solve energy supplies shortage and global environment problems, nevertheless the limited energy capacity and low power density of present electrode materials is still not enough to meet the electric vehicle requirements for extended range [1,2]. Therefore, it is essential to explore new cathodes with higher specific capacity to increase the energy density of battery system [3,4]. Based on light-weight elements and multi-electron reactions, sulfur is one of the most promising candidates among all conventional cathode materials for Li secondary cells due to its high theoretical capacity  $(1675 \text{ mAhg}^{-1})$  [5], which is nearly five times higher than that of existing transition metal oxide and phosphate materials [6,7]. Besides, sulfur has an advantage of natural abundance, low cost, and environmental friendliness. Therefore, sulfur becomes a promising cathode material for the next generation of high energy density rechargeable batteries. However, in spite of these advantages, there are several crucial technical problems to tackle [8–10]. First of all, a major hurdle is the electrical insulating nature of sulfur. The second one is the capacity degradation of the sulfur cathode upon cycling due mainly to the shuttle phenomenon. Third, the deposition of insulating Li<sub>2</sub>S on reaction interface during the discharge process increases the resistance of the cell.

To overcome these problems, many methods have been intensively investigated including surface coating [11-13], conductive substrates [14,15], multifunctional binders and novel electrolytes with inorganic additives [16-18]. Among the above strategies, carbon-based materials with controlled morphology and structure, particularly those derived from cheap sustainable sources constitute a rational solution for the preparation of practical carbon-sulfur composite electrodes [19,20]. In comparison with other carbon materials such as graphene [21] and carbon nanotubes [22], porous carbon materials was believed to be an ideal electrode material for lithium-sulfur batteries due to their interconnected porous structure, high specific surface area and pore volume [23-25]. Nowadays, many researchers focus on designing the composite by optimizing the porous structure of carbon. For example, Ye invented a series of uniform porous carbon spheres through a KOH activation process, and they claim that the pore structure of the carbon host can be easily controlled by adjusting the activation concentration of KOH [23], meanwhile, Zhao has reported the fabrication of novelstructured porous carbon microspheres with a controllable multi-modal pore size distribution, and they claimed that they can control the pore size by adding into silica sols with different particle sizes [26]. In most

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cases, researchers mainly concentrate on these two methods, but it always followed with high expenditure or complicated synthesis, which hinders the practical applications of mesoporous carbon in large scale.

Herein, mesoporous carbon spheres with tunable porosity have been prepared by a simple, cost-effective and template-free method, which then were employed to the design and fabrication of sulfur-impregnated porous carbon composite cathode materials for lithium-sulfur battery. In comparison with the traditional sulfur cathode and normal sulfur/ carbon composite cathode, the novel S/MCS composite cathode shows several advantages. Firstly, the MCS was prepared through a spray drying process with chitosan as a precursor. The method is relatively simple, flexible and easily scalable for industrialization and the precursor is sustainable biomass. Secondly, the surface area, pore volume and the unique bimodal pore size distribution of the MCSs can be easily tuned by just mixing different volume ratio of ethanol into the suspension, and no pore directing agent or template is needed. Thirdly, an autogenetic pressure technique (APT) at high temperature based on a swagelok structured stainless autoclave was exploited for loading sulfur into the pores of the MCS spheres. By this autogenetic pressure technique, sulfur-impregnated mesoporous carbon spheres with controlled sulfur loading content were obtained efficiently and no extra heating process to remove the excess sulfur is required, avoiding high expenditure or complicated synthesis.

### 2. Experimental section

## 2.1. Preparation of S/MCS composites

The high porosity MCSs were prepared through a spray drying process with chitosan as a precursor. In a typical preparation, 4g chitosan was dissolved in 200 ml acetic acid solution using water/ ethanol mixture with different volume ratio (e.g. 10 vol% and 20 vol% ratio of ethanol) as solvent for the solution. The solution of chitosan was stirred for 2 h, and it was then sprayed into the chamber of the spray dryer at 180 °C using hot air as carrier gas, and dried composite samples were simultaneously collected by a connected cyclone separator. Then, the obtained chitosan spheres were firstly cured at 400 °C for 2 h and then was carbonized at 900 °C for 5 h under a high purity nitrogen atmosphere. Three samples, designated as MCS-0, MCS-10 and MCS-20 were prepared with different ethanol/water volume ratios in the mixed solvent for dissolving chitosan, namely 0:100, 10:100 and 20:100. The obtained MCS-0, MCS-10, and MCS-20 spheres were then utilized as matrices for the preparation of S/MCS composite spheres with different sulfur loading contents, e.g. 50 and 60 wt%. The mixture of sulfur and MCS was loaded into a swagelok structured stainless autoclave and cured at 155 °C for 6 h, and then the temperature was increased to 300 °C and kept at this temperature for 5 h to guarantee melted sulfur infiltrate into the pores of the porous carbon spheres. Finally, when the autoclave was cooled to room temperature, S/MCS composite spheres named as S/MCS-0-50, S/MCS-10-50 and S/ MCS-20-50 were collected (where -50 stands for the loading content of sulfur in the composite spheres). Similarly, sample of S/MCS-20-60 was prepared by the same process with 60 wt% sulfur content. A proposed formation mechanism of the sulfur-impregnated mesoporous carbon composite spheres is illustrated in Scheme 1.

#### 2.2. Characterization

X-ray diffraction (XRD) patterns were collected on a Rigaku Ultima IV X-ray diffractometer with Cu-K $\alpha$  radiation ( $\lambda = 0.15418$  nm) as the X-ray source. The thermo gravimetric analysis (TGA) was performed on a Mettler Toledo TGA-2 thermal gravimetric analyzer under Ar atmosphere with a heating rate of 10 °C min<sup>-1</sup>. X-ray photoelectron spectroscopy (XPS) data were accumulated on a PHI VersaProbe III (ULVAC-PHI INC.) X-ray photoelectron spectrometer with a monochromatized Al Ka standard X-ray source and the binding energies were calibrated by referencing the C1s to 283.8 eV. Nitrogen adsorption/desorption isotherms were measured using a Quantachrome Autosorb-IQ-MP/XR. The specific surface areas were estimated with the Brunauer-Emmett-Teller (BET) method with N2 adsorption data in the relative pressure range of  $P/P_0 = 0.05-0.35$ . The pore size distributions were calculated using the Barrett-Joyner-Halenda (BJH) model applied to the desorption branch of the N<sub>2</sub> isotherms. The morphology and structure of the samples were examined by a JEOL JSM-7800F field emission scanning electron microscope (FESEM) and a JEOL JEM-2100plus transmission electron microscope (TEM).

## 2.3. Electrochemical measurement

The working electrodes were prepared by making a slurry consisting of 80 wt% active material, 10 wt% conductive agent (acetylene black) and 10 wt% polyvinylidene fluoride (PVDF) as binder. The slurry was coated on an aluminum foil. After drying at 55 °C under vacuum over night, the electrodes were punched to fit into 2016 coin-type cells in a glove box filled with Ar gas. Lithium metal was used as the counter electrode, a Cellgard 2400 microporous membrane was employed as the separator, and 50 µL of 1 M bis-(trifluoromethane) sulfonimide lithium (LiTFSI, Alfa Corp.) in a mixed solvent of dimethoxyethane (DME) and 1,3-dioxolane (DOL) (1:1, vol.%) as the electrolyte. The charge--discharge tests were carried out using a LAND Cell Test System (2001A, Wuhan, China) between cutoff voltage of 3 V and 1.5 V. Cyclic voltammetry (CV) measurements were conducted using a two-electrode coin-type cell performed between 1.5 V and 3 V at 0.1 mVs<sup>-1</sup> on a CHI760D electrochemical working station. Electrochemical impedance spectroscopy (EIS) profiles were recorded on a CHI760D electrochemical working station in the frequency range between 100 kHz and 0.01 Hz with amplitude of 5 mV.

## 3. Results and discussion

Fig. 1(a) shows the XRD patterns of the sublimed sulfur, MCS-20, S/ MCS-0-50, S/MCS-10-50, and S/MCS-20-50 samples. The XRD pattern of elemental sulfur exhibits several sharp and intensive peaks throughout the entire diffraction range, indicating a well-defined crystal structure. For the carbon sphere of MCS-20, the strong peak at two theta of 22.0° indicates the presence of graphitic domains while the small peak at two theta of 44.0° represents the quasi-amorphous nature of the hard carbon [27–29]. However, typical crystallized sulfur diffraction peaks in S/MCS-10-50 and S/MCS-20-50 disappear entirely, indicating that most of the sulfur is incorporated into the interior of the pore structure and homogeneously dispersed therein. Differently, for S/ MCS-0-50 sample the intensity of crystalline sulfur peaks grows to be detectable in the XRD patterns. It can be proposed that the excessive



**Scheme 1.** Illustration for the formation process of the S/MCS composite spheres.



Fig. 1. (a) XRD patterns of pristine sulfur, MCS-20, S/MCS-0-50, S/MCS-10-50, and S/MCS-20-50 samples; (b) TGA curves of S/MCS-20-50 and S/MCS-20-60 composites; (c) XPS full survey of the MCS-20 and (d) high resolution survey in N 1s region.

sulfur maybe almost overfill the pore volume of the carbon substrate, and a portion of sulfur crystallized on the outer surface of MCS-0, such a speculation is in agreement with the N<sub>2</sub> adsorption-desorption measurement and will be discussed in the following section. To confirm the sulfur loading efficiency by the ATP process and the exact sulfur loading content in the composite spheres, TGA were conducted in an Ar flow. Fig. 1(b) shows the typical TGA curves of S/MCS-20-50 and S/MCS-20-60 composites. As can be seen from the curves, the S/MCS-20-50 and S/ MCS-20-60 samples display weight loss of 49.6 and 59.7 wt%, respectively, in the temperature range between 180 and 450 °C, and the weight losses are closed to the sulfur contents as set in their raw materials. The detected weight loss temperatures are relatively higher than that of the sublimation temperature for elemental sulfur and no obvious weight loss has been observed in these TGA curves below the temperature of 180 °C, suggesting that most of the sulfur is confined inside the pores of the MCS. XPS measurements have been performed to verify the composition of the carbon spheres since the chitosan precursor contains N elements. Fig. 1(c) and (d) display the XPS full survey and the high resolution spectra in the N1s region of MCS-20 sample. From the surveys one found that there are mainly C, N and O atoms on the samples surface. The binding energy at 397.4, 400.2 and 402.1 eV can be attributed to pyridinic, pyrrolic and graphitic nitrogen, respectively. An content of 1.73 atm.% for nitrogen has been calculated based on the XPS data. Usually, the doping of carbon with nitrogen is expected to improve the electrochemical performance of carbon based composite materials, and in our cases which may be beneficial for that of the S/ MCS composites [14,25].

The N<sub>2</sub> adsorption-desorption isotherms in Fig. 2 a and b illustrate the variation of porous characters of the MCS-X (x = 0, 10, and 20) samples before and after 50 wt% sulfur loading. From the curve one can see that the MCS-10 and MCS-20 show hysteresis loops and obvious capillary condensation steps, suggesting the existence of mesosized pores in them [30–32]. However, the large hysteresis observed for MCS-10 and MCS-20 samples decreases significantly after sulfur encapsulation, for example, N<sub>2</sub> adsorption-desorption measurements show the MCS-20 exhibits a high surface area of  $1290 \text{ m}^2 \text{ g}^{-1}$  and a large pore volume of  $1.29 \text{ cm}^3 \text{ g}^{-1}$ . When 50 wt% sulfur is embedded, the specific surface area and total pore volume for sample S/MCS-20-50 then decrease to  $121 \text{ m}^2 \text{ g}^{-1}$  and  $0.29 \text{ cm}^3 \text{ g}^{-1}$ , respectively. The changes of the porosity of these samples before and after sulfur loading were summarized in Table 1.

The pore size distribution curves of MCS-0, MCS-10 and MCS-20 samples have been illustrated in Fig. 2b. It can be seen that the MCS-0 sample shows only a very weak distribution peaks around 4 nm, likely originating from the interspaces in the carbon spheres. With the addition of ethanol at a volume ratio of 10% (sample MCS-10), the peak around 4 nm increase remarkably and an additional characteristic peak around 7 nm appears, demonstrating a bimodal pore size distribution character. Another interesting phenomenon is that with the increase of volume ratio of ethanol to 20 vol% (sample MCS-20), it shows still bimodal pore size distribution character, while the percentage of large sized pore around 7 nm increases obviously. Such a change of the porosity in these samples can be explained as due to the solvent effect during the spray drying process. The addition of ethanol to the suspension changes the viscosity of the chitosan solution and increases the volatility of the solvent. The increase of the solvent volatility improved the interspaces in the derived chitosan spheres from spray drying, which then led to the increase of the porosity of the obtained carbon spheres by the subsequent calcinations. However, considering the explosion risk of organic solvent at high temperatures, one cannot increase the ratio of ethanol immoderately in our preparation. The pore size distribution curves depicted in Fig. 4 d reveal more clearly the bimodal pore size distribution character in MCS and the preferred inhalation of sulfur in different sized pores. After the sulfur impregnation into the carbon matrix, the small sized pore filled preferentially due to the strong capillary force, which shows more obvious decreasing of the pore size distribution intensity than the larger one. The hierarchical porous structure facilitates the diffusion of molten sulfur and sulfur gas



Fig. 2. Nitrogen adsorption-desorption isotherms (a, c) measured at 77 K and pore size distribution curves (b, d) for MCS-10, MCS-20 before and after sulfur loading.

 Table 1

 BET specific surface area and pore volume of different samples.

Samples	BET Surface Area $(m^2 g^{-1})$	Pore Volume (m <sup>3</sup> ·g <sup>-1</sup> )
MCS-0	645	0.33
MCS-10	1141	0.88
MCS-20	1292	1.29
S/MCS-0-50	-	-
S/MCS-10-50	63	0.1
S/MCS-20-50	121	0.29

Not available.

adsorption, making sulfur exist in a highly dispersed state and avoiding aggregation of the sulfur after condensation.

Pictures A-C in Fig. 3 display the SEM images of MCS-0, MCS-10 and MCS-20 derived from the spray-drying process and a subsequent high temperature carbonization. It can be seen that the MCS-0 samples consist of a large quantity of carbon spheres with diameter in the range of 1-5 µm and some of which shows a wrinkled surface. When mixture solvent of water/ethanol was applied with ethanol ratio of 10 vol%, the obtained carbon spheres become perfect spherical morphology and show a very smooth surface without cracks. When the volume ratio of ethanol is increased from 10 to 20 vol%, the derived MCS-20 sample shows a quite similar morphology as that of MCS-10. However, some loopholes on the surface of the carbon spheres can be observed. Images C and F show the macroscopic morphologies of MCS-20 and S/MCS-20-50. From the comparison one cannot identify the difference between them. No sulfur particles can be observed on the external surface of the carbon sphere substrates. Pictures D and E in Fig. 3 depict the TEM image of MCS-0 and MCS-20 samples, and they illustrate the porous characteristics of the MCS-20 sample. A zoom-in image of the region marked by the white rectangle shows the presence of mesopores in MCS-20, which will be in favor of the infiltration of the electrolyte and the fast transport of Li ions during the charging/discharging processes. Whereas, MCS-0 sample shows a more condense TEM image, and the pores on its surface is vague even under a high magnification mode (see the insert in picture D). The elemental mapping of sulfur and carbon for S/MCS-20-50 has been shown in Fig. 3F, it clearly reveals the existence of sulfur and its homogeneous dispersion inside the porous MCS-20 substrate.

Fig. 4a depicts the cyclic voltammogram (CV) curves of the S/MCS-20-50 composite cathode. The plots show typical electrochemical reaction characteristics of elemental sulfur. During the first cathodic scan, two remarkable reduction peaks at 1.95 and 2.25 V can be observed. The upper plateau at 2.25 V corresponds to the reduction of elemental sulfur (S<sub>8</sub>) or highly oxidized polysulfides such as Li<sub>2</sub>S<sub>8</sub> and Li<sub>2</sub>S<sub>6</sub> to Li<sub>2</sub>S<sub>4</sub> [33–35], and the lower plateau at 1.95 V represents the reduction of Li<sub>2</sub>S<sub>4</sub> or lower sulfides to Li<sub>2</sub>S<sub>2</sub> or Li<sub>2</sub>S. In the anodic scan, only one sharp oxidation peak is observed in the potential of 2.55 V, which corresponds to the oxidation process of Li<sub>2</sub>S [36,37]. The cathodic and anodic peak current densities of the sulfur/carbon nanocomposite show no obvious change during the 3rd cycling, illustrating that the cathode materials have excellent electrochemical reversibility due to the porous hollow structure and good electronic conductivity.

The initial discharge-charge voltage profiles of the S/MCS-0-50, S/ MCS-10-50 and S/MCS-20-50 cathodes at a 0.2C rate are compared in Fig. 4b. In the DME/DOL-based electrolyte, Li-S battery theoretically has two typical discharge potential plateaus which are observed for all cathodes in accordance with the CV curves. For the S/MCS-20-50 composite cathode, the initial discharge capacity is as high as  $1163 \text{ mAhg}^{-1}$ , which reaches nearly up to 70% of theoretical specific capacity of sulfur. In contrast, the discharge capacities of the cathodes made of S/MCS-10-50 and S/MCS-0-50 present an obvious decrease to 937 and 815 mAhg<sup>-1</sup>, respectively. Meanwhile, the initial dischargecharge voltage profiles of the three samples are accompanied with successive increasing of potential polarization in a sequence of S/MCS-0-50 > S/MCS-10-50 > S/MCS-20-50. One can see that the discharge voltage decreased continuously and the charge voltage increased significantly. The strong potential polarization of S/MCS-0-50 can be ascribed to the poor utilization of sulfur due to the lower pore volume and surface area of MCS-0-50 to uptake lithium ions.

Fig. 5a depicts the discharge and charge capacities of S/MCS-0-50,



Fig. 3. SEM images of MCS-0 (A), MCS-10 (B), MCS-20 (C) samples, TEM image of MCS-0 (D) and MCS-20 (E) (the inserts at the bottom left in image D and E show a high magnification view of the as labeled areas in the spheres), and SEM image of S/MCS-20-50 (F) (the red and the green insets in picture F showed the elemental mapping of carbon and sulfur, respectively). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

S/MCS-10-50 and S/MCS-20-50 composites cathodes at different current rates. One can see that the discharge capacities decrease gradually as the rate increased from 0.2 to 2 C for all of these electrodes. It can be explained by the probable formation of a thin S layer on the external surface of the carbon spheres owing to the strong affinity of sulfur to carbon. However, it also can be find S/MCS-20-50 is completely superior to the other two composite cathodes in all the rate performances. After decaying rapidly from 1163 in the first cycle to  $1055 \text{ mAhg}^{-1}$  in the second one at a rate of 0.2 C, the fading trend turns to slow in the following cycles even with an increase of current rate. In addition, the S/MCS-20-50 can operate at rate as high as 2 C, and it still delivers a capacity of  $510 \text{ mAhg}^{-1}$ . When the rate is reset back to 0.2 C regime after more than 50 cycles, the S/MCS-20-50 electrode resumes the original capacity of 809 mAhg<sup>-1</sup> without abrupt capacity fading. However, for the other two composite cathodes, the decrease of reversible capacity with the increase of current density can be clearly observed. We speculate that for the three composites with the same sulfur loading content, their electrical conductivity decrease due to the presence of insulative elemental sulfur and the ability for lithium ions accommodation is low especially in S/MCS-0-50 spheres due to its relative low pore volume, which then result in the decrease of capacity in comparison with S/MCS-10-50 and S/MCS-20-50 samples. The same is true of the explanation for the difference between the latter two

composite cathodes. Fig. 5b shows the cycle performance of S/MCS-0-50, S/MCS-10-50 and S/MCS-20-50 cathodes at a 0.2 C rate in terms of up to 100 repeated discharge-charge galvanostatic cycles. It demonstrates that the S/MCS-20-50 composite cathode delivers the higher electrochemical performance with an initial capacity of 1138 mAhg<sup>-1</sup> and the capacity remains at  $715 \,\mathrm{mAhg}^{-1}$  after 100 cycles, which is higher than that of S/MCS-0-50 and S/MCS-10-50. The relatively high cycle capability for S/MCS-20-50 electrode can be attributed to the high pore volume and the relative large specific surface area and also to the bimodal pore size distribution in the spherical structure, which could reduce the electric pathways to arrive to the external surface and enhance the transportation rates of lithium ions and solvated electrolyte. The charge/discharge capacity of S/MCS-20-50 composite cathode at a current rate of 0.2 C and the corresponding coulombic efficiency are shown in Fig. 5c. A high coulombic efficiency of 93% is obtained after 100 cycles, demonstrating an enhanced capacity reversibility and cycle stability, meanwhile, the negative effects of dissolution of polysulfide and the insulation of sulfur was minimized effectively. As can be seen in Fig. 5 a and b, capacity fluctuations have been observed for the cycling tests, which might be due to the temperature changes during the test. In order to improve the energy density of the composite cathode and further investigate the limitation of MCS-20 as conductive matrices, MCS-20 spheres were utilized as support for the preparation of



Fig. 4. CV curve of S/MCS-20-50 cathode measured under the potential window of 1.5–3.0 V at a scan rate of 0.1 mVs<sup>-1</sup> (a), and the initial discharge-charge voltage profiles of the three different composite cathodes at a rate of 0.2 C (b).



Fig. 5. Multi-rate capabilities (a) and their cycling performance at 0.2 C rate (b) of the three different composite cathodes, the charge and discharge capability and the corresponding coulombic efficiency of S/MCS-20-50 (c) and those of S/MCS-20-60 (d) at a current rate of 0.2 C.

composite cathode materials with 60 wt% sulfur loading content and the cycle performance of the S/MCS-20-60 is presented in Fig. 5d. It can be seen that the S/MCS-20-60 composite cathode could also deliver an initial capacity of 969 mAh g<sup>-1</sup> at 0.2 C and the capacity remained at  $642 \text{ mAhg}^{-1}$  after 100 cycles with a coulombic efficiency of about 95%, showing still very excellent performance and potential to industrial application. The specific capacity of S/MCS-20-60 is a little bit lower than that of S/MCS-20-50, which can be ascribed to the reducing of the conductivity of the composite spheres with the increase of sulfur content.

The different electrochemical performances of the three cathodes can be ascribed to the porosity differences between these carbon hosts with different specific surface area, pore volume and bimodal pore distribution. In the case of S/MCS-20-50 sample, firstly, the relative high specific surface area originated from the mesosized channels provides the large interfacial contact area between sulfur and carbon at the nanoscale and the boundless interconnects of the MCS-20 framework for electron conduction. The relatively high specific surface area could also introduce electrolyte into the active cathode material to maintain the intimate contact with conductive carbon matrix and supply more electrochemical reaction sites. Secondly, the mesopores with relative large size provide a higher volume to allow easy electrolyte diffusion and Li+ transportation, and in the meantime, accommodate sulfur volume expansion during cycling. Meanwhile the smallsized mesopores can bridge the larger mesopores and enhance the contact between carbon and sulfur, thus lowering the resistance in charge transfer and diffusion. Furthermore, the small-sized mesopores play also the roles in trapping polysulfides and preventing the escape of active sulfur material from the carbon framework. Consequently, the kinetic of the reactions in the charge-discharge plateau is constrained mainly in the mesopore of the OMC/S-20-50 and could be highly reversible. Whereas for the S/MCS-0-50, the excess sulfur crowed in the

mesopore of MCS-0 might block the paths for electron transport and the stuffed mesopores lack flexible volume for uptaking lithium ions, resulting in poorer cycle performance. All in all, MCS-20 can be considered as the most optimistic substrate among them due to its unique bimodal pore structure, relative large pore volume and high specific surface area, all of which are crucial for achieving both high sulfur loading and good electrochemical performance.

To verify further the improved electrochemical performance, the electrochemical impedance spectroscopy (EIS) measurements of the S/MCS-20-50 cathodes at a rate of 0.2C after different cycles have been carried out. As can be seen from Fig. 6, the impedance plots are composed of a semicircle in the high frequency domain corresponding to



Fig. 6. Electrochemical impedance spectra of the S/MCS-20-50 cathode after 1st, 10th and 100th charge/discharge cycles.

the charge transfer impedance and interfacial impedance, and a sloping straight line in the low frequency domain corresponding to the Warburg impedance [38,39]. It is obvious that the S/MCS-20-50 composite electrode exhibited a low and gradually decreased charge transfer resistance from the 1st to the 10th galvanostatic charge, and turned to be stable during the following test. The decrease of impedance with cycling can be mainly attributed to a much high conductivity and improved reaction kinetics of the composite cathode during the charge discharge processes. In addition, this impedance evolution matches well the excellent electrochemical performance of OMC/S-20-50 composite electrode with a high reversible cycle capacity.

## 4. Conclusions

In summary, a promising approach to the total-preparation of sulfur-impregnated mesoporous carbon composite sphere as cathode materials for Li-S battery has been demonstrated. As good conductive matrix and inclusion substrate for sulfur, the mesoporous carbon spheres (MCS) with unique mesosized bimodal pore structures, large pore volume and high specific surface areas have been successfully prepared through a simple, cost-effective and template-free spray-dying process combined with calcinations. Three kinds of mesoporous carbon spheres (MCS-0, MCS-10 and MCS-20) with controlled specific surface area from 645 to  $1292 \, m^2 g^{-1}$  and pore volume from 0.33 to  $1.29 \text{ cm}^3 \text{g}^{-1}$  are obtained by manipulating the volume ratio of ethanol in the solution and no pore directing agent or template has been introduced. The three kinds of mesoprous carbon spheres with 50 wt% sulfur loading content can be used as electrodes for rechargeable Li-S batteries through a one-step autogenetic pressure technique (APT). It has been demonstrated that the S/MCS-20-50 composite electrode shows the best electrochemical performance, and a discharge capacity of 510 mAhg<sup>-1</sup> is achieved at current density of 2 C and the capacity can be maintained at  $715 \text{ mAhg}^{-1}$  after 100 cycles at 0.2 C. More importantly, even at 60 wt% sulfur loading content the derived S/MCS-20-60 sample could still remain  $642 \text{ mAhg}^{-1}$  after 100 cycles at 0.2 C. These results illustrate that the cyclability and the utilization of sulfur for the Li-S batteries have been significantly improved. It can be expected that the simple, cost-effective approach developed for the preparation of these S/MCS composite could be a promising strategy to make the rechargeable lithium-sulfur batteries a commercial reality.

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