Discrete Hollow Carbon Spheres Derived from Pyrolytic Copolymer Microspheres for Li-S Batteries

Yeseul Choi, Naemn Yoon, Nahyeon Kim, Changil Oh, Hyejeong Park, and Jung Kyoo Lee

Department of Chemical Engineering, Dong-A University, Busan 49315, Korea

Discrete hollow carbon spheres (HCSs) with a high surface-to-volume ratio and distinct conducting shell have attracted immense attention as electrode materials for batteries and supercapacitors. In this study, we developed a novel and scalable method to synthesize well-defined HCSs. The HCSs were prepared using a pyrolytic soft template of styrene/acrylic acid copolymer microspheres. Sulfur could be effectively confined inside the pores of the uniform-sized HCSs (average diameter = 320 nm, shell thickness = 40–50 nm) to produce a S/HCS-65-IM (S content = 65 wt%) Li-S cathode using a modified sulfur-loading method involving solution impregnation followed by melt-diffusion (IM). S/HCS-65-IM delivered much higher capacity and greater cycling stability over 200 cycles and showed much lower impedance build up than S/HCS-65-PM prepared via the conventional melt-diffusion of a physical mixture of sulfur powder and HCSs. The sulfur utilization of S/HCS-65-IM was further improved by more than 20% by suppressing its lithium-polysulfide shuttle effect using a carbon-coated separator (CCS). The S/HCS-65-IM cathode (with CCS) also exhibited excellent cycling stability (capacity retention of >81% after 200 cycles at 0.5 C) and high rate capability with a reduced interfacial charge transfer resistance, suggesting that S/HCS-65-IM (with CCS) is a promising cathode for Li-S batteries.

© The Author(s) 2018. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/2.0151903jes]

Manuscript submitted September 5, 2018; revised manuscript received October 22, 2018. Published November 28, 2018. This paper is part of the JES Focus Issue of Selected Papers from IMLB 2018.

Porous carbon materials of various structures with high surface area, excellent conductivity, and light weight have been widely used as sulfur hosts for the cathodes of lithium-sulfur (Li-S) batteries, which are regarded as one of the most promising rechargeable battery systems in terms of energy density and cost.1–21 A Li-S battery composed of a sulfur cathode (1675 mAh g−1) and a lithium-metal anode (3860 mAh g−1) can offer a practical energy density (400–600 Wh kg−1) more than twice that of offered by state-of-the-art lithium-ion batteries (LIBs), providing a 500 km driving range per charge for an electric vehicle.1–4 However, the widespread use of Li-S batteries is still hindered by the low electrochemical activity of sulfur species (insulating nature of both S and the discharge product, Li2S), structural instability of electrodes because of the large volume expansion (80%) caused by sulfur reduction, and a short cycle life owing to the anode instability associated with the lithium-polysulfide (LPS) shuttle effect.3,22–24 The host materials for sulfur play an extremely important role in overcoming these limitations. Hence, the encapsulation of sulfur in porous carbon materials is considered as one of the most effective approaches for the development of high-performance Li-S batteries.25 Among these materials, hollow carbon spheres (HCSs)15,16,18,20,26,27 have been widely used as sulfur hosts to develop Li-S batteries with outstanding electrochemical properties. HCSs as sulfur hosts offer unique advantages: 1) the large internal void space can accommodate not only a relatively high level of sulfur loading but also a large volume expansion because of the reduction of sulfur into Li2S, 2) efficient confinement of the soluble LPS by the shell of HCSs which acts as transfer barrier limiting LPS shuttling, and 3) a large contact area between the insulating sulfur and Li2S with carbon facilitating the electron and ion transports. Furthermore, hollow carbon structures doped with nitrogen18,20 and metal oxides28 as sulfur hosts show stronger chemical binding to the polar LPS and hence much enhanced electrochemical performances than those with nonpolar C-C bonds. However, the synthesis of HCSs is usually carried out using hard templates such as silica particles15,20,29 or hollow spheres of metal oxides (SnO2 or TiO2).18,26 These templates have to be removed by tedious, time-consuming, and toxic acid treatments. Therefore, the development of a facile and scalable method to synthesize well-defined HCSs is imperative not only for energy-storage devices but also for the other potential applications such as catalyst supports, fuel cells, gas storage, separation, sensors, and delivery devices for drugs and contrast imaging agents.29,30

Herein, we report a facile method to synthesize well-defined HCSs by using pyrolytic styrene/acrylic acid copolymer (referred to as PS-COOH henceforth) microspheres as the template (Scheme 1). The monodispersed copolymer beads were readily obtained by the emulsifier-free emulsion copolymerization of styrene and acrylic acid.31 The obtained PS-COOH microspheres whose surface was functionalized with –COOH groups were coated with a carbon-gel with succrose as the carbon source in an acid solution. The carbon-gel coated PS-COOH microspheres were then heated in Ar flow in order to carbonize the shell and pyrolyze the copolymer core at the same time to obtain well-defined HCSs with a diameter of 320 nm and a shell thickness of 40–50 nm. To encapsulate sulfur into the pores of the HCSs (for S/HCS composites), we employed a solution impregnation method which was followed by melt-diffusion (denoted as IM, henceforth). The capillary forces facilitated the even infiltration of elemental sulfur into the pores through the shell of the HCSs, as described in our previous report.32 The S/HCS composites showed very stable cycling performances because of the confinement of sulfur

Supporting Information

Scheme 1. Schematic of the synthesis of the HCSs using a pyrolytic template of styrene-acrylic acid copolymer microspheres.

E-mail: jklee88@daum.ac.kr

Received March 27, 2018; revised October 22, 2018; accepted November 28, 2018.

Journal of The Electrochemical Society, 166 (3) A5099-A5108 (2019)
inside the pores of the HCSs, which is further manifested by the transfer barrier of their shells. When the S/HCS composites were coupled with a carbon-coated separator (CCS), they delivered much enhanced capacity (high sulfur utilization) and rate capability (low interfacial resistance) as Li-S battery cathodes.

**Experimental**

**Synthesis of PS-COOH microspheres by emulsion polymerization.**—The microspheres of styrene (St) and acrylic acid (AA) copolymer (PS-COOH) were prepared by the batch emulsifier-free emulsion copolymerization of St with AA using ammonium persulfate (APS) as the initiator. In a typical procedure, St (10.0 g, 99.5%, Junsei) and AA (1.5 g, 99%, Sigma-Aldrich) were added to a jacket reactor containing N2-bubbled DI water at 70 °C to remove dissolved oxygen. The APS (0.05 g, ≥98.0%, Sigma-Aldrich) dissolved in N2-bubbled DI water was added into the St-AA solution. The reaction was carried out under a N2 atmosphere at 70 °C for 4 h. The reaction temperature was increased to 120 °C and the reaction mixture was stirred overnight at this temperature under reflux to coat a carbon gel on the surface of the PS-COOH microspheres. The carbon-gel coated PS-COOH microspheres were purified by carrying out at least three centrifugation/dispersion cycles in DI water.

**Preparation of HCSs and S/HCS composites.**—HCSs were prepared by using sucrose (≥99.5%, Sigma-Aldrich) as the carbon precursor and PS-COOH as the template. In a typical procedure, a PS-COOH solution (28.2 mL of 7.1 wt% PS-COOH in DI water corresponding to 2.0 g of dried PS-COOH) was prepared in a reaction flask. A sucrose solution (20.0 g of sucrose dissolved in 20.0 mL of DI water) was prepared separately and was added dropwise into the PS-COOH solution at 60 °C under reflux conditions over 2 h. The reaction was further carried out for 1 h. Then, the reaction temperature was increased to 120 °C and the reaction mixture was stirred overnight at this temperature under reflux to coat a carbon gel on the surface of the PS-COOH microspheres. The carbon-gel coated PS-COOH microspheres were purified by three centrifugation/dispersion cycles in DI water and were then dried at 80 °C in air overnight. The dried carbon-gel coated PS-COOH microspheres were heated in a tube furnace under the flow of Ar at 800 °C for 4 h to obtain the HCSs (0.94 g).

To prepare the sulfur-loaded S/HCS composites, we carried out the wet-impregnation of a sulfur solution on the HCSs followed by the melt-diffusion of the sulfur-impregnated samples. In a typical procedure, a sulfur solution prepared by dissolving elemental sulfur in the St-AAA solution at 60 °C under reflux conditions over 2 h. The reaction was further carried out for 1 h. Then, the reaction temperature was increased to 120 °C and the reaction mixture was stirred overnight at this temperature under reflux to coat a carbon gel on the surface of the PS-COOH microspheres. The carbon-gel coated PS-COOH microspheres were purified by three centrifugation/dispersion cycles in DI water and were then dried at 80 °C in air overnight. The dried carbon-gel coated PS-COOH microspheres were heated in a tube furnace under the flow of Ar at 800 °C for 4 h to obtain the HCSs (0.94 g).

To prepare the sulfur-loaded S/HCS composites, we carried out the wet-impregnation of a sulfur solution on the HCSs followed by the melt-diffusion of the sulfur-impregnated samples. In a typical procedure, a sulfur solution prepared by dissolving elemental sulfur powder (0.31 g) in carbon disulfide (CS2, 3.0 mL) was impregnated into the HCSs (0.15 g) and then the solvent was removed by air-drying in a well-ventilated fume hood. The impregnation-drying step was repeated several times to load a desired amount of sulfur on the HCSs. After further drying at 50 °C overnight in a fume hood, the sulfur-impregnated sample was transferred into a Teflon-lined autoclave vessel in an Ar-filled glove box. The sample vessel was heated at 160 °C for 12 h to facilitate the melt diffusion of sulfur into the pores of the HCSs. The sulfur-loaded sample so obtained was named as S/HCS-65-1M, where “65” and “1M” denote the target sulfur content (wt%) and the sulfur loading method of impregnation followed by melt-diffusion, respectively. For comparison, control sulfur-loaded samples (S/HCS-51-1M (sulfur content = 51 wt%) and S/HCS-65-1M (sulfur content = 65 wt%)) were prepared by the conventional sulfur-loading method involving the physical mixing of sulfur powder (0.3 g) and the HCSs (0.15 g) followed by melt-diffusion (referred to as the PM method henceforth). The melt-diffusion was carried out at 160 °C for 12 h in a tube furnace under the flow of Ar for the S/HCS-51-PM sample and in a Teflon-lined autoclave for the S/HCS-65-PM sample. The properties of the S/HCS composite samples used in this study are given in Table I.

**Preparation of CCS.**—The CCS was prepared using the procedure reported elsewhere. A slurry of thin-flake type graphite (0.2 g) and polyvinylidene fluoride (PVdF) dissolved in N-Methyl-2-Pyrrolidone (NMP) with a graphite-PVdF weight ratio of 9:1 was coated on a commercial polypropylene (PP) membrane separator (Cellgard 2400, 25 μm thick). The coated separator was first dried in air at room temperature for 1 h and then in a vacuum oven at 50 °C for 6 h. Finally, the coated film was roll-pressed to prepare the CCS.

**Characterizations.**—Field-emission scanning electron microscopy (FE-SEM, JEOL JSM-35CF operated at 10 kV) and Field-emission transmission electron microscopy (FE-TEM, JEOL JEM-2100F operated at 200 kV) equipped with energy-dispersive X-ray spectroscopy (EDS) element-mapping functionality, were employed to investigate the structure and morphology of the PS-COOH, HCS, and S/HCS samples. A B-TEM (Hitachi, H-7500 operated at 80 kV) with a low accelerating voltage (to minimize the sample damage by electron beam energy) was also used to investigate the morphology of the S/HCS samples under the high contrast mode. The Fourier-transform infrared (FT-IR) spectra of the samples were obtained on a Thermo Scientific Nicolet 380 spectrometer using the KBr pellet method. The specific Brunauer-Emmet-Teller (BET) surface area and pore size distribution of the HCSs were measured using their nitrogen adsorption/desorption isotherms obtained using a Micromeritics ASAP 2000 at liquid-N2 temperature. The X-ray diffraction (XRD) patterns of the HCS and S/HCS composite samples were recorded on a diffractometer (Rigaku Miniflex 600, 40 kV, 15 mA, Cu-Kα radiation, λ = 1.5418 Å). The sulfur contents in the S/HCS composites were determined by carrying out their thermogravimetric analysis (TGA) by heating them to 800 °C at a rate of 10 °C min−1 under the flow of N2. The ionic conductivities (σ) of the pristine PP separator and CCS were evaluated by the equation of σ = h/(RbRc), where h = thickness, Rb = bulk resistance measured by using an impedance analyzer, Rc = contact area between the separator (diameter = 1.6 cm) and the stainless steel blocking electrode.

**Electrochemical measurements.**—CR2032 coin-type cells assembled in an Ar-filled glove box with Li foil as the counter electrode were used to obtain the electrochemical responses of the S/HCS samples. The working electrodes were prepared by coating homogeneous pastes (in active material (S/HCS composites):conductive additive (Super P Li, Timcal Ltd.)) of PVdF(Solef 5130, Solvay, 5 wt% dissolved in N-methyl-2-pyrrolidone) binder mass ratio of 7:1:2 onto an aluminum foil using a Meyer-Bar coating device (Kipae E&T, Korea). The working electrodes were roll-pressed and then cut into 1.5 cm-diameter disks. The total mass loading was in the range of 1.5–2.0 mg cm−2. The working electrode disks were dried at 60 °C for 4 h in a glass vacuum cell. The vacuum cell containing the electrodes was transferred into an Ar-filled glove box to avoid exposure to air. A Celgard 2400 polypropylene membrane or the CCS was used as the separator. A mixture of 1.0 M lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) and 0.4 M LiNO3 in a 1:1 (volume) mixture of dioxolane (DOL) and dimethoxyethane (DME) was used as the electrolyte with the electrolyte-to-sulfur weight ratio of 20 μL/mg S. A cut-off voltage in the range of 1.8–2.8 V (vs. Li/Li+) was used for carrying out the electrochemical tests (1 C rate = 1675 mA g−1 sulfur = 1.50 mA cm−2 (for active material with 65 wt% S)). The cyclic

| Table I. Properties of HCSs and S/HCS composites. |
|-----------------------------------------------|
| HCS properties | S.A. a, m2 g−1 | Vp b, cm3 g−1 | Dp c, nm |
|-----------------|-----------------|-----------------|--------|
| S/HCS samples   | S/HCS-65-1M IM | S/HCS-51-PM IM | S/HCS-65-PM IM |
| S content %     | 64.1           | 51.1           | 64.9   |
| S loading method| IM             | PM             | PM     |

a BET surface area.
b Total pore volume P/V P = 0.99.
c Adsorption average pore width by BET.
d Determined by TGA.

See main text.
voltammetry (CV) tests were carried out at a scan rate of 0.1 mVs$^{-1}$ on a galvanostat/potentiostat system (WonATech Co., Ltd., Korea). Electrochemical impedance spectroscopy (EIS) was carried out on a ZIVE SP2 analyzer (WonATech Co., Ltd., Korea) over a frequency range of 1 MHz–10 mHz with an AC amplitude of 10 mV.

**Results and Discussion**

Fig. 1a and Fig. 1b show the SEM and TEM images of the PS-COOH template, respectively. The images showed that the PS-COOH templates had a spherical morphology and a uniform size distribution with an average diameter of 320 nm. The FT-IR spectrum of the PS-COOH templates (Fig. 1c) confirmed that styrene and acrylic acid formed a copolymer with surface carboxylic acid (R-COOH) groups. Unlike polystyrene, which is completely pyrolytic with almost zero carbon yield$^{25}$, the PS-COOH templates retained about 20.6 wt% of carbonaceous residue after carbonization at 800°C under the flow of nitrogen, as shown in the TGA profile shown in Fig. 1d.

Fig. 2a and Fig. 2b show the SEM and TEM images of the HCS samples, respectively. The images revealed that the HCSs with a diameter of about 320 nm were successfully synthesized without aggregation by using the pyrolytic PS-COOH copolymer microspheres as the template. As can be observed from Fig. 2b, the HCS samples had
a uniform shell thickness in the range of 40–50 nm. The out-diameter of the HCS samples was similar to that of the PS-COOH templates. This can be attributed to the thermal-shrinkage of the carbon gel coated on the surface of the PS-COOH templates during carbonization. Figs. 2c and 2d show the N\textsubscript{2} adsorption/desorption isotherms and pore size distribution of the HCSs, respectively. The isotherm in Fig. 2c shows a slight increase in the adsorption of the HCSs and a small adsorption/desorption hysteresis loop because of the pore (capillary) condensation at high relative pressures (P/P\textsubscript{0}). The BET surface area of the HCSs was 499 m\textsuperscript{2} g\textsuperscript{-1}, and their total pore volume was 0.48 cm\textsuperscript{3} g\textsuperscript{-1}. The pore volume was dominated in the pore diameter range of 2–4 nm, as shown in Fig. 2d.

The sulfur contents in the S/HCS samples were determined by their TGA analysis (Fig. 3a). The S/HCS-51-PM, S/HCS-65-IM, and S/HCS-65-PM samples had the sulfur contents of 51.1, 64.1, and 64.9 wt\%, respectively. Note that elemental sulfur and the HCSs were mixed in a 2:1 weight ratio to obtain a final sulfur content of around 65 wt\% for both the S/HCS-51-PM and S/HCS-65-PM samples. However, the S/HCS-51-PM sample lost a substantial amount of sulfur upon being heated at 160 \degree C for melt-diffusion of sulfur in a tube furnace under the flow of Ar and only 51.1 wt\% of sulfur was left. On the other hand, the S/HCS-65-IM and S/HCS-65-PM samples showed a negligible sulfur loss during the melt-diffusion process in an autoclave vessel. Fig. 3b shows the XRD patterns of elemental sulfur and the HCSs and S/HCS composite samples. Apart from the crystalline \( \alpha\)-S\textsubscript{8} phase of elemental sulfur before impregnation, the \( \gamma\)-S\textsubscript{8} phase (Rosickyite, JCPDS card no. 01-071-0137), a polymorph of sulfur, was formed in the S/HCS samples through crystallization during the thermal treatment for the melt-diffusion process at 160 \degree C. This is consistent with the results reported previously. Among the S/HCS samples, the S/HCS-51-PM sample showed the lowest sulfur peak intensity, indicating that the lowest amount of sulfur was present in this sample. The sulfur peak intensity of the S/HCS-65-IM sample was lower than that of the S/HCS-65-PM sample, indicating that sulfur was more deeply embedded into the HCS pores of S/HCS-65-IM.

The structural features of the S/HCS samples were further investigated by FE-SEM and FE-TEM. As shown by the SEM image in Fig. 4a, the morphology and size of the S/HCS-65-IM sample were almost the same as those of the HCSs (Fig. 2a). The strong sulfur signal in the energy-dispersive X-ray (EDX) spectrum of the sample collected from the full-area scan (Fig. 4b) indicates that sulfur was present throughout the HCSs. The FE-TEM image (Fig. 4c) shows bright circular cavities in each HCS in S/HCS-65-IM, possibly due to sulfur sublimation under high vacuum with the heating effect of the electronic beam. The dark area around bright circular cavities in the HCSs can be ascribed to residual sulfur. On the other hand, the FE-TEM image of the HCSs (Fig. 2b) showed homogeneous contrast in each HCS. Since in conventional TEM measurements, sulfur sublimates and redistributes because of the electron beam heating under high vacuum conditions, a B-TEM operating at a low accelerating voltage (80 kV) was also used in the high-contrast mode to investigate the structure of the S/HCS-65-IM samples. As shown in Fig. 4d and its inset, agglomerated sulfur particles present separately from HCSs were not observed. Most of the sulfur species were uniformly confined into the pores of the HCS hosts. The overall morphology and shell thickness of the HCSs remained unchanged even after the impregnation of sulfur.

In order to examine the distribution of sulfur throughout the HCSs, FE-TEM elemental mapping of S/HCS-65-IM and S/HCS-65-PM was carried out for carbon and sulfur. In both the samples, the shell of the HCSs was carbon-rich (green color), as seen in Fig. 5a and Fig. 5d. On the other hand, S/HCS-65-IM showed a much more uniform sulfur (yellow color) distribution (throughout the HCSs, Fig. 5b) than S/HCS-65-PM, in which sulfur was largely present in the shell part of the HCSs, as shown in Fig. 5e. Fig. 5c and Fig. 5f show the EDS line scans along the center of a single HCS for both the samples. The EDS scan of S/HCS-65-IM showed a carbon signal much more intense than the sulfur signal, indicating that most of the sulfur species were infiltrated into the HCS pores. On the other hand, the sulfur signal was more intense than the carbon signal in the case of S/HCS-65-PM, indicating that sulfur was mainly present on the shell part or the HCS surface in this sample. The EDS line scan results were in good agreement with those obtained from the elemental mapping analysis (Fig. 5b and Fig. 5c). Hence, it can be stated that the IM method resulted in a better encapsulation of sulfur into the HCS pores than the conventional PM method. In a previous study, the infiltration of sulfur deep inside carbon particles by melt infusion of a physical mixture of elemental sulfur and carbon hosts was examined by...
cryo-TEM. It was found that sulfur infiltration into the carbon particles was unsuccessful or inefficient, leaving much of the sulfur outside the host carbon particles.37

As shown in Fig. 6a, the carbon coating layer is 9 μm thick and the thin graphite flakes are densely packed and aligned in parallel to the surface of PP separator. As compared in Fig. 6b, electrolyte wettability was much better on the CCS than on the pristine PP separator. The bulk resistance ($R_b$) of the separator was larger on the CCS than that on the pristine PP separator by carbon coating (Fig. 6c). However, the ionic conductivity ($\sigma$) of the CCS was measured to be slightly larger than that of PP separator.

Fig. 7a shows the voltage profile of S/HCS-65-IM for the first cycle. A typical two-plateau discharge profile was obtained at 2.3–2.0 V vs. Li/Li$^+$. The first plateau at 2.3–2.1 V can be attributed to the reduction of elemental sulfur to higher order lithium poly sulfides (LPS) (Li$_2$S$_x$, $6 \leq x \leq 8$). On the other hand, the second plateau at 2.1–2.0 V can be attributed to the conversion of the higher order LPS to lower order LPS (Li$_2$S$_x$, $2 \leq x \leq 6$) and Li$_2$S.$^8,11$ The first charge profile showed two plateaus at 2.2–2.3 and 2.3–2.4 V corresponding to the oxidation of the low and high order LPS, respectively.$^8$ In the first cycle, a small voltage hysteresis (about 0.17 V vs. Li/Li$^+$) was obtained between the charging and discharging processes at the average capacity. The small voltage hysteresis indicates that the over-potential of the cell was insignificant due to the uniform dispersion of sulfur in the composite.$^9$ The first discharge capacity (based on sulfur weight in the composite) was about 900 mAh g$^{-1}$sulfur. Fig. 7b shows the corresponding CV profile of S/HCS-65-IM. In the cathodic scan, two reduction peaks centered at around 2.3 and 2.0 V appeared, while two overlapping oxidation peaks at around 2.3 and 2.4 V appeared in the anodic scan. This is consistent with the voltage profile shown in Fig. 7a. These redox responses provide an insight into the typical two-step consecutive reduction and oxidation processes involved in Li-S cells.

The cycling performances of the S/HCS composites are compared in Fig. 7c. All the samples were cycled at 0.1 C for the first five cycles followed by cycling at 0.5 C for the next 200 cycles. All the samples showed fast capacity fading during the initial five cycles at 0.1 C possibly because of the dissolution of LPS mainly present on the outer surface of the HCSs. All the samples, however, exhibited very stable cycling performances at 0.5 C for 200 cycles. The S/HCS-65-IM, S/HCS-65-PM, and S/HCS-65-PM samples showed initial reversible capacities (at 0.5 C) of 567, 549, and 300 mAh g$^{-1}$sulfur, and their corresponding capacity retentions during the 205th cycle were 88.9, 97.4, and 81.6%, respectively. S/HCS-65-IM showed a rather high Coulombic efficiency of 97.4–99.0% during cycling at 0.5 C for 200 cycles (Fig. 7c). For the same sulfur content of around 65 wt%, S/HCS-65-IM exhibited not only much higher capacity but better cycling stability than S/HCS-65-PM. The XRD patterns (Fig. 3b) and FE-TEM...
images with the EDS line scan results (Fig. 5) of the samples show that S/HCS-65-IM showed much better encapsulation of sulfur in the pores of HCS than S/HCS-65-PM. In addition, S/HCS-65-IM showed a more uniform distribution of sulfur throughout the HCS structure than S/HCS-65-PM. Thus, the LPS dissolution in S/HCS-65-IM was more effectively retarded by the shell (diffusion barrier) than that in S/HCS-65-PM. In addition, in S/HCS-65-IM, a large fraction of sulfur participated in the electrochemical reactions with lithium than that in S/HCS-65-PM. As seen in Fig. 7c, S/HCS-65-IM and S/HCS-51-PM showed similar sulfur-capacities. On the other hand, S/HCS-65-IM showed a much higher composite-capacity (based on composite (sulfur and HCS) weight) than S/HCS-51-PM, (Fig. 7d). S/HCS-51-PM showed a much higher composite-capacity as well as sulfur-capacity than S/HCS-65-PM. This can be attributed to the poor sulfur

Figure 4. (a) SEM image, (b) EDX spectra of full-area scan in (a), (c) FE-TEM image and (d) B-TEM (at 80 kV) image of S/HCS-65-IM with an enlarged image in the inset.

Figure 5. FE-TEM elemental mapping images for (a, d) carbon (green), and (b, e) sulfur (yellow) and (c, f) EDS line scan curves of the S/HCS composites. (a, b, and c) for S/HCS-65-IM and (d, e, and f) for S/HCS-PM.
Figure 6. (a) SEM image of the cross-section of the CCS (insets are the SEM images of the CCS(top) and PP separator surface), (b) photographs of electrolyte droplets on PP separator and CCS and (c) EIS spectra of PP and CCS (inset is parameters used for ionic conductivity).

Figure 7. (a) Charge/discharge voltage profiles and (b) CV profiles of S/HCS-65-IM at the first cycle, respectively, and specific capacities per gram of (c) sulfur and (d) composite for various S/HCS samples.
encapsulation and distribution throughout the HCSs in S/HCS-65-PM. These results suggest that the conventional “PM” method cannot encapsulate and disperse insulating sulfur throughout the porous carbon hosts, especially at high levels of sulfur-loading.

Although S/HCS-65-IM showed higher capacity and better cycling stability than S/HCS-65-PM, the S/HCS-65-IM cell delivered sulfur-capacities in the range of 700–900 mAh g\(^{-1}\)sulfur at 0.1 C. This corresponds to only 42–54% of the theoretical capacity of sulfur (1675 mAh g\(^{-1}\)sulfur). The low sulfur utilization in S/HCS-65-IM can also be ascribed to the dissolution and diffusion of LPS away from the cathode, thus leading to initial capacity fading, as seen in Fig. 7c. In order to improve the sulfur utilization in S/HCS-65-IM cell, a carbon-coated separator (CCS) was employed. For the preparation of this separator, thin flake-type graphite was used as the carbon material. As shown in Fig. 8a, the first discharge capacity of the S/HCS-65-IM cell assembled with the CCS increased to about 1000 mAh g\(^{-1}\)sulfur from about 900 mAh g\(^{-1}\)sulfur obtained from the same cell assembled with a pristine PP separator (Fig. 7a). The reversible capacity of the S/HCS-65-IM (with CCS) at 0.1 C is still much lower than the theoretical capacity of sulfur mainly due to the low conductivity of sulfur present in the large pore (diameter = 230 nm). The reversible capacity could be further improved by employing HCS with much smaller pore size than that of the HCS used in this study.

The rate responses of the cells assembled with or without CCS are compared in Fig. 8b. The S/HCS-65-IM cell with the CCS delivered much higher capacities for all the current densities in the range of 0.1–5.0 C-rate than the S/HCS-65-IM cell assembled with a pristine PP separator. In particular at 2.0 C rate, S/HCS-65-IM (with CCS) delivered capacities of 500–592 mAh g\(^{-1}\)sulfur, while the S/HCS-65-IM cell assembled with the pristine PP separator delivered only 196–411 mAh g\(^{-1}\)sulfur. Both the cells, however, showed poor capacity retention at 5.0 C possibly because of the inherent high internal resistance of the coin-cell system employed here. The effect of the CCS on cycling performance is shown in Fig. 8c. The S/HCS-65-IM (with CCS) cell delivered capacities of 969–1023 mAh g\(^{-1}\)sulfur at 0.1 C and 667–835 mAh g\(^{-1}\)sulfur at 0.5 C, which were about 20% higher than the corresponding capacities obtained from the cell assembled with the PP separator. For the initial five cycles at 0.1 C, the capacity retention of the S/HCS-65-IM (with CCS) cell was 94.5% while that of the S/HCS-65-IM (PP separator) was only 79%, suggesting that CCS significantly suppressed the LPS dissolution and diffusion away from the cathode part. Even after 200 cycles at 0.5 C, S/HCS-65-IM (with CCS) showed a capacity retention of more than 81%, indicating its very stable cycling performance. Thus, the CCS improved not only the sulfur utilization by about 20% but also the rate capability at high rate. As seen in Fig. 8c, the long-term cycling stability of the S/HCS-65-IM (with CCS) at 0.5 C is not as good as that of the S/HCS-65-IM possibly due to the slow but steady transfer of LPS to the anode side. That is the LPS accumulated between the cathode and CCS can migrate along the edge of electrode to the lithium anode in the small coin cell (CR2032). This LPS carry-over would be much suppressed in an actual battery cell configuration with much large dimension.

The cycled electrodes were further examined by electrochemical impedance spectrometry (EIS). Fig. 9 shows the Nyquist plots of the electrodes and their corresponding equivalent circuits to fit the EIS profile (inset). \(R_s\), \(R_1\)–\(R_3\) (\(R_{ct}\)), and \(W\) denote the resistances of the electrolyte, three different interfacial charge transfers, and lithium diffusion, respectively. All the cells showed very low \(R_s\) values in the range of 2.8–4.3 \(\Omega\). Three semicircles, one with a small diameter at high frequency and two at medium-to-low frequencies, were observed.
in the EIS spectra. The small semicircles at high frequency are magnified in the inset of Fig. 9. They can be attributed to the charge transfer occurring at the anode surface although the resistances of $R_1$ were very small (≈2 Ω) because of the low surface area of the anode compared to the cathode.\(^\text{40}\) The two semicircles at medium-to-low frequencies can be attributed to the charge transfer of sulfur intermediates in the cathode.\(^\text{40}\) The S/HCS-65-PM cell showed the largest charge transfer resistance through the S/HCS cathode ($R_2 + R_3$) possibly because of the poor sulfur encapsulation and/or poor sulfur dispersion throughout the HCS hosts, as shown by the EE-TEM images in Fig. 5. The charge transfer resistance at medium frequency (mainly $R_2$) is the most common factor affecting the performance of Li-S batteries.\(^\text{41}\) Hence, it can be stated that S/HCS-65-PM showed very low capacity (low sulfur utilization) compared to S/HCS-65-IM because of the large charge transfer resistance in the cathode. S/HCS-65-IM (CCS) showed a slightly smaller resistance value of $R_2$ than S/HCS-65-IM because of the enhanced charge transfer through the conductive carbon film on the PP separator. As compared in Fig. 6, the CCS showed higher ionic conductivity and much better electrolyte wettability than the pristine PP separator. A small decrease in the resistance and enhanced ionic conductivity through the CCS along with good electrolyte wettability on the CCS resulted in a large improvement in the rate capability of the S/HCS-65-IM (CCS) at high C-rate, as shown in Fig. 8b.

Conclusions

We successfully developed a novel and scalable synthetic procedure to design well-defined HCSs by using a pyrolytic soft template of styrene/acrylic acid copolymer microspheres. In order to effectively encapsulate sulfur inside the pores of the uniform-sized HCSs in the S/HCS composites for Li-S cathodes, we employed two different sulfur-loading methods; a modified sulfur-loading method involving solution impregnation of sulfur followed by melt-diffusion (IM) and the conventional physical mixing of sulfur powder and HCSs followed by melt-diffusion (PM). In the S/HCS-65-IM (sulfur content = 65 wt\%) sample, sulfur was well-confined inside the pores of the HCSs. On the other hand, the S/HCS-65-PM sample showed a poor sulfur dispersion. Hence, S/HCS-65-IM delivered much higher capacity (higher sulfur utilization) and greater cycling stability (reduced LPS shuttling) over 200 cycles and showed much lower impedance build up than S/HCS-65-PM. However, S/HCS-65-IM showed a limited sulfur utilization of ~54% at 0.1 C (actual/theoretical capacity of ~900/1675 mAh g\(^{-1}\) sulfur, indicating that substantial LPS dissolution and shuttling occurred in the cell. Sulfur utilization was improved up to ~62% by suppressing the LPS shuttle effect by using a CCS. The S/HCS-65-IM cell with the CCS also exhibited excellent cycling stability (capacity retention of >81% after 200 cycles at 0.5 C) and much improved rate capability because of the enhanced ionic conductivity and decreased interfacial charge transfer resistance.

Acknowledgment

This work was supported by the National Research Foundation of Korea grant funded by the Ministry of Education (NRF-2017R1A2B4002940).

ORCID

Jung Kyoo Lee \(\text{https://orcid.org/0000-0003-1673-7587}\)

References

1. P. G. Bruce, S. A. Freunberger, L. J. Hardwick, and J. M. Tarascon, \textit{Nat. Mater.}, 11, 19 (2012).
2. A. Manthiram, S. H. Chung, and C. X. Zu, \textit{Adv. Mater.}, 27, 1980 (2015).
3. A. Rosenman, E. Markevich, G. Salitra, D. Aurbach, A. Garusuch, and F. F. Chesneau, \textit{Adv. Energy Materials}, 5 (2015).
4. R. P. Fang, S. Y. Zhao, Z. H. Sun, W. Wang, H. M. Cheng, and F. Li, \textit{Advanced Materials}, 29 (2017).
5. D. Li, F. Han, S. Wang, F. Cheng, Q. Sun, and W. C. Li, \textit{Adv. Mater. Interfaces}, 5, 2208 (2018).
6. J. T. Lee, Y. Y. Zhao, S. Thieme, H. Kim, M. Oschatz, L. Borchardt, A. Magasinski, W. I. Cho, S. Kaskel, and G. Yushin, \textit{Adv. Materials}, 25, 4573 (2013).
7. B. Zhang, M. Xiao, S. J. Wang, D. M. Han, S. Q. Song, G. H. Chen, and Y. Z. Meng, \textit{Adv. Mater. Interfaces}, 6, 13174 (2014).
8. J. X. Song, T. Xu, M. L. Gordin, P. Y. Zhu, D. P. Lv, Y. B. Jiang, Y. S. Chen, Y. H. Duan, and D. H. Wang, \textit{Adv. Functional Materials}, 24, 1243 (2014).
9. Z. W. Zhang, Z. Q. Li, F. B. Hao, X. K. Wang, Q. Li, Y. X. Qi, R. H. Pan, and L. W. Yin, \textit{Adv. Functional Materials}, 24, 2500 (2014).
10. Z. Li, Y. Jiang, L. X. Yuan, Z. Q. Yi, C. Wu, Y. Liu, P. Strasser, and Y. H. Huang, \textit{Acta Nano}, 8, 9295 (2014).
11. X. L. Ji, K. T. Lee, and L. F. Nazar, \textit{Nature Materials}, 8, 500 (2009).
12. B. Zhang, X. Qin, G. R. Li, and X. P. Gao, \textit{Energy & Environmental Science}, 3, 1531 (2010).
13. S. Xin, L. Gu, N. H. Zhao, Y. X. Yin, L. J. Zhou, Y. G. Guo, and L. J. Wan, \textit{J. Am. Chem. Soc.}, 134, 18510 (2012).
14. S. Y. Zheng, P. Han, Z. Han, H. J. Zhang, Z. H. Tang, and J. H. Yang, \textit{Scientific Reports}, 4 (2014).
15. N. Jayaprakash, J. Shen, S. S. Moganty, A. Corona, and L. A. Archer, \textit{Adv. Mater. Int. Ed.}, 50, 5004 (2011).
16. J. Schuster, G. He, B. Mandlmeier, T. Yim, K. T. Lee, T. Bein, and L. F. Nazar, \textit{Angew. Chem.-Int. Ed.}, 51, 3591 (2012).

Figure 9. Nyquist plots of the cycled S/HCS cells (insets are equivalent circuits and magnified Nyquist plots in the high frequency region).

![Figure 9](image-url)
17. W. Y. Li, Q. F. Zhang, G. Y. Zheng, Z. W. Seh, H. B. Yao, and Y. Cui, *Nano Lett.*, **13**, 5534 (2013).

18. G. M. Zhou, Y. B. Zhao, and A. Manthiram, *Advanced Energy Materials*, **5** (2015).

19. F. Xu, Z. W. Tang, S. Q. Huang, L. Y. Chen, Y. R. Liang, W. C. Mai, H. Zhong, R. W. Fu, and D. C. Wu, *Nat. Commun.*, **6** (2015).

20. W. D. Zhou, X. C. Xiao, M. Cai, and L. Yang, *Nano Lett.*, **14**, 5250 (2014).

21. Q. Li, Z. A. Zhang, Z. P. Guo, Y. Q. Lai, K. Zhang, and J. Li, *Carbon*, **78**, 1 (2014).

22. Z. L. Gao, R. Li, Bin Zhang, and Zhan Lin, *Frontiers in Energy Research*, **3**, 1 (2015).

23. Q. Li, Z. A. Zhang, Z. P. Guo, Y. Q. Lai, K. Zhang, and J. Li, *Carbon*, **78**, 1 (2014).

24. Z. Li, H. B. Wu, and X. W. Lou, *Energy & Environmental Science*, **9**, 3061 (2016).

25. C. F. Zhang, H. B. Wu, C. Z. Yuan, Z. F. Guo, and X. W. Lou, *Angew. Chem. Int. Edit.*, **51**, 9592 (2012).

26. Y. H. Qu, Z. A. Zhang, X. W. Wang, Y. Q. Lai, Y. X. Liu, and J. Li, *J. Mater. Chem. A*, **1**, 14306 (2013).

27. Z. Li, J. T. Zhang, B. Y. Guan, D. Wang, L. M. Liu, and X. W. Lou, *Nat. Commun.*, **7** (2016).

28. R. Liu, S. M. Maharin, C. Li, R. R. Unocic, J. C. Iderbo, H. J. Gao, S. J. Pennycook, and S. Dai, *Angew. Chem. Int. Edit.*, **59**, 6799 (2011).