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7 Self-Assembling Hollow Carbon Nanobeads into
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11 Double-Shell Microspheres as a Hierarchical Sulfur
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15 Host for Sustainable Room-Temperature Sodium-
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19 Sulfur Batteries
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53 batteries.
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ABSTRACT

We report the use of double-carbon-shell passion fruit-like porous carbon microspheres (PCMs) as the sulfur substrate in the room temperature sodium sulfur (RT Na-S) batteries. PCMs are covered by the micro-sized carbon shells on the outside and consisted of the carbon nanobeads with hollow structure inside, leading to a unique multidimensional scaling double-carbon-shell structure with high electronic conductivity and strengthened mechanical properties. Sulfur was filled inside the PCMs (PCMs-S) and protected by the unique double-carbon-shell, which means the following generated intermediate sodium polysulfide species cannot be exposed to the electrolyte directly and well protected inside. In addition, the inside interconnected porous structure provides rooms for the volume expansion of sulfur during discharge processes. It is found that the PCMs-S with a 63.6 % initial coulombic efficiency contributed 290 mAh g⁻¹ at the current density of 100 mA g⁻¹ after 350 cycling test. More importantly, PCMs-S exhibited good rate performance with a capacity of 113 and 56 mAh g⁻¹ at the current densities of 1000 and 2000 mA g⁻¹, respectively.

1. Introduction

Sodium-sulfur (Na-S) battery is a promising energy storage system because of the natural abundance of Na in the earth's crust. Compared with high-temperature (HT) Na-S batteries, room-temperature (RT) Na-S batteries are more promising for practical application because they can avoid the safety problems caused by high operation temperature (>300 °C). Unfortunately, the RT Na-S batteries show some disadvantages similar to Li-S batteries, such as low electric conductivity of sulfur and the generated sodium polysulfide (NaPS) species (such as Na₂S) during the discharge process, the solubility of high ordered NaPS, and huge volume change

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3 between sulfur and Na_2S species.¹⁻⁸ These issues lead to rapid capacity fade, limiting their
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5 application as the energy storage systems.⁹⁻¹⁹
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9 To meet the multiple challenges, it is effective to design a novel sulfur substrate with high
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11 conductivity and porous structure. The porous structure inside the substrate can play a role as the
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13 protect barrier to prevent transition of the intermediate NaPS into the electrolyte. In addition, the
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15 inside void space allows the volume change of sulfur. From this point of view, encapsulating
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17 sulfur into porous carbon is helpful for both Li-S and Na-S batteries. In 2016, sulfur embedded
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19 carbon nanofibers (CNFs)^{5,14}, graphene films^{16,20} and porous carbon^{2,6,19} have been extensively
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21 reported as cathode electrodes for Na-S batteries. However, since the embedded sulfur inside the
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23 matrices is exposed directly to the electrolyte, the loss of polysulfide species from the porous
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25 matrices is inevitable. In addition, the mechanical strength of this open-style structured electrode
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27 is poor, especially under continue huge volume expansion/contraction processes. Moreover, the
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29 continue volume changes of sulfur can lead to serious structural damage along with the solid
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31 electrolyte interphase (SEI) generation on the fresh sulfur surfaces, which can lead to a large
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33 capacity fade. Therefore, future study of the RT Na-S batteries can be focused on the
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35 development of the porous but sealed structured sulfur/carbon composites to prevent polysulfide
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37 migration and improve structure stability.
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44 To do so, the double-carbon-shell passion fruit structured porous carbon microspheres (PCMs)
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46 were employed as the novel carbon sulfur substrate in this work. PCMs were covered by the
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48 micro-sized carbon shells (outer-carbon-shell) and consisted of the hollow carbon nanobeads
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50 (inside-carbon-shell), which can result in a novel multidimensional scaling double-carbon-shell.

51 **Scheme 1** illustrates the fabrication procedure of the final sulfur filled PCMs (PCMs-S). For
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53 PCMs, calcium carbonate@silica ($\text{CaCO}_3@\text{SiO}_2$) microspheres consisting of CaCO_3 -coated
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SiO₂ nanobeads (CaCO₃@SiO₂) were initially produced around 3 min. Then, C@CaCO₃@SiO₂ composite with double-carbon-shell structure was produced after a carbon deposition through a chemical vapour deposition (CVD) way by using acetylene as the carbon resource. The double-carbon-shell can be attained in this way since the carbon coating layers can be formed on the CaCO₃@SiO₂ microspheres surface and inside CaCO₃@SiO₂ nanobead. PCMs were obtained after removal of CaCO₃ and SiO₂ templates. The final PCMs-S composite was generated after sulfur filling. The sulfur sealed inside PCMs can be well protected, and the diffusion region of the following generated NaPS are also limited not only by the inside porous carbon but also the outer carbon shell. In addition, the overall structural stability, electronic conductivity and mechanic strength of the composite can be improved at the same time due to the introduction of the double-carbon-shell structure. On the other hand, some void space is still maintained inside PCMs-S after sulfur filling. The inside porous structure can absorb NaPS and leave room for sulfur expansion during discharging, benefiting the cycling stability. In order to better understand the difference in electrochemical performance between nanoporous and microporous structure, sulfur-filled hollow carbon microspheres (HCMs-S) were also prepared and tested. It is found that, the PCMs-S shows much improved cycling stability and rate performance.

Scheme 1. Schematic demonstration of the fabrication process of PCMs-S.

2. Results and Discussion

Figure 1 shows the SEM images of the samples. HCMs microspheres with a uniform size distribution (3–5 μm in diameter) in a lower magnification are shown in Figure 1a. Based on the enlarged SEM picture of one single broken microsphere in Figure 1b, the micro-sized sphere has a hollow structure. After sulfur filling, the structure of HCMs-S (Figure 1c) shows a significant difference. The hollow structure of the as-obtained HCMs disappears and is filled with solid particles. Figure 1d exhibits the image of PCMs in a lower magnification. Compared with HCMs, PCMs show a similar size distribution. However, based on the magnified part of PCMs in Figure 1e, it can be seen that the inside carbon beads are interconnected and covered with the carbon shells on the outer side. The multidimensional scaling double-carbon-shell is composed of the inside nanosized carbon shell and the outside micro-sized hollow carbon shell in the PCMs can be clearly observed. The structure of PCMs is significantly different from HCMs, which means that the function of silica during the $\text{CaCO}_3@\text{SiO}_2$ microspheres fabrication is very important. After sulfur filling treatment, no obvious structural difference can be found between PCMs and PCMs-S (Figure 1f). The overall structure of PCMs-S is well protected even after sulfur filling treatment at 300 $^\circ\text{C}$ for 24 h, which means that the novel double-shell structure plays a crucial role in maintaining the structure stability.

Figure 1. Morphologies of the samples in different magnifications. (a, b) SEM images of HCMs, (c) HCMs-S, (d, e) PCMs, and (f) PCMs-S

Figure 2 shows the TEM and elemental mapping images of the samples. A carbon sphere with around 3 μm in diameter and hollow structure is seen in Figure 2a. In addition, carbon tubes are generated on the HCMs surface during the carbonization process. Figure 2b illustrates the thickness of the carbon layer in HCMs is about 20 nm. Figure 2c shows a single HCMs-S microsphere. After sulfur filling, most of the voids inside the hollow HCMs disappear and are filled with particles which agglomerated into microsize. According to the elemental mapping results (Figure 2d to 2f) of a single HCMs-S microsphere, sulfur is well filled inside the hollow carbon. Figure 2g shows a single PCMs microsphere. The inside porous network is covered with carbon shells with a multilayered structure (Figure 2h). The thickness of each coating shell is 5–7 nm. **Figure S1** shows the inside part of PCMs. It can be seen that all of the inside carbon beads with hollow structure are interconnected, with a diameter about 50–70 nm. The porous structure of PCMs is filled with sulfur and becomes much denser after sulfur impregnation

(Figure 2i). The elemental mapping results (Figure 2k to 2l) of a single PCMs-S microsphere (Figure 2j) show that the sulfur is uniformly dispersed inside PCMs.

Figure 2. TEM images and elemental mapping results of the samples. TEM images of (a and b) HCMs, (c and d) HCMs-S and (e to f) their corresponding elemental mapping results; TEM images of (g and h) PCMs, (i and j) PCMs-S and (k to l) their corresponding elemental mapping results.

Figure 3a shows the XRD patterns of HCMs-S and PCMs-S. Compared the well-resolved peaks corresponding to bulk crystalline sulfur in HCMs-S, most peaks disappear and become broader in PCMs-S. The weak intensity of sulfur peak in PCMs-S indicates that the sulfur particles are successfully filled inside PCMs and covered with the double-carbon-shell.²¹ Another distinct diffraction peak at $2\theta = 26.5$ is the (002) plane of carbon (JCPDS No. 65-6212). Figure 3b shows the pore size distribution (PSD) results. Besides the peaks located at 3.5 and 5.5 nm which are related to the small mesopores, the pores with the sized around 10–50 nm can also be found inside PCMs. However, only 3.8 and 6.5 nm small mesopores can be seen in HCMs. In addition, the larger sized pores (10–50 nm) in PCMs are related to the inside interconnected hollow carbon nanobeads. The surface area is $128 \text{ m}^2 \text{ g}^{-1}$ for HCMs and $165 \text{ m}^2 \text{ g}^{-1}$ for PCMs. The increased surface area of PCMs is mainly derived from the inner porous structure. Figure 3c shows the TG curves of HCMs-S and PCMs-S measured in N_2 . For HCMs-S, there is only one weight loss in the temperature range of 200–300 °C, and the weight curve become quite flattening when temperature above 300 °C. The weight loss for HCMs-S is around 44 wt% and it is attributed to the sublimation of sulfur from the hollow carbon microspheres. For PCMs-S, it can be see that there are two separated weight losses derived from sulfur sublimation. The first 6 wt% weight loss is located in the same range as HCMs-S (200–300 °C) and the second 28 wt% weight loss is around 600–780 °C. The increased sublimation temperature of sulfur during the second one is due to the more difficult evaporation of the sulfur which is filled inside the carbon beads with

hollow structure.²¹ Therefore, we believe that 28 wt% of encapsulated sulfur in the PCMs-S is fully embedded inside the hollow carbon nanobeads and the last 6 wt% sulfur is filled in the void spaces inside the microspheres. Based on the above analysis, the different embedding modes of sulfur in HCMs-S and PCMs-S are illustrated in Figure 3d. For HCMs-S, 44 wt% of sulfur is filled inside the micro-sized hollow carbon. The higher sulfur content inside HCMs-S is mainly because of the hollow structure which can provide more space for sulfur filling. On the other hand, for PCMs-S, 28 wt% of sulfur is encapsulated in the inner interconnected hollow carbon nanobeads and 6 wt% of sulfur is filled in the void spaces among the inside carbon nanobeads. As a result, most of the sulfur inside PCMs-S is fully enclosed inside which can effectively prevent the polysulfides from dissolving into the electrolyte.

Figure 3. Materials Characterization. (a) XRD patterns, (b) the pore size distribution, (c) the TG curves under N₂, and (d) the schematic illustration of different sulfur embedding status of the samples.

The charge/discharge capacities at 100 mA g⁻¹ of PCMs-S and HCMs-S are shown in **Figure 4a**. For HCMs-S, a significant charge capacity decrease from 873 to 59 mAh g⁻¹ can be found during the first 50 cycles, which means more than 93 % (814 mAh g⁻¹) of the original capacity was irreversible and lost. The capacity fade was mainly due to the continuous diffusion of the high ordered NaPS from the electrode to the electrolyte via the broken holes on the carbon shells, leading to poor cycling stability. On the other hand, for PCMs-S, the charge capacity is kept stable after a capacity decrease from 700 to 390 mAh g⁻¹ after the first 50 cycles, indicating the higher utilization and activity of sulfur in PCMs-S. As a result, the unique double-carbon-shell structure in PCMs-S is crucial to the final electrochemical performance, a reflection of the NaPS species generated inside PCMs-S have a better protection and less direct contact to the electrolyte. Moreover, the interconnected porous structure inside PCMs-S can offer more active positions to encapsulate sulfur inside.²¹ Figure 4b shows the first and the second charge/discharge curves of PCMs-S at 100 mA g⁻¹. The discharge and charge capacity for PCMs-S is 1100 and 699 mAh g⁻¹ in the first run, and 795 and 664 mAh g⁻¹ in the second run. As a result, the coulombic efficiency for PCMs-S during the first cycling test is 63.6 %, and then it reaches 83.5 % in the following cycling test. The irreversible capacity during the first cycle is 401 mAh g⁻¹. According to Figure 4b, the capacity loss mainly derives from the voltage plateau which is below 1.4 V, leading to the disappear of the discharge platform during the second cycling test. **Figure S2** shows the SEM pictures of PCMs electrode after long cycling test. The structure of PCMs-S was well maintained, supporting the result from Figure 4b. The improved

cycling performance for PCMs-S is stemmed from the following advantages: (1) the nanosized porous structure inside PCMs-S results in a better sulfur dispersion than that of the micro-sized hollow structured HCMs-S, leading to the improved structural stability of sulfur during volume expansion process; (2) the double-carbon-shell structure improves the strength property of PCMs-S and effectively limits the diffusion of NaPS into electrolyte.²²⁻²⁵

The rate ability of PCMs-S is provided in Figure 4c. The charge capacity of PCMs-S at 10th cycle is 402 mAh g⁻¹ under 100 mA g⁻¹, and capacity retentions after 200, 500, 1000 and 2000 and 100 mA g⁻¹ is 51.0, 18.4 and 28.1 and 14.2%. More importantly, the charge capacity is still remained at 407 mAh g⁻¹ when turns back to 100 mA g⁻¹ after the high rates test, indicating the outstanding rate performance of PCMs-S. For better understand the kinetic properties of the PCMs-S and HCMs-s samples, electrochemical impedance spectroscopy (EIS) measurement were carried out. Figure 4d shows Nyquist plots of the PCMs-S and HCMs-s (Inset of Figure 4d shows the equivalent circuit of PCMs-S). A semicircle and a straight line can be found in both of the plots in the higher and lower frequency range, respectively. Compared with HCMs-S which shows a charge transfer resistance (R_{ct}) value of 900 Ω , PCMs-S has the R_{ct} value of 499 Ω (see **Table S1** in the supporting information), demonstrating faster diffusion of electrons and ions through the interface between the electrode and electrolyte, because of the close contact between the sulfur particles and the carbon matrix inside PCMs. The smaller R_{ct} value of PCMs-S is also a reflection of the high electroactivity of sulfur with the improvement derived from PCMs. **Figure S3** illustrates the enlarged part from the EIS curves in the high frequency region. Table S1 indicates that PCMs-S and HCMs-S show different solution resistance (R_s). Compared with HCMs-S, PCMs-S has a lower R_s value, which is result from the enhanced electronic conductivity. Small R_s values make contribution to the power performance of the electrodes.

Therefore, PCMs-S shows improved cycling and rate abilities when employed as the cathode material in RT Na-S batteries.

Figure 4. Electrochemical performance of the samples. (a) the cycling property of HCMs-S and PCMs-S at 100 mA g⁻¹ in a voltage window from 0.8 to 2.8 V (vs. Na/Na⁺), (b) the first and the second charge/discharge curves of PCMs-S, (c) the rate performance of PCMs-S, and (d) the EIS plots of PCMs-S and HCMs-S (inset: equivalent circuit; W is the Warburg impedance and CPE (constant phase element) is the double layer capacitor).

For further insight the detailed electrochemical performance of PCMs-S, we employed the Powder Diffraction Beamline at the Australian Synchrotron to collect the *in-situ* synchrotron XRD data ($\lambda = 0.6885$ Å) which reflects the oxidation-state changes of sulfur species during

discharge/charge processes. The various changes of sulfur oxidation states during the initial cycle along with the initial discharge-charge curves are presented in **Figure 5**. The peaks located at 7.00° , 10.34° , and 11.76° collected from the fresh half-cell can be assigned to the (113), (222), and (026) planes of S_8 (JCPDF no. 77-0145). At the beginning of the initial discharge process from 2.2 V to 1.5 V, all the S_8 peaks were disappeared and a new peak at 12.05° evolved, indicating the S_8 rings broken and multi-step reduction of S_8 species.²¹ For this work, the new developed peak at 12.05° can be ascribed to the (020) plane of the initial generated polysulfide species Na_2S_5 (JCPDF no. 77-0294). In the discharge process, there are a couple of new cathodic peaks evolved at 1.2 and 0.8 V in the CV curve, respectively. Specifically, the first cathodic peak in the CV plot from 1.5 V to 1.0 V was associated with the formation of Na_2S_4 and Na_2S_2 , which can be confirmed by the following generated new peaks at 13.31° and 18.71° . The first XRD peak at 13.31° could be assigned to the (213) plane of Na_2S_4 (JCPDF no. 71-0516), while the peak at 18.71° was associated with the (002) plane of Na_2S_2 (JCPDF no. 81-1764). It is notable that the position of (002) peak in this work is slightly higher than that of the standard Na_2S_2 , which means the interlayer spacing distance of the (002) peak is smaller. The further reduction of Na_2S_2 was processed between 1.2 V to 0.8 V, leading to another cathodic peak which located at 0.8 V. During this process, a new peak was developed at 17.07° , corresponding to the (220) plane of Na_2S (JCPDF no. 77-2149). In the following charging process, the predominant reaction was the multi-step oxidation from Na_2S_2 to Na_2S_4 , Na_2S_4 to Na_2S_x ($5 \leq x \leq 8$), and Na_2S_x ($5 \leq x \leq 8$) to S_8 . However, Na_2S was not reduced to long-chain polysulfides during the charging process since it first appeared, because there was no intensity changes of the Na_2S peak could be found. Therefore, the generated Na_2S was inactive and irreversible. Based on the *in-situ* synchrotron XRD data analysis, it is believed that for the RT Na-S batteries, the active electrochemical

reactions should be the reversible multi-step reduction/oxidation between S_8 and Na_2S_2 . The high discharge capacity (more than 1100 mAh g^{-1}) during the first discharge process was due to the fully reduction of S_8 to Na_2S , and the large capacity loss (401 mAh g^{-1}) during the first cycling test was because of the irreversibility of Na_2S .

Figure 5. *In-situ* synchrotron XRD analysis of the electrochemical behavior towards Na^+ for PCMs-S ($\lambda = 0.6885 \text{ \AA}$). *In-situ* synchrotron XRD patterns (middle) of the RT Na-S half cell using PCMs-S as the cathode along with the initial CV plot (left) and the initial charge/discharge curves (right).

3. Conclusion

In summary, the PCMs-S composite exhibits improved cycling stability and excellent rate capability due to the following factors: (1) the double-carbon-shell structure improves the electronic conductivity and suppresses the polysulfide shuttle to the anode; (2) the inside porous structure accommodates the volume expansion of sulfur during discharge processes; (3) the encapsulated sulfur inside the interconnected hollow carbon nanobeads is endowed with uniform

dispersion in the range of nanosize which improves the structural stability of sulfur and shortens the distance of sodium ions diffusion.

Associate Content

Supporting Information

Experimental Section, SEM image of PCMs-S, Charge resistance and solution resistance of PCMs-S and HCMs-S obtained from Nyquist Plots, EIS curves of PCMs-S and HCMs-S

Author Contributions

‡Lei Zhang, Binwei Zhang and Yuhai Dou contributed equally.

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Experimental Section

Synthesis of $\text{CaCO}_3@\text{SiO}_2$ microspheres: All the chemicals used in this work were purchased from Sigma Aldrich. Stoichiometric sodium carbonate (Na_2CO_3), 800 mg SiO_2 (~80 nm) and 0.5 g sodium dodecyl benzene sulfonate (SDBS) were added to 400 ml deionized (DI) water under stirring for 30 min to get a uniform suspension (a). In addition, stoichiometric calcium chloride (CaCl_2) was dissolved in 400 ml DI water to achieve solution (b). After that, suspension (a) was mixed with solution (b) under stirring for 5 min to obtain $\text{CaCO}_3@\text{SiO}_2$ suspension. Then the

CaCO₃@SiO₂ suspension was centrifuged and washed by DI water to obtain pure CaCO₃@SiO₂ powder. For a comparison, CaCO₃ microspheres without SiO₂ were also fabricated under the same conditions as described above.

Carbon coating on CaCO₃@SiO₂ composites (C@CaCO₃@SiO₂): The prepared CaCO₃@SiO₂ powder was put in a furnace filled with purified Ar flow and heated to 650 °C at a heating rate of 5 °C min⁻¹. Subsequently, acetylene (95% Ar mixed with 5% acetylene) was introduced into the furnace at the same temperature at a flow rate of 30 mL min⁻¹ for 2 h. The final C@CaCO₃@SiO₂ composite was attained after the furnace was cooled down under Ar atmosphere. Due to the good permeability of acetylene, the carbon layers can be fabricated not only on the outer of the whole microsized spheres but also the inside every single nanospheres, leading to the unique double-carbon-shell structure. For a comparison, CaCO₃ microspheres were also coated with carbon via the same process to form C@CaCO₃ composite.

CaCO₃ layer and silica etching: C@CaCO₃@SiO₂ was first washed with HCl (1 mol L⁻¹) to remove CaCO₃ for 0.5 hour and then washed by NaOH (2 mol L⁻¹) solution for another 3 days to remove SiO₂ to form the final product, named as PCMs. For C@CaCO₃, the powders were only treated by HCl washing to remove CaCO₃ and named as HCMs.

Sulfur filling in PCMs and HCMs: The as-obtained PCMs or HCMs were mixed with sulfur by grinding in a carbon/sulfur ratio of 1:4, and the mixture was transferred into a 25 mL stainless-steel Teflon-lined autoclave. In order to obtain a better dispersion between the sulfur and carbon matrixes, the autoclave was sealed and maintained at 180 °C for 24 h. The obtained preliminary sulfur-doped PCMs or HCMs mixture was transferred into a sealed but vacuumed vessel, heated at 300 °C for another 24 h to ensure complete diffusion of melt sulfur into the interior pores of

the carbon matrix. After being naturally cooled down to room temperature, the S-PCMs and S-HCMs were finally obtained.

Materials Characterization: The products S-PCMs and S-HCMs were analyzed by X-ray diffraction (XRD; GBC MMA) with Cu K α radiation; field-emission scanning electron microscopy (FESEM; JEOL 7500); and transmission electron microscopy (TEM; JEOL ARM-200F) with high-resolution TEM (HRTEM). The specific surface area was determined according to the Brunauer–Emmett–Teller (BET) method in the relative pressure range of 0.05–0.2. The pore volume and pore size distributions were derived from the adsorption branches of isotherms by using the Barrett-Joyner-Halenda (BJH) model. The sulfur content of the products was measured by a Mettler Toledo TGA/SDTA851 analyzer from 30 to 900 °C in Ar at a heating rate of 5 °C min⁻¹.

Electrochemical measurements: The tests were conducted by assembling coin-type half cells in an argon-filled glove box. Lithium foil was employed as both reference and counter electrode. The working electrode consisted of 70 wt% active material (S-PCMs and S-HCMs, respectively), 20 wt% carbon black, and 10 wt% carboxymethyl cellulose (CMC) binder. Electrolyte consisting of 1.0 mol L⁻¹ NaClO₄ in propylene carbonate/ethylene carbonate, in a volume ratio of 1:1, and 5 wt% fluoroethylene carbonate additive (PC/EC + 5 wt% FEC), was prepared and utilized in this work. Electrochemical cycling of electrodes was conducted by galvanostatic test at 100 mA g⁻¹ in a voltage window from 0.8 to 2.8 V (vs. Na/Na⁺). Cyclic voltammetry and impedance testing were performed using a Biologic VMP-3 electrochemical workstation from 0.8 to 2.8 V at a scan rate of 0.1 mV s⁻¹.

In-situ synchrotron XRD measurements: The preparation process of the half-cells which were used for *in-situ* synchrotron XRD test was similar to the fabrication process of coin-cells for the normal electrochemical behavior testing. The only difference is that two holes with a diameter of 4 mm were punched on the cathode- and anode-side caps to make sure that the X-ray beams could catch the sodiation/desodiation reactions. In addition, the above mentioned holes were coated with the Kapton film which has slight peaks under XRD measurements, followed by fully covering with AB glue. During the *in-situ* synchrotron XRD test, a Neware battery test system was connected to the cell to carry out the charge/discharge process.

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