Sulfur/Oxygen Codoped Porous Hard Carbon Microspheres for High-Performance Potassium-Ion Batteries

Mei Chen, Wei Wang, Xiao Liang, Sheng Gong, Jie Liu, Qian Wang,* Shaojun Guo,* and Huai Yang*

Potassium-ion batteries (KIBs) are very promising alternatives to lithium-ion batteries (LIBs) for large-scale energy storage. However, traditional carbon anode materials usually show poor performance in KIBs due to the large size of K ions. Herein, a carbonization-etching strategy is reported for making a class of sulfur (S) and oxygen (O) codoped porous hard carbon microspheres (PCMs) material as a novel anode for KIBs through pyrolysis of the polymer microspheres (PMs) composed of a liquid crystal/epoxy monomer/thiol hardener system. The as-made PCMs possess a porous architecture with a large Brunauer–Emmett–Teller surface area (983.2 m² g⁻¹), an enlarged interlayer distance (0.393 nm), structural defects induced by the S/O codoping and also amorphous carbon nature. These new features are important for boosting potassium ion storage, allowing the PCMs to deliver a high potassiation capacity of 226.6 mA h g⁻¹ at 50 mA g⁻¹ over 100 cycles and be displaying high stability by showing a potassiation capacity of 108.4 mA h g⁻¹ over 2000 cycles at 1000 mA g⁻¹. The density functional theory calculations demonstrate that S/O codoping not only favors the adsorption of K to the PCMs electrode but also reduces its structural deformation during the potassiation/depotassiation. The present work highlights the important role of hierarchical porosity and S/O codoping in potassium storage.
monomer/thiol hardener system. The resulting PCMs possess an amorphous nature, an expanded interlayer distance (0.393 nm), large Brunauer–Emmett–Teller (BET) surface area (983.2 m$^2$ g$^{-1}$), and hierarchical micro/mesopore structure. These important features make PCMs exhibit a highly reversible potassiation capacity of 226.6 mA h g$^{-1}$ at the current density of 50 mA g$^{-1}$ (0.18 C, the C rate was calculated based on the theoretical capacity of graphite (279 mA h g$^{-1}$). The present PCMs are highly stable for KIBs, by retaining almost no decrease of capacity (108.4 mA h g$^{-1}$) over 2000 cycles at a high current density of 1000 mA g$^{-1}$ (3.6 C), one of the best cycling stabilities reported to date.

The typical procedures for preparing the PCMs are illustrated in Scheme 1. We first synthesized polymer microspheres (PMs) with the controlled diameter within a liquid crystal (LC)/epoxy monomer/thiol hardener system. Then, the S/O codoped porous carbon microspheres (PCMs) were made from a carbonization-etching procedure employing the PMs as the precursors (Details in Supporting Information). Figure 1a shows scanning electron microscopy (SEM) image of the PMs synthesized at 80 °C with an LC concentration of 50.0 wt%, an epoxy monomer/thiol mass ratio of 1:1, an accelerant content of 5.0 wt%. It is found that the synthesized PMs were spherical in shape with a narrow size distribution. The inset of Figure 1a reveals that the as-made PMs have a mean diameter of 2.51 µm. The chemical structure of the crosslinked epoxy-thiol-based PMs was confirmed by Fourier transform infrared spectrometer (FT-IR) (Figure S1, Supporting Information). The vibration bands at 3490, 2938–2854, 2562, 1730, 1170, and 1030 cm$^{-1}$ were representative of the $\nu$(O–H), $\nu$(C–H), $\nu$(S–H), $\nu$(C=O), $\nu$(C=O–C) and $\nu$(C–O–H) groups, respectively. Interestingly, the diameter of the as-made PMs is tunable from 1.56 to 7.82 µm by varying the parameters such as the curing temperature (ranging from 60 to 120 °C), LCs content (50.0 to 80.0 wt%) and accelerant content (2.0 to 10.0 wt%) (Table S1 and Figures S2–S4, Supporting Information). The effect of different curing parameters on the sizes of PMs can be attributed to the curing kinetics.[36–39] Taking the LC content parameter as an example (Figure S2, Supporting Information), obviously, the curing rate of the epoxy increased as LC content decreased. Thus, as the curing process was conducted (the initial isotropic syrup gradually phase-separated into LC-rich and epoxy-rich domains), the coagulation of epoxy-rich domains was limited by the rapid formation of the epoxy seeds, resulting in much smaller epoxy-rich domains. Thus, PMs with smaller sizes were produced as the polymerization between epoxy monomers and thiol occurred within smaller reaction domains.[36,40] Similarly, increasing the curing temperature and accelerant content also led to an increase of the curing rate, thus producing smaller sizes of PMs (Figures S3 and S4, Supporting Information).

Carbonizing the PMs at 800 °C for 3 h under a H$_2$/Ar mixture (with a volume ratio of 1:9) produced the uniformed carbon microspheres (CMSs) with tunable diameters (Table S1, Supporting Information). Figure 1b shows the SEM image of the carbonized PMs. We found the dehydrogenized CMSs preserved the initial spherical shape with a smooth surface (inset of Figure 1b; Figure S5a, Supporting Information), but the size of the CMSs slightly shranked into a smaller diameter of 1.53 µm. Nitrogen sorption measurements show that the BET surface area of the as-made CMSs is 99.3 m$^2$ g$^{-1}$ (Figure S5b,
Supporting Information). The XRD spectra show the nongrafitic, hard carbon nature of the product with an interlayer distance of 0.377 nm, revealed by the position of the (002) peak with \( 2\theta = 23.59^\circ \) (Figure S5c, Supporting Information). In order to increase the surface area of the as-made smooth CMs, the CMs subsequently underwent an etching process using KOH as the etchant. This process led to the production of porous carbon microspheres (PCMs) with enormous micro-/meso-sized pores (Figure 1c,d). Furthermore, the PCMs retain their original spherical morphology with a mean diameter of 1.47 \( \mu \)m. It is worth noting that the activation time for the CMs in the KOH (aq) was crucial to the final morphologies of the PCM products. As shown in Figure S6 (Supporting Information), the size and porosity of the PCM products increased as activation time of CMs in the KOH solution increased. However, the structure of the carbon microspheres product would collapse if the activation time was too long. The optimum activation time for CMs was set as 2 h (Figure S6, Supporting Information).

The porosity and architecture of the as-made PCMs were verified by nitrogen absorption–desorption isotherms and pore-size distribution analyses, respectively (Figure 2a). The hysteresis loop (Figure 2a) demonstrates that the product possesses the characteristic of the H4-type adsorbent feature (IUPAC definition), generally observed in materials containing both micropores and mesopores.\[41\] The high isotherm in the low-pressure region suggests the presence of high microporosity in the PCMs. The BET surface area was calculated as high as 983.2 m\(^2\) g\(^{-1}\) based on the linear portion of the isotherm, significantly higher than the value of 99.3 m\(^2\) g\(^{-1}\) of original CM precursors. Also, the pore size distribution of the PCMs (inset of Figure 2a) indicates a high portion of micropores with a pore width of \( \approx 1.32 \) nm. Moreover, X-ray diffraction (XRD) and Raman spectra reveal the amorphous, hard carbon nature of the PCMs (Figure 2b,c). The broad (002) peak in the XRD pattern indicates the stacking height of the graphene layers in the PCMs is low, and the diffraction peak at \( 2\theta = 22.85^\circ \) shows that the PCMs have an interlayer spacing of \( \approx 0.393 \) nm, much larger than the d-spacing value of the (002) plane in crystal-line graphite (0.334 nm).\[24\] The Raman spectrum of the PCMs shows a typical nongraphitic carbon characteristic with a more intense D-band (ascribed to \( A_{1g} \) vibration mode of sp\(^2\) carbon rings caused by the defects) than the G-band (ascribed to \( E_{2g} \) vibration mode of sp\(^2\) carbon atoms).\[24,29\] Besides, the porous morphology and amorphous nature of the PCMs were also observed in the TEM and high-resolution TEM (HR-TEM) images (Figure 2d,e) and selected area electron diffraction (SAED, inset of Figure 2e), agreeing with the results of the XRD patterns and Raman spectra, further demonstrating the amorphous nature of PCMs.\[29\]

The energy-dispersive X-ray spectrometry (EDS) mappings were used to characterize the composition of the PCMs (Figure 2f). The results clearly show that C (95.14%), O (3.92%), and S (0.94%) have uniform distribution in the PCMs. XPS analysis of the PCMs was carried out to determine the S/O bonding configurations. As shown in the O 1s spectrum in Figure 2g, an apparent peak at 532.3 eV was observed, corresponding to the C–O bond.\[43\] In the S 2p spectrum, there were two peaks centered at 163.8 and 165.1 eV, attributed to the S 2p\(_{3/2}\) and S 2p\(_{1/2}\) peaks for the C–S–C covalent bond, respectively, which is similar to thiophene-type sulfur (Figure 2h).\[43,44\] The EDS mapping and XPS analysis indicate that the O and S atoms had been successfully doped into the carbon structure of the PCMs from the original PMs after the carbonization-etching process.
The as-prepared S/O codoped PCMs were used as the anode materials for KIBs. We first investigated the K-ion storage behaviors of the PCMs using potassium half cells. As shown in Figure S7a (Supporting Information), the initial potassiation and depotassiation capacities of the PCMs electrode were 358.6 and 221.3 mA h g⁻¹, respectively, and the Coulombic efficiency was determined to be 61.7% at the current density of 50 mA g⁻¹ in the first cycle. The irreversible capacity loss (LCL) in Figure S7a (Supporting Information) in the initial cycle was primarily attributed to the formation of a solid electrolyte interphase (SEI) film on the surface of the PCMs electrode,[27] well agreeing with the cyclic voltammetry (CV) result (Figure S7b, Supporting Information).

Figure 3a shows typical charge/discharge curves of the hard carbon nature for PCMs. A voltage plateau well above the plating potential of K metal is observed, which can help inhibit the formation of potassium metal dendrite. The unconspicuous voltage plateau is observed during charge/discharge process due to the following reasons. In the aspect of electrochemistry, the adsorption/desorption on the electrode surface can lead to the monotonic slope that derives from the homogeneous chemical reaction with potential dependence.[29,45,46] In this work, owing to the large specific surface area, a large number of K ions can adsorb/desorb onto/from the PCMs, resulting in the unconspicuous voltage plateaus. Besides, the K ions with the large size have the sluggish kinetics, which can also cause the unobvious voltage plateaus.[7]

Figure 3b shows the cycle performance and Coulombic efficiency of PCMs at 50 mA g⁻¹ (0.18 C). A large LCL and poor Coulombic efficiency were observed in the first few cycles. Nevertheless, high capacity and much improved Coulombic efficiency were maintained during the subsequent cycles, demonstrating good electrochemical reversibility during the potassiation and depotassiation. Indeed, a high potassiation capacity was sustained at 226.6 mA h g⁻¹ after 100 cycles, and the Coulombic efficiency approached as high as 97%. However, under the same condition, the reversible capacity of the smooth
CMs electrode continuously decreased to ≈25 mA h g\(^{-1}\) after 100 cycles at the same current density (Figure 3a, Supporting Information), demonstrating a poor cycling stability. The PCMs also show the superior rate ability. Reversible capacities of 230, 213, 176, and 158 mA h g\(^{-1}\) were obtained at 50, 200, 500, 1000 mA g\(^{-1}\), respectively. After 80 cycles at various current densities, the capacity of PCMs restored to ≈225 mA h g\(^{-1}\) when the current density goes back to 50 mA g\(^{-1}\) (Figure 3c). Furthermore, the remarkable stability and reversibility of the PCMs were further demonstrated by its cycle performance at different current densities (Figure 3d). In Figure 3d, the capacities of the PCMs electrode remained 201, 173, and 133 mA h g\(^{-1}\) at 0.72 C, 1.8 C, and 3.6 C, respectively, after 200 cycles. By contrast, the capacities of the CMs electrode were only 20, 15, and 10 mA h g\(^{-1}\) at the same rates (Figure 3d; Figure S8b, Supporting Information). The long-term cycle performance of the PCMs at a high current density of 1000 mA g\(^{-1}\) was further evaluated (Figure 3e). Impressively, the electrode was stabilized at a reversible capacity of 108.4 mA h g\(^{-1}\), and this capacity was maintained over more than 2000 cycles, indicating the good stability of the carbon structure and excellent durability of the PCMs electrode. This long-term cycling stability of the PCMs electrode represents one of the best performances of all carbonaceous anode materials used in KIBs.

Figure 3. Electrochemical potassium storage performances for the PCMs anode: a) The 2nd, 3rd, 5th, 10th, 50th, and 100th potassiation and depotassiation profiles of PCMs at 50 mA g\(^{-1}\). b) Potassiation and depotassiation capacity and Coulombic efficiency of PCMs at 50 mA g\(^{-1}\). c) Rate capability of PCMs from 50 to 1000 mA g\(^{-1}\). d) Cycle life and Coulombic efficiency of PCMs measured under different current densities from 200 to 1000 mA g\(^{-1}\). e) Long-term cycle stability and Coulombic efficiency at a high current density of 1000 mA g\(^{-1}\) over 2000 cycles.

To further understand the mechanism during the potassium insertion/desorption, we carried out the ex situ XRD analysis of the PCMs in the original, potassiated, and depotassiated states, respectively (Figure 4a). The results show that the diffraction peak for the (002) plane gradually shifted to a smaller angle during the potassiation process, indicating that interlayer spacing gradually increased, ascribed to the continuously intercalation of K ions into the PCMs electrode. The corresponding peak gradually shifted to a wider angle during depotassiation process, indicating that the carbon interlayer spacing continuously decreased during the process, resulted from the deintercalation of K ions from the PCMs.[7,10,47] It is worth mentioning
that the diffraction peak of the (002) plane appeared to return to its original position when the PCMs electrode was charged to 2.5 V. We believed that this was a clear indication of the reversibility of the potassiation/depotassiation process in the PCMs electrode.\[29\] Besides, we also carried out the high-angle annular dark-field (HAADF) imaging and corresponding EDS mapping (Figure 4b) when the electrode was discharged to 0.01 V. These results reveal that C and K were uniformly distributed in the sample with no phase separation, further confirming the successful intercalation of K ions into the PCMs.

Moreover, the morphologies of the PCMs material after 500, 1000, and 5000 cycles were also examined using SEM (Figure S9, Supporting Information). The spherical shape of the material was well preserved even after 5000 cycles, indicating high structure stability of the PCMs. Since the intensity ratio of D-band and G-band in Raman spectra represents the degree of graphitization for the carbon materials, we carried out ex situ Raman analysis of the PCMs under different states to further elucidate the potassiation and depotassiation process (Figure 4c). During the potassiation process, the ratio of $I_D/I_G$ decreased from 1.04 to 0.90 as the discharge voltage of the cell decreased from the initial state to 0.01 V, indicating a higher degree of graphitization. On the other hand, during the depotassiation process, the value of $I_D/I_G$ increased from 0.90 to 0.97 as the charge voltage increased from 0.01 to 2.5 V, indicating a lower degree of graphitization.\[29\]

The superior K-storage performance of the PCMs anode can be attributed to the hierarchical architecture composed of enormous micro-/mesopores within the microsphere matrixes as well as the defects and the enlarged interlayer distance induced by the S/O codoping. Generally, because of the restricted interlayer spacing of the graphite and the large size of the K ions, it would be difficult for the K ions to squeeze into the interlayer spacing during the potassiation process, leading to a significantly reduced capacity and poor stability.\[10,29\] By contrast, the expanded interlayer spacing of the PCMs could accommodate more K ions and tolerate the variation of interlayer spacing during the K$^+$ charge/discharge process.\[48\] In addition, based on the “adsorption–intercalation” mechanism,\[45,46\] the presence of defects, nanovoids and doped S/O heteroatoms in the PCMs would further facilitate the adsorption of K ions onto the active sites, which contribute to the improved capacity.\[25,34\] It should be noted that rather than intercalating into the carbon layers, the adsorption of K ions on the active sites will not directly result in the expansion of the interlayer spacing, which is beneficial to the stability of carbon structure. The abundant micro- and mesopores of the PCMs would provide not only good access for the electrolyte to the electrode surface, but would also reduce the distance for K ions diffusion.\[35\] The microsized spherical morphology could further provide strong adhesion between the current collector and the PCMs electrode, ensuring the long-term stability of PCMs electrode.\[34\]

To get insight into the relationship between high stability of the PCMs anode and S and O codoping, density functional theory (DFT) calculations are performed. A two-layer S/C codoped carbon structure (Figure 5a) is constructed to investigate the effect of the S and O codoping on the K-adsorption capability at low K contents, where S and O exist in the form of thiophene-type sulfur and C=O bonding, respectively. In order to evaluate the energy change before and after K intercalation, the insertion energy ($E_{in}$) is defined as Equation (1)

$$E_{in} = E_2 - E_1 - \mu_K$$  

(1)
Table 1. K insertion energies (in eV) and volumes (in Å³) of the structures with K adsorbed at S₁, S₂, and S₃, respectively. The values listed in the parentheses are the percentages of volume expansion of K adsorbed structures compared with PCMs.

<table>
<thead>
<tr>
<th>Structure</th>
<th>PCMs</th>
<th>K adsorbed at S₁</th>
<th>K adsorbed at S₂</th>
<th>K adsorbed at S₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Insertion energy</td>
<td>−</td>
<td>1.13</td>
<td>−0.96</td>
<td>−0.05</td>
</tr>
<tr>
<td>Volume</td>
<td>1187</td>
<td>1313 (10.6%)</td>
<td>1273 (7.2%)</td>
<td>1284 (8.2%)</td>
</tr>
</tbody>
</table>

where $E₁$ and $E₂$ are the total energies of the system before and after introducing potassium atoms, respectively, and $μ_K$ is the chemical potential of potassium bulk. A positive $E_{in}$ indicates an endothermic and unstable K insertion reaction while a negative $E_{in}$ suggests an exothermic and stable reaction. Meanwhile, the structural deformation after K insertion is evaluated by volume change,\(^{[49,50]}\) as it is proposed that the degree of volume expansion is directly related to the stability of electrodes.\(^{[51]}\) Here, we consider three K adsorption sites (S₁, S₂, and S₃) to evaluate the effect of S and O codoping towards K adsorption (Figure 5). We calculate the insertion energy and volume change of these K adsorbed structures (Table 1). It is found that K atom insertion into the S₁ site is energetically unfavorable with a large volume expansion, which is consistent with the poor electrochemical performance of the graphite anode.\(^{[52]}\) However, when we introduce K atoms at sites near S or O doping site, just like the cases of S₂ and S₃ site, the insertion energies become negative, which suggests that K atoms are stably adsorbed, and S and O doping are helpful to enhance the K adsorption ability and increase the specific capacity. In addition, we also find that S and O doping could help to alleviate the structural deformation, as the percentages of volume expansions of structures with K adsorbed at S₂ and S₃ site are smaller than that of S₁ site. Therefore, we can conclude that S and O codoping could facilitate the adsorption of K and reduced structural deformation.

Figure 5. Graphical illustrations of the structures of a) PCMs, and K adsorbed at b) S₁, c) S₂, and d) S₃ sites, respectively.

To summarize, we demonstrate the synthesis of a S/O codoped porous hard carbon microspheres (PCMs) material as a novel anode for boosting KIBs in term of capacity, rate ability and cycling stability, through first synthesizing polymer microspheres (PMs) via thermally curing the epoxy monomers/thiol hardeners within a LCs solvent, followed by a carbonization-etching process. The as-made PMs material was found to exhibit amorphous carbon nature and possess an enlarged interlayer spacing (0.393 nm), high BET surface area (983.2 m² g⁻¹) and enormous structural defects, resulted from the hierarchichal porous framework and the codoped S/O heteroatoms. Also, revealed by DFT calculations, these characteristics could not only facilitate the K ions adsorption to PCMs electrode but also reduce its structural deformation during the potassiation/depotassiation. Consequently, the PMs exhibit a high capacity (226.6 mA h g⁻¹ at 50 mA g⁻¹ after 100 cycles) and superior rate capability (158.1 mA h g⁻¹ at 1000 mA g⁻¹). More impressively, it can also maintain a highly reversible storage capacity of above 108.4 mA h g⁻¹ for more than 2000 cycles at 1000 mA g⁻¹, representing one of the best long-term cycling stabilities among all carbonaceous anodes for KIBs.

Experimental Section

Preparation of Polymer Microspheres (PMs): In a typical synthesis of the PMs with 2.5 μm diameter, 1.5 g of dipentaerythritol hexakis(3-mercaptopropionate) (6S) and 1.5 g of diglycidyl 1,2-cyclohexanedicarboxylate (DCD) were introduced into 3.0 g of LCs by vigorous stirring at 70 °C to form a homogenous solution. The LC mixtures used as solvent in this study was made in-house by mixing different liquid-crystalline monomers to reach a desirable compatibility, wide nematic temperature range (−40–85 °C) and suitable viscosity (45.0 mPa s⁻¹). After that, 0.15 g of 4-dimethylaminopyridine (DMAP) as accelerator was quickly added into the above mixtures and stirred at room temperature. Subsequently, the sample was cured in an oven at 80 °C for 2 h. Then, after dipping in cyclohexane (AR) for two weeks to fully extract the LCs solvent and drying in vacuum for 48 h, monodisperse polymer microspheres (PMs) were made.

Preparation of Carbon Microspheres (CMs) and Porous Carbon Microspheres (PCMs): The as-prepared PMs were pyrolyzed under following H₂/Air mixture (with a volume ratio of 1:9) atmosphere at 800 °C for 3 h to obtain the carbon microspheres (CMs). Regards activation, 600 mg CMs powder was dispersed in 30 mL 7 M aqueous KOH solution and stirred for 2 h at a speed of 400 rpm. The excess KOH solution was removed by centrifugation. The mixture was dried at 80 °C for 24 h. The dried CMs/KOH mixture was heated at 800 °C for 1 h under a nitrogen flow. After cooling down in vacuum, the sample was repeatedly washed by deionized water until a pH value of 7 was reached. Then the sample was dried at 80 °C for 24 h, followed by thermal annealing at 800 °C for 2 h under a nitrogen flow, to generate the activated porous carbon microspheres (PCMs). Please note that the carbonization processes were proceeded with a gas flow of 150 sccm and the heating rate was 5 °C min⁻¹.

Computational Methods: All the calculations are conducted by using density functional theory (DFT) implemented in Vienna Ab initio Simulation Package (VASP).\(^{[53]}\) The projector augmented wave
(PAW) method was used with a kinetic energy cutoff of 500 eV. The first Brillouin zone was sampled by a $3 \times 3 \times 4$ k-point grid within the Monkhorst–Pack scheme. The exchange–correlation interactions are treated by Perdew–Burke–Ernzerhof (PBE) functional. To consider the van der Waals forces, a DFT-D2 dispersion-correlation approach was used. The convergence criteria of 10–4 eV for the total energy and 10–2 eV Å$^{-1}$ for atomic forces were used.

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

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Conflict of Interest
The authors declare no conflict of interest.

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