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Selenium@Hollow mesoporous carbon composites for high-rate and long-cycling lithium/sodium-ion batteries

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Abstract

© 2019 Elsevier B.V. Selenium (Se) is a prospective candidate of electrode material for high-energy batteries. However, the low Se loading, volumetric expansion and polyselenide shuttling between cathode and anode are major factors to limit further development. To overcome above issues, the hollow carbon structure with interconnected mesopores is used to confine Se composite via a facile annealing treatment route. The Se/HMCS electrode exhibits excellent performance, including a long cycle life (710 mA h g⁻¹ at the 800th cycle at 0.5 A g⁻¹ for LIBs and 291 mA h g⁻¹ at the 1500th cycle at 0.5 A g⁻¹ for SIBs). When coupled with LiCoO₂ and Na₃V₂(PO₄)₃/C in full cells, this electrode also exhibits superior rate capability (181 Wh kg⁻¹total at 20 W kg⁻¹ for LIBs and 130 Wh kg⁻¹total at 52 W kg⁻¹ for SIBs). The excellent electrochemical performance is attributed to the unique hollow structure of HMCS and a large amount of Se encapsulated within mesoporous, which not only promote electronic/ionic transport but also provide additional buffer space to adjust the volumetric expansion of Se and polyselenide during long cycling. This facile and novelty strategy could be easily extended to other materials with low electronic conductivity for advanced energy storage systems.

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Selenium@Hollow Mesoporous Carbon Composites for High-Rate and Long-Cycling Lithium/Sodium-Ion Batteries

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Abstract

Selenium (Se) is a prospective candidate of electrode material for high-energy batteries. However, the low Se loading, volumetric expansion and polyselenide shuttling between cathode and anode are major factors to limit the further development. To overcome above issues, the hollow carbon structure with interconnected mesopores is used to confine Se composite via a facile annealing treatment route. The Se/HMCS electrode exhibits excellent performance, including a long cycle life (710 mA h g⁻¹ at the 800th cycle at 0.5 A g⁻¹ for LIBs and 291 mA h g⁻¹ at the 1500th cycle at 0.5 A g⁻¹ for SIBs). When coupled with LiCoO₂ and Na₃V₂(PO₄)₃/C in full cells, this electrode also exhibits superior rate capability (181 Wh kg⁻¹_{total} at 20 W kg⁻¹ for LIBs and 130 Wh kg⁻¹_{total} at 52 W kg⁻¹ for SIBs). The excellent electrochemical performance is attributed to the unique hollow structure of HMCS and a large amount of Se encapsulated within mesoporous, which not only promote electronic/ionic transport but also provide additional buffer space to adjust the volumetric expansion of Se and polyselenide during long cycling. This facile and novelty strategy could be easily extended to other materials with low electronic conductivity for advanced energy storage systems.

Keywords Hollow mesoporous sphere structure, Selenium anode, Lithium-ion batteries, Sodium-ion batteries, Full-cell

1.Introduction

The burning of fossil fuels in the world exacerbates the energy crisis and greenhouse effect, which prompt scientists to develop renewable energy sources such as solar energy, wind, and tides [1]. However, the discontinuity and instability originated from the time-space constraints make the application of these renewable energies are critically limited. Therefore, the development of high-efficient and low-cost energy storage and conversion systems plays a core role to integrate these renewable energies into the smart grid. Rechargeable batteries (LIBs/SIBs), as new and efficient energy storage systems, have been successfully used in many fields such as portable electronics and electric vehicles [2-5]. However, the anode materials (graphite) of LIBs cannot meet the high energy density demand of the future devices due to its inherent low theoretical specific capacity (372 mA h g^{-1}) [6-8]. Besides, the limitation of lithium source restricts the LIBs large-scale applications. SIBs as the promising replacement of LIBs in grid scale application has aroused great attention in recent years. However, it is even worse for SIBs because the Na^+ ion is larger than Li^+ ion ($1.02 \text{ \AA}$ vs $0.76 \text{ \AA}$ in radius), which makes Na^+ ion more difficult to intercalate into graphite interlayer (only 31 mA h g^{-1}) [9-11]. Thus, it is crucial to search for novel anode materials having a high specific capacity and long cycling life to improve the batteries system (LIBs/SIBs).

Recently, Se has attracted considerable attention as electrode materials because of the high volumetric capacity ($3253 \text{ mA h cm}^{-3}$) and the high electronic conductivity ($1 \times 10^{-3} \text{ S m}^{-1}$) [12-17]. However, there are yet great challenges exist in Se electrode materials that impede their practical applications. Such challenges mainly involve the

pulverization aroused by the volume variation of Se and polyselenide, which leads to great loss of the active material and rapid deterioration of cycling stability [18, 19]. In order to highlight advantages of Se electrode materials and make it a practical SIBs/LIBs anode material, one of the common and feasible methods is to confine Se and polyselenides into the carbonaceous matrix, which not only increase electrical conductivity, but also accommodate volume change [11, 20-24]. For example, Sen Xin et al. synthesized Se/micropores carbon composite that maintained a capacity of 300 mA h g⁻¹ at a current density of 50 mA g⁻¹ in LIBs [25]. Zeng and co-workers synthesized a flexible and free-standing porous carbon nanofiber/selenium composite electrode, which delivered a reversible capacity of 500 mA h g⁻¹ at a current density of 50 mA g⁻¹ after 80 cycles in SIBs [26]. Among all the porous carbon materials, mesoporous carbon hollow spheres (MCHS) with porous shells, accessible interior space, high surface area, and large pore volume is considered to be the most suitable carbon matrix for hosting the Se to improve the electrochemical performance [22, 23, 25, 26].

Herein, we design and prepare a Se electrode material with hollow mesoporous sphere structure, in which Se is impregnated into the mesoporous carbon sphere (Se/HMCS) with a simple melt-diffusion method. The Se@HCMS electrode delivers superior lithium storage performances in half cell, including an ultralong cycle lifespan (710 mA h g⁻¹ at 0.5 A g⁻¹ after 800th cycles), and superior rate capability (303 mA h g⁻¹ at 3 A g⁻¹). More importantly, by coupling with the commercial LiCoO₂, it also exhibits excellent performances in full cells. Even at a high power density of 20 W kg⁻¹, the

energy density of full-cell could still be kept at 181 Wh kg⁻¹_{total}. Meanwhile, the electrochemical properties of the Se/HMCS were examined comprehensively as anode materials for sodium ion half-cell. It delivers a high specific capacity of 291 mA h g⁻¹ at 0.5 A·g⁻¹ after 1500th cycles. The rate performance is also excellent (263 mA h g⁻¹ at 3 A g⁻¹). When coupled with homemade Na₃V₂(PO₄)₃/C in full cells, it also maintains a reversible capacity of 180 mA h g⁻¹ after 100 cycles at 0.5 A g⁻¹. The superior electrochemical properties are attributed to the unique hollow mesoporous carbon structure and Se encapsulated within mesoporous carbon matrix, improving the conductivity, alleviating the volume change and thus enhancing the cycling stability.

2. Experimental

2.1 Samples Preparation

2.1.1 Hollow Mesoporous Carbon Spheres (HMCS)

Synthesis of SiO₂@SiO₂/RF: Firstly, 3.46 mL Tetraethylorthosilicate (TEOS) was added to the solution of 70 mL ethanol, 10 mL H₂O and 3 mL ammonia (25 wt%) at room temperature with 15 min stirring; Secondly, 0.4 g of resorcinol and 0.56 mL of formaldehyde (37 wt%) were added to the prepared solution under stirring for 24 h at room temperature. The final solution was carefully collected and washed with distilled water and ethanol three times, and dried in a vacuum oven at 60 °C for 12 h.

Synthesis of SiO₂@SiO₂/C: The as-prepared samples were annealed at 700 °C (2 °C min⁻¹) for 5 h in N₂ gas to carbonize the polymer into carbon.

Synthesis of HMCS: The black product after annealing was dispersed into 1 M NaOH to remove the silica template, forming hollow mesoporous carbon spheres.

2.1.2 Selenium@Hollow Mesoporous Carbon Spheres (Se@HMCS) Composite

Se powder (99.99%) and HMCS with a weight ratio of 110:45 were mixed and heated at 160 °C for 12 h followed by 350 °C for 3 h in N₂ atmosphere to obtain Se@HMCS.

2.2 Samples Characterization

General microstructure and morphology of the samples were performed by a scanning electron microscopy (SEM) (JEOL JSM-7100F) and a transmission electron microscope (TEM) (JEOL JEM 1011 and JEOL2100, Japan). X-ray diffraction (Bruker D8 Adv, Germany) was employed to identify the composition and crystal structure of the synthesized samples. XPS measurements were recorded on a Thermo Scientific K-Alpha using an Al K α X-ray source. Thermo-gravimetric analysis (TGA) was used to examine the Se content in the composite (in N₂ atmosphere). Raman spectra were acquired on a NEXUS 670 Raman spectrometer, using excitation at 632 nm at room temperature. N₂ adsorption-desorption isotherms of the prepared composites were measured using an ASAP-2010 surface area analyzer.

2.3 Electrochemical Measurements

The electrode fabricated by Se@HMCS composites, acetylene black and carboxymethyl cellulose (CMC) with a weight ratio of 8:1:1, and using DI water as a solvent. The forming slurries were pasted onto copper foil and then dried under vacuum at 60 °C for 12 h. The loading mass of active materials on the individual electrode was about 1.0 mg cm⁻². Afterwards, CR2032-type coin cell was assembled in an argon-filled glove box. The Li-ion battery electrolyte was 1 M LiPF₆ in ethylene carbonate (EC),

dimethyl carbonate (DMC) and ethyl methyl carbonate (EMC) (v/v/v 1 : 1 : 1). The electrolyte was 1 M NaClO₄ dissolved in a mixture of EC and propylene carbonate (PC) (1:1, by volume ratio) with 5 wt% fluoroethylene carbonate (FEC) solution as the Na-ion battery electrolyte. The cyclic voltammetry (CV) curves were studied by a CHI760E electrochemistry workstation from 3.0 V to 0.01 V (vs. Li/Li⁺ and vs. Na/Na⁺) at a scan rate of 0.1 mV s⁻¹. Galvanostatic measurements were conducted on LAND CT2001A battery test system between 3.0 V to 0.01 V.

For the cathode material as Li-ion half cells, the cathode was used of commercial LiCoO₂, acetylene black, and polyvinylidene fluoride (PVDF) in a weight ratio of 8:1:1 on an aluminum foil. Galvanostatic measurements were conducted on LAND CT2001A battery test system between 4.5 V to 3.2 V. For Li-ion full cells, the anode (Se@HMCS) need not pre-lithium. The capacity ratio of anode (Se@HMCS)/cathode (LiCoO₂) was controlled around 1:1.3. Galvanostatic measurements were conducted on LAND CT2001A battery test system between 4.0 V to 0.8 V.

For the cathode material as Na-ion half cells, the cathode was used of homemade Na₃V₂(PO₄)₃/C, acetylene black, and polyvinylidene fluoride (PVDF) in a weight ratio of 8:1:1 on an aluminum foil. Galvanostatic measurements were conducted on LAND CT2001A battery test system between 3.8 V to 2.5 V. For Na-ion full cells, the anode (Se@HMCS) also need not pre-sodium. The capacity ratio of anode (Se@HMCS)/cathode (Na₃V₂(PO₄)₃/C) was controlled around 1:1.3. Galvanostatic measurements were conducted on LAND CT2001A battery test system between 4.2 V to 1.2 V. The capacity of Se/HCMS calculated based on the mass of Se/HCMS

composite.

3. Results and discussion

Scheme 1. Illustrates the fabrication process of Se@HMCS composites.

The strategy for synthesizing the Se@HMCS is shown in **Scheme 1**. Firstly, tetraethylorthosilicate (TEOS) and resorcinol formaldehyde (RF) oligomers were co-condensed on SiO₂ core particles to form the SiO₂@SiO₂/RF with a uniform average size of ~300 nm core-shell nanospheres (**Figure S1**) (step I, Scheme 1). Secondly, the SiO₂@SiO₂/RF was thermally treated at 700 °C for 5 h in N₂ gas to carbonize the polymer into carbon (**Figure S2**) (step II, Scheme 1), followed by treatment by NaOH to remove SiO₂ template, achieving hollow mesoporous carbon spheres (HMCS) (**Figure S3**) (step III, Scheme 1). Afterwards, Se@HMCS composite was obtained through a facile melt diffusion procedure (step IV, Scheme 1).

Figure 1. (a) Low and (b, c) High resolution SEM images of the Se@HMCS composites. (d) Low and (e, f) High resolution TEM images of the Se@HMCS composites. (g) High resolution TEM image of the Se@HMCS composites. (h-j) Elemental mapping of the Se@HMCS composites.

Figure 1 reveals the microstructures and morphologies of the Se@HMCS composites by SEM and TEM. The SEM images of Se@HMCS composites exhibit similar morphological of HMCS with a diameter of ~ 300 nm and shell thickness of ~ 10 nm (**Figure 1a-c and f**). The hollow structure is disclosed by some broken spheres (**Figure 1b**). This result is supported by the TEM images. As shown in **Figure 1d and e**, the obvious contrast indicates the hollow and porous structure nature of Se@HMCS. The HRTEM lattice diagram (**Figure 1g**) shows that there are no distinct lattice fringes for Se@HCMS composites, indicating the amorphous Se and carbon in the Se@HCMS

composites. The elemental mapping of Se@HCMS composites (**Figure 1h-j**) demonstrates the homogenous distribution of Se in the carbon material without any Se bulk. All the above results indicate that the Se has been impregnated into the mesoporous of HCMS.

Figure 2. (a) XRD patterns of the Se and Se@HCMS. (b) Raman spectrum of the Se and Se@HCMS. XPS spectra of Se@HCMS: (c) C 1s. (d) Se 3d. (e) Nitrogen adsorption-desorption isotherms of HMCS and Se@HMCS composites. (f) corresponding pore size distributions curves of HMCS and Se@HMCS composites.

The composition of the samples was analyzed by the X-ray diffraction (XRD).

Figure 2a displays the highly crystalline of pristine Se. After impregnated into the carbon materials, all the characteristic peaks of Se disappear. The disappearance of Se peaks in XRD patterns indicates there is no bulk crystalline Se in the composite after heat treatment, which may lead to better electrochemical performance [27-29]. The results of the XRD analysis are also consistent with Raman spectra. As shown in **Figure 2b**, the pristine Se shows one peak at 142 cm^{-1} (ring structure of Se) and one peak at

236 cm^{-1} (chain structure of Se) [30]. However, there is no obvious the peaks of Se in the Se@HMCS composites, demonstrating all of the pristine Se powder is diffused into the pores of mesoporous carbon spheres after the heating process [31]. The two distinct peaks at 1345 and 1570 cm^{-1} are ascribed to the disordered carbon (D band) and graphitized carbon (G band), respectively [32]. The intensity ratio of I_D/I_G (about 1.03) reflects low graphitization degree of the carbon [33]. The Se content in the Se@HMCS composites was elevated by the thermogravimetric analysis (TGA) in N_2 flow from room temperature to 800 $^{\circ}\text{C}$ (**Figure S4**). The Se content in the Se@HMCS is 55.7 wt% determined by the TGA curve.

The chemical bonding state of the Se@HMCS composites was further examined by X-ray photoelectron spectroscopy (XPS) measurements. The survey spectrum of Se@HMCS composites shows the presence of the elements C, Se and O (**Figure S5**). The $\text{C}1\text{s}$ spectrum in **Figure 2c** is divided into C-C (284.7 eV), C-O (286.2 eV) and C=O (288.6 eV) peaks [34]. The Se spectrum is fitted into three peaks at 55.4 eV, 56.3 eV and 58.4 eV, corresponding to Se $3\text{d}_{5/2}$, Se $3\text{d}_{3/2}$ and Se-C/Se-O, respectively (**Figure 2d**) [35, 36]. Nitrogen adsorption-desorption tests were used to analyses the specific surface area and pore size distribution of the HMCS and Se@HMCS composites. **Figure 2e** shows the Brunauer-Emmett-Teller (BET) surface area decreases from 690 of the HMCS to 81 $\text{m}^2 \text{g}^{-1}$ of the Se@HMCS, implying a significant reduction in pore-size in the mesoporous region (about 3.9 nm) due to the Se loading in HMCS (**Figure 2f**), which is consistent with the XRD and Raman results.

Figure 3. The Se@HMCS composites as anode materials for LIBs: (a) CV curves at a scan rate of 0.1 mV s^{-1} for the first three cycles. (b) Cycle stability of Se@HMCS composites, HMCS and Se at 0.05 A g^{-1} . (c) Rate performance of Se@HMCS composites, HMCS and Se. (d) b value obtained by plots of $\log(i)$ versus $\log(v)$, calculated from reduction and oxidation states of CV curves. (e) Diagram of the capacitive contribution to the total capacity at different scan rates. (f) CV profile showing the capacitive contribution (the filled part) of the Se@HMCS electrode at a scan rate of 4.0 mV s^{-1} .

The electrochemical performances of the Se@HMCS electrode were evaluated in the voltage window of $0.01\text{-}3.0 \text{ V}$ (vs. Li^+/Li). **Figure 3a** shows the typical cyclic voltammetry (CV) curves of the Se@HMCS electrode in the first three cycles at 0.1 mV s^{-1} . During the initial cathodic process, a board peak of 1.67 V and a weak peak centered at 0.69 V are attributed to the reduction of elemental Se to Li_2Se_n ($n \geq 4$), as well as the formation of solid electrolyte interphase (SEI) layer [30, 37]. Two oxidation peaks at 1.96 V and 2.24 V are observed in the anodic process, which is attributed to the delithiation of Li_2Se . After the first cycle, the cathodic peak at 1.67 V shifts to a

higher voltage of 1.83 V, while the peak at 0.69 V remains at its original position with decreased intensity due to the irreversible formation of SEI layer. The CV peaks almost overlap each other in the subsequent cycles, suggesting the good cycling stability of the Se@HMCS electrode in the lithium half-cell.

Figure S6 displays the 1st, 50th and 100th charge/discharge profiles of the Se@HMCS electrode at a current density of 0.05 A g⁻¹. The discharge profile presents two slope voltage plateaus, demonstrating the two step reactions during the lithiation process, which is agreement with CV examination. Interestingly, the charge and discharge profiles of 50th and 100th cycle basically overlap with each other, and the Se@HMCS electrode can still maintain an excellent reversible capacity of 603.4 mA h g⁻¹ after 100 cycles (Figure 3b), suggesting its outstanding stability and reversibility in the half cell of LIBs.

The rate capability of Se@HMCS was assessed at various current densities. As shown in Figure 3c, the synthesized sample delivered specific capacities of 486, 415, 389, 345 and 303 mA h g⁻¹ at rates of 0.1, 0.5, 1, 2 and 3 A g⁻¹, respectively. Furthermore, its capacity recovers back to the initial value (485 mA h g⁻¹) when the current density returns to 0.1 A g⁻¹. In contrast, the HCMS and Se materials deliver much lower reversible capacity and rate performance than the Se@HMCS electrode due to the low electronic conductivity (Figure 3b, c). Figure S7a reveals the long cycling performance of Se@HMCS electrode at 0.5 A g⁻¹ for 800th cycles. It delivers a reversible capacity of 710 mA h g⁻¹ after 800th cycles which is higher than the initial cycles is due to the electrode activation (Figure S7b) [20]. In the first several cycles,

the irreversible capacity results from some side reactions and the formation of SEI [30, 37]. In addition, the activation of the electrode materials may be another possible reason to the increasing trend. The superior electrochemical performance of Se@HMCS come from its unique structure, which can not only enhance the electron conductivity, but also accommodate the volume expansion [36, 38]. More importantly, the Se@HMCS composites electrode kept its structure after cycling (**Figure S8**). In addition, the long cycling and rate performance of the Se@HMCS electrode are superior to other Se-based electrodes for LIBs (**Figure S9a**).

In order to further understand the excellent cycle stability and high rate capacity of the Se@HMCS electrode as anode for LIBs, the CV curves of the Se@HMCS electrode at different scan rates, from 0.2 to 100 mV s⁻¹, were collected to analyze the kinetic properties (**Figure S9b**). The similar shape of CV curves in the range of 0.2-100 mV s⁻¹ indicates the characteristic of pseudocapacitive behavior [39]. **Figure 3d** shows the *b* values obtained by the slope of the plot of log (*i*) versus log (*v*) according to the following equation [39-41]:

$$i = a v^b \quad (1)$$

(*i*: current density; *v*: sweep rate; *a*, *b*: constants). Previous reports have indicated that the *b* value of 1.0 reflects a surface capacitive contribution (capacitor-type) (*k*₁*v*), while the *b* value of 0.5 is diffusion-controlled contribution (battery-type) (*k*₂*v*^{1/2}). For Se@HMCS electrode as LIBs from 0.2 to 4 mV s⁻¹, the *b* values of the anodic peak 1 and 2 are 0.801 and 0.834. The *b* values of the cathodic peak 3 and 4 are 0.911 and 0.973, respectively, illustrating the high contribution of capacitive behavior. Meanwhile,

the cathodic peak 4 shifts a little (< 0.18 V) (**Figure S9c**), indicating small polarization and fast kinetics [42]. Larger than the scan rate of 4 mV s^{-1} , the b values of the anodic peak 1 and 2 decreases to 0.607 and 0.620, and the b values of the cathodic peak 3 and 4 are 0.623 and 0.746, respectively. The results may be due to the increasing resistance and diffusion constraints **at a high rate**.

The relationship between the normalized capacity and sweep rate distinguishes the charge storage mechanism, could be divided into two regions (**Figure S9d**) [43]. When the sweep rate is less than 4 mV s^{-1} , the normalized capacitance is approximately linear with $v^{-1/2}$, which demonstrates the independence of the capacitance contribution relative to sweep rate. Therefore, the process is attributed to surface capacitive contribution. Interestingly, with increasing of sweep rate above 4 mV s^{-1} , the normalized capacity decreases rapidly, indicating the contribution of diffusion-controlled. The equation:

$$i(V) = k_1 v + k_2 v^{1/2} \quad (2)$$

could clearly and quantitatively distinguish the contributions capacitor-type and battery-type at a fixed voltage. As shown in **Figure 3e**, the capacitive contribution rises with increasing sweep rate. When the sweep rate up to 4 mV s^{-1} , the rate of capacitive contribution can reach 87% of the total capacity (**Figure 3f**). The long cycling stability and high rate capacity are attributed to the pseudocapacitive behavior.

Figure 4. The Se@HMCS composites as anode materials for SIBs: (a) CV curves at a scan rate of 0.1 mV s^{-1} for the first three cycles. (b) Cycle stability of HMCS and Se@HMCS composites at 0.05 A g^{-1} . (c) Rate performance of Se@HMCS composites, HMCS and Se. (d) b value obtained by plots of $\log(i)$ versus $\log(v)$, calculated from reduction and oxidation states of CV curves. (e) Diagram of the capacitive contribution to the total capacity at different scan rates. (f) CV profile showing the capacitive contribution (the filled part) of the Se@HMCS electrode at a scan rate of 4.0 mV s^{-1} .

The sodium half-cell performances of the Se@HMCS electrode are comprehensively evaluated in the voltage window of $0.01\text{--}3.0 \text{ V}$ (vs. Na^+/Na). The CV curves of the initial 3 cycles for the Se@HMCS electrode is shown in **Figure 4a**. In the first cathodic process, the two peaks at 1.55 V and 0.96 V are attributed to the reduction of Se to generate Na_2Se [39]. Another peak at 0.44 V disappears after the first cycle, indicating the formation of solid electrolyte interphase (SEI) film [44, 33]. The two cathodic peaks shift towards a higher voltage (1.2 V and 1.6 V) from the second cycle due to the electrode activity. In the anodic process, the two peaks at 1.62 V and 2.08 V correspond to the conversion reaction of Na_2Se , reversibly producing of elemental Se

[45, 46]. After the first cycle, CV curves exhibit excellent overlapping, suggesting good cycling stability of electrode reactions during the discharge/charge processes [33]. The CV results are well consistent with the discharge/charge profiles at a current density of 0.05 A g^{-1} (**Figure S10**).

The cycling performance of Se@HMCS electrode as anode for half-cell of SIBs was first examined at a current density of 0.05 A g^{-1} (**Figure 4b**). It remained a capacity of about 400 mA h g^{-1} after 100 cycles. The rate performance of Se@HMCS electrode was also studied, and shown in **Figure 4c**. It delivered specific capacities of 370 mA h g^{-1} at 0.1 A g^{-1} , 342 mA h g^{-1} at 0.5 A g^{-1} , 315 mA h g^{-1} at 1.0 A g^{-1} , 289 mA h g^{-1} at 2.0 A g^{-1} , and 280 mA h g^{-1} at 3.0 A g^{-1} . When current density backs to 0.1 A g^{-1} , a capacity of 370 mA h g^{-1} was returned. High reversible capacity of 291 mA h g^{-1} was achieved after 1500 cycles at a high rate of 0.5 A g^{-1} (**Figure S11**). In comparison, Se and HCMS electrodes displayed lower specific capacity and inferior rate capabilities than Se@HMCS electrode (**Figure 4b, c**). Furthermore, the Se@HMCS electrode delivered longer cycling stability and higher rate performance in comparison to others Se-based electrode for SIBs (**Figure S13a**). The high specific capacity, long cycling stability and good rate performance make Se@HMCS composites a promising anode for advanced SIBs. Those results demonstrated that the HMCS played an essential role in improving the electrochemical of Se due to the enhanced electronic conductivity, buffering space to accommodate the volumetric expansion of Se and restriction of polyselenide during long cycling. Importantly, the micromorphology of the Se@HMCS composites electrode could keep its original structure after cycling (**Figure S12**).

For better understanding the outstanding electrochemical performance of Se@HCMS electrode as anode for SIBs, the CV curves at different scan rates (0.2–100 mV s^{-1}) were detected to analyze the kinetic properties (**Figure S13b**) [47]. Through explaining for LIBs, we know that the b value of 1.0 reflects a capacitor-type, while the b value of 0.5 is a battery-type. For Se@HMCS electrode as SIBs from 0.2 to 4 mV s^{-1} , the b values of the anodic peak 1 and 2 are 0.829 and 0.939, and the b values of the cathodic peak 3 and 4 are 0.893 and 0.887 (**Figure 4d**), respectively, indicating the high contribution of capacitor-type [48, 49]. At the same time, slightly moving the cathode peak 4 ($< 0.18\text{V}$) indicates that the polarization is smaller, and the kinetic is faster (**Figure S13c**). Above the scan rate of 4 mV s^{-1} , the b values of the anodic peak 1 and 2 decreases to 0.672 and 0.760, and the b values of the cathodic peak 3 and 4 are 0.698 and 0.633, respectively, which is due to the increased resistance at a high rate.

As shown in **Figure S13d**, it should be noted that there are two different regions in the diagram. For the sweep rates $< 4.0 \text{ mV s}^{-1}$, the normalized capacity is largely independent of the sweep rates, indicating the high contribution of surface capacity. For the sweep rates $> 4.0 \text{ mV s}^{-1}$, the normalized capacity is dependent on the sweep rates, indicating the high contribution of diffusion capacity. The capacitive contribution (the filled part) gradually improves with increasing of sweep rates (**Figure 4e**), and reaches 88% up to 4 mV s^{-1} (**Figure 4f**). The result indicates that the high rate capability is attributed to the suppressed diffusion.

Figure 5. (a) Discharge and charge profiles of the fifth cycle for SIBs. (b) XRD patterns of the Se@HCMS electrode at each stage labeled in (a).

The gradual sodium insertion/extraction of Se during the fifth cycle was examined by ex situ XRD (**Figure 5**). After discharge to 1.46 V in **Figure 5a**, the Se is converted to Na₂Se₂, as the characteristic diffraction peaks of Na₂Se₂ appear at 23.4°, 27.7°, 34.0°, 52.0°, and 57.1° (**Figure 5b**). The peaks of Na₂Se₂ completely disappear when discharge to 0.1 V, and all the peaks correspond to Na₂Se (22.5°, 37.2°, and 58.9°). These results demonstrate that Se first undergoes sodiation into Na₂Se₂, and then to Na₂Se. In the charging process, the XRD patterns show the gradual desodiation of Na₂Se, which first forms Na₂Se₂ and then returns to the original Se. Therefore, the presence of two typical plateaus at 1.6/2.08 V and 1.2/1.62 V correspond to the reaction of $\text{Se} \leftrightarrow \text{Na}_2\text{Se}_2$ and $\text{Na}_2\text{Se}_2 \leftrightarrow \text{Na}_2\text{Se}$, respectively. This is total agreement with our CV results.

Figure 6. Se@HMCS//LiCoO₂ Li-ion full cell: (a) Schematic illustration of the full cell with Se@HMCS anode and LiCoO₂ cathode. (b) Charge/discharge curves at different rates (the capacity is calculated by the mass of anode). (c) Rate performance at different rates (the capacity is calculated by the mass of anode). (d) Ragone plot of this full battery about the power and energy density (they are evaluated by the mass of total). (e) Cycling performance at 0.5 A g⁻¹ anode (the capacity is calculated by the mass of anode and the digital inset “TYUT” image of the light-emitting diode lit by the LIBs full battery).

The excellent electrochemical properties of Se@HMCS electrode urge us to study the performance of lithium ion full-cell. In the full-cell, we selected the Se@HMCS material as anode and the commercial LiCoO₂ as the cathode (**Figure S14** and **Figure 6a**). **Figure S15** showed the excellent cycling and high rate performance of the commercial LiCoO₂, which delivered a high capacity of 180 mA h g⁻¹ at the current density of 0.1 A g⁻¹. **Figure 6b** displayed charge/discharge curves at different rates of Se@HMCS//LiCoO₂ full-cell in the voltage range of 0.8–4.0 V. With the increasing of rates, the voltage platform and reversible capacity decrease slightly, which prove to be a better rate performance for the Li-ion full-cell. The rate performance of the Li-ion full-cell was tested and shown in **Figure 6c**. Se@HMCS//LiCoO₂ full-cell exhibited specific capacities of 470, 308, 245, 194, and 170 mA h g⁻¹ at 0.1, 0.5, 1, 2, and 3 A g⁻¹_{anode}, respectively. More impressive, when the current density backs to 0.1 A g⁻¹, the capacity recovered to 467 mA h g⁻¹, indicating that the structure of Se@HMCS composites material can withstand different current densities. As shown in **Figure 6d**, the energy density of Li-ion full-cell could reach 181 Wh kg⁻¹ at power density of 0.02 kW kg⁻¹_{total}. Moreover, the Li-ion full cell exhibits a reversible capacity of 256 mA h g⁻¹ at the current density of 0.5 A g⁻¹, even after 150 cycles. It is inescapably clear that the digital inset “TYUT” image of the light-emitting diode lit by the LIBs full battery.

Figure 7. Se@HMCS//Na₃V₂(PO₄)₃/C Na-ion full cell: (a) Schematic illustration of the full cell with Se@HMCS anode and Na₃V₂(PO₄)₃/C cathode. (b) Charge/discharge curves at different rates (the capacity is calculated by the mass of anode). (c) Rate performance at different rates (the capacity is calculated by the mass of anode). (d) Ragone plot of this full battery about the power and energy density (they are evaluated by the mass of total). (e) Cycling performance at 0.5 A g⁻¹_{anode} (the capacity is calculated by the mass of anode and the light-emitting diode lit by the SIBs full battery).

The electrochemical performance of Na-ion full-cell was investigated and shown in **Figure 7**, which assembled by Se@HMCS material as anode and the home-made

Na₃V₂(PO₄)₃/C nanocomposite (NVP/C) as the cathode (**Figure S16** and **Figure 7a**) [38]. The NVP/C powder exhibits outstanding cycling stability and high rate capability in the half cell (**Figure S17**). **Figure 7b** show the electrochemical behavior of Se@HMCS//Na₃V₂(PO₄)₃/C full cell measured at different rates in the voltage range of 1.2–4.2 V. **Figure 7c** presented the rate capability measurements of the Na-ion full-cell at various current rates from 0.1 to 3 A g⁻¹. It delivers high average reversible capacity of 251, 208, 167, 127, and 95 mA h g⁻¹ at 0.1, 0.5, 1, 2, and 3 A g⁻¹ anode, respectively. When the current density is back to 0.1 A g⁻¹, the reversible capacities almost recover to their initial values, once again indicating their stable structures during the cycling. At a power density of 52 W kg⁻¹, the energy density is up to 130 Wh kg⁻¹ total (**Figure 7d**). The Na-ion full-cell still maintains a reversible capacity of 180 mA h g⁻¹ after 100 cycles at 0.5 A g⁻¹, with the CE almost approaching 99.9% (**Figure 7e**). It can be evidently seen that the light emitting diode (LED) was emitting light when the Na-ion full cell was turned on.

4. Conclusion

In summary, Se@HCMS were prepared by a simple template process followed by a melt-diffusion method. The electrochemical results demonstrated Se@HCMS composite was an active and durable anode for long cycle life of LIBs/SIBs. The superior electrochemical properties are attributed to the unique hollow mesoporous carbon spheres, improving the conductivity, accommodating volumetric expansion of Se and polyselenide during long cycling. This facile and novelty strategy could be easily extended to other materials with low electronic conductivity for advanced energy

storage systems.

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