

通过温和碱性蚀刻法制备蛋黄-壳/多孔硅氧碳负极材料

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摘 要: 硅氧碳(SiOC)负极材料具有理论比容量高、机械柔性好、结构稳定和价格低等一系列优良性能, 被认为是极具潜力的锂离子电池负极材料之一。本工作通过溶胶-凝胶法, 精确控制前驱体添加的顺序和时间, 合成了一种具有独特蛋黄-壳结构且内核多孔的 SiOC 材料, 在低能耗且温和的反应条件下使硅和碳在微观上均匀有效结合分布, 该结构促进电极高倍率与长寿命的统一。所用原料为 1,4-双(三乙氧基硅基)苯和四乙氧基硅烷的混合物, 并在温和碱性条件下进行蚀刻处理。采用扫描电子显微镜、透射电子显微镜和 X 射线衍射等多种表征技术, 细致地表征了材料的微观结构, 阐明了温和碱性蚀刻如何影响材料形貌和孔结构的机理。蛋黄-壳(YS@C)和多孔(P@C)SiOC 负极材料的比表面积分别为 $17.041 \text{ m}^2 \cdot \text{g}^{-1}$ 和 $27.458 \text{ m}^2 \cdot \text{g}^{-1}$ 。在 $0.5 \text{ A} \cdot \text{g}^{-1}$ 的电流密度下, YS@C 和 P@C 可稳定循环 550 次, 比容量分别为 $453 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$ 和 $384 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$ 。即使在 $1 \text{ A} \cdot \text{g}^{-1}$ 的高电流密度下, YS@C 仍能稳定循环 1000 次, 比容量达 $354 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$ 。总体而言, 本工作提供了一种高效温和的新方法来制备高性能蛋黄-壳/多孔结构材料, 为解决硅基负极膨胀核心痛点, 有效抑制电极粉化与固体电解质界面膜破裂提供了新思路新方法, 并有利于商业化生产。

关键词: 温和蚀刻法; 硅氧碳基负极; 高能量密度电池; 碳包覆; 溶胶-凝胶法

中图分类号: TM912.9 文献标志码: A 文章编号: 0454-5648(2026)07-2470-11

网络出版时间: 2026-04-28



1 Introduction

In recent years, silicon oxycarbide (SiOC) anodes have attracted widespread attention owing to their high cycling stability, suitable potential platform, low cost, and environmental friendliness. In addition, SiOC materials exhibit better cycling performance than silicon-based anodes because of the uniform distribution of silicon and carbon in these materials and the formation of Li_2O and silicates during initial lithiation^[1-2]. These compounds function as protective and buffering layers, reducing the volume expansion of silicon. Therefore, the cycling performance of SiOC materials is superior to that of silicon-based materials. Despite these advantages, SiOC anodes still suffer from low intrinsic electronic conductivity, low ionic conductivity, and large volume expansion, which has led to a series of problems, such as electrode material comminution, loss of electrical contact with the collector, and excessive growth of the solid-electrolyte interphase (SEI)^[3-5]. These issues seriously hinder the commercialization of SiOC-based anodes.

In the past few decades, researchers have proposed

various methods for addressing the issues related to SiOC-based anodes. Common modification strategies include nanostructure design, compositing with carbon-based materials, and surface or interface modification^[6]. In particular, carbon modification is an efficient method for solving the aforementioned issues because it can substantially improve the conductivity, optimize the electrochemical kinetics, and partially alleviate the volume expansion of SiOC. Notably, SiOC repeatedly expands during long-term cycling, ultimately leading to its fragmentation and pulverization. Nanostructured design can reduce the size of active material particles or reserve a certain amount of void space for them, thereby alleviating the volume expansion and contraction of SiOC during lithiation and embrittlement^[7-9]. Unfortunately, nanostructured active materials typically have a large specific surface area, leading to extensive contact between the active material and electrolyte, resulting in SEI overgrowth and a decrease in the initial Coulombic efficiency. Surface modification that results in the formation of a core-shell or yolk-shell structure can effectively reduce the interfacial contact between the electrode and electrolyte,

收稿日期: 2025-07-18。 修订日期: 2026-03-28。

基金项目: 国家自然科学基金(92163121)。

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Received date: 2025-07-18. Revised date: 2026-03-28.

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thereby minimizing side reactions^[10–13]. Therefore, surface modification is also a considerably useful means of stabilizing SEI. In summary, designing a reasonable gradient structure for SiOC materials and combining various modification strategies are considerably promising in terms of improving battery performance but face substantial challenges.

Herein, different organic–inorganic hybrid silicon dioxide (SiO₂) spheres were synthesized through the sol–gel method. The hybrid SiO₂ spheres were selectively etched with a weak alkaline solution to obtain SiO₂ spheres with egg yolk–shell and porous structures. Finally, a carbon coating was applied to these structures to obtain SiOC anode materials with an egg yolk–shell gradient structure (YS@C) and a porous structure (P@C). At the atomic scale, silicon and carbon were found to be uniformly distributed within the core of the prepared materials, considerably enhancing their conductivity. The intermediate void layer effectively mitigated the volume expansion of the materials during lithiation. The shell comprised SiO₂ and conductive carbon, which not only improved the conductivity of the materials but also reduced the interfacial contact between the active material and the electrolyte, thereby minimizing side reactions.

2 Experimental

2.1 Synthesis of egg yolk–shell-structured YS@C

To a 200 mL three-necked flask, 70 mL of deionized water, 30 mL of anhydrous ethanol, and 200 mg of cetyltrimethylammonium bromide (CTAB) were added, followed by stirring at 35 °C for 10 min and the addition of 1 mL of ammonia water (25%, in mass fraction). After 1 h of reaction, 0.25 mL of 1,4-bis (triethoxysilyl) benzene (BTEB) was dropped into the mixture and the reaction was continued for 12 h. The reacted solution was centrifuged, and the precipitate was dried and mixed with 30 mL of anhydrous ethanol, 70 mL of deionized water, and 200 mg of CTAB. After stirring for 10 min, 1 mL of ammonia water (25%, in mass fraction) was added, the mixture was further stirred for 1 h, and 0.25 mL of tetraethoxysilane (TEOS) was added. After an additional 12 h of reaction, the mixture was centrifuged, and the obtained precipitate was dried to obtain the core–shell structure. The obtained product was added to 30 mL of a 2.4 mol/L Na₂CO₃ solution and stirred for 3 h, after which the mixture was centrifuged and the precipitate was dried to obtain SiOC particles with an egg yolk–shell structure (YS-PMOs). YS-PMOs (1.5 g) were mixed with 280 mL of deionized water, 120 mL of anhydrous ethanol, and 800 mg of CTAB and allowed to react for 10 min. Subsequently, 4 mL of 25% ammonia water was added and the reaction was allowed to proceed for another 30 min. Thereafter, 700 mg of resorcinol was added and the reaction was continued for another

30 min. Then, 1 mL of formaldehyde was added and the reaction was allowed to proceed for 24 h. After this, the mixture was centrifuged and the obtained precipitate was dried. Finally, the obtained solid was calcined at 800 °C for 3 h in a mixed H₂/Ar₂ atmosphere, yielding YS@C.

2.2 Synthesis of porous P@C

To a 200 mL flask, 200 mg of CTAB, 70 mL of deionized water, and 30 mL of anhydrous ethanol were added and stirred at 35 °C for 10 min. Subsequently, 1 mL of ammonia water (25%) was added and the reaction was allowed to proceed for 1 h. Thereafter, 0.25 mL of TEOS and 0.25 mL of BTEB were added and the reaction was continued for an additional 12 h. After the reaction, the mixture was centrifuged and the precipitate was dried. The obtained product was etched with 30 mL of Na₂CO₃ (2.4 mol/L) for 3 h, the mixture was centrifuged, and the precipitate was dried, yielding a porous product, referred to as P-PMOs. P-PMOs (1.5 g) were mixed with 280 mL of deionized water, 120 mL of anhydrous ethanol, and 800 mg of CTAB and allowed to react for 10 min. Then, 4 mL of ammonia water (25%) was added and the reaction was continued for an additional 30 min. Thereafter, 700 mg of resorcinol was added and the reaction was allowed to proceed for another 30 min. Subsequently, 1 mL of formaldehyde was added, the reaction was continued for an additional 24 h, the mixture was centrifuged, and the obtained precipitate was dried. The product was calcined at 800 °C for 3 h in a 10% H₂/Ar₂ atmosphere, yielding black P@C.

2.3 Characterization and electrochemical testing of materials

The surface microstructure of the prepared materials was characterized *via* field-emission scanning electron microscopy (FE-SEM; MAIA3LM). The morphology of the samples was analyzed *via* transmission electron microscopy (TEM; Talos F200s, Thermo Fisher Scientific). Energy dispersive X-ray spectroscopy was performed using a spectrometer attached to the SEM instrument. Powder X-ray diffraction was performed in the 10°–80° range using a Bruker D8 ADVANCE instrument equipped with a CuK_α radiation source ($\lambda = 0.154\ 18\ \text{nm}$). The surface condition of the samples was examined using an Autosorb-iQ nitrogen adsorption–desorption instrument, and the specific surface area was determined using the Brunauer–Emmett–Teller method.

To prepare electrodes for electrochemical tests, the prepared active material, conductive carbon black (conductive agent), and carboxymethyl cellulose sodium (binder) were mixed in a mass ratio of 7.0:1.5:1.5 in an agate mortar for 30 min. Then, a small amount of deionized water was added, followed by grinding in a planetary shaker. Depending on the viscosity of the mixture, deionized water was added as

appropriate. After grinding, the mixture was coated on the surface of Cu foil and vacuum-dried at 80 °C for 12 h. The obtained foil samples were cut into 10 mm disks and pressed under 15–20 MPa, yielding the working electrodes. In the test cells, the diaphragm was made of Celgard2300, and the electrolyte was 1 mol/L $\text{LiPF}_6/(\text{EC} + \text{DMC} + \text{EMC})$ (volume ratio of 1:1:1). The assembled battery cells were sealed with a sealing machine and left to stand for 7–8 h. Battery performance tests were conducted using the Shenzhen Neware Battery Testing System, and constant-current charge and discharge tests were conducted in the voltage range of 0.01–5.00 V. Cyclic voltammetry (CV) and alternating current (AC) impedance testing were performed on an electrochemical workstation (CHI660, Shanghai Chenhua).

3 Results and discussion

The SEM and TEM images revealed the morphology and particle size of $\text{YS}@C$ and $\text{P}@C$. After etching with sodium carbonate, YS-PMOs transform into monodisperse particles (Fig. 1a), with sizes mainly

distributed in the range of 250–270 nm. Broken particles can be found in the SEM image in Fig. 1b, proving the existence of cavities. TEM images (Fig. 1d–Fig. 1f) show that the interior near the outer shell was gradually etched and that the gaps expanded to form an eggshell structure. The surface of the “yolk” is rough and located at the center of the particles. The $\text{YS}@PMOs$ monodisperse particles were coated with phenolic resin (RF), with the RF-converted carbon uniformly covering the surface of $\text{YS}@PMOs$ after calcination (Fig. 1c).

When BTEB and TEOS were added as mixed silica sources, only a portion of inorganic silica was etched away during the same sodium carbonate etching process. The particle size of the hybrid P-PMOs obtained after etching is mainly distributed in the range of 280–300 nm (Fig. 2a), slightly larger than the particle size of YS-PMOs . P-PMOs appear as monodisperse particles with uniform size, crosslinked surface structure, and uniformly distributed internal pores. After coating with RF and calcination, the particle size of prepared $\text{P}@C$ increased to 320–350 nm (Fig. 2c and Fig. 2f).

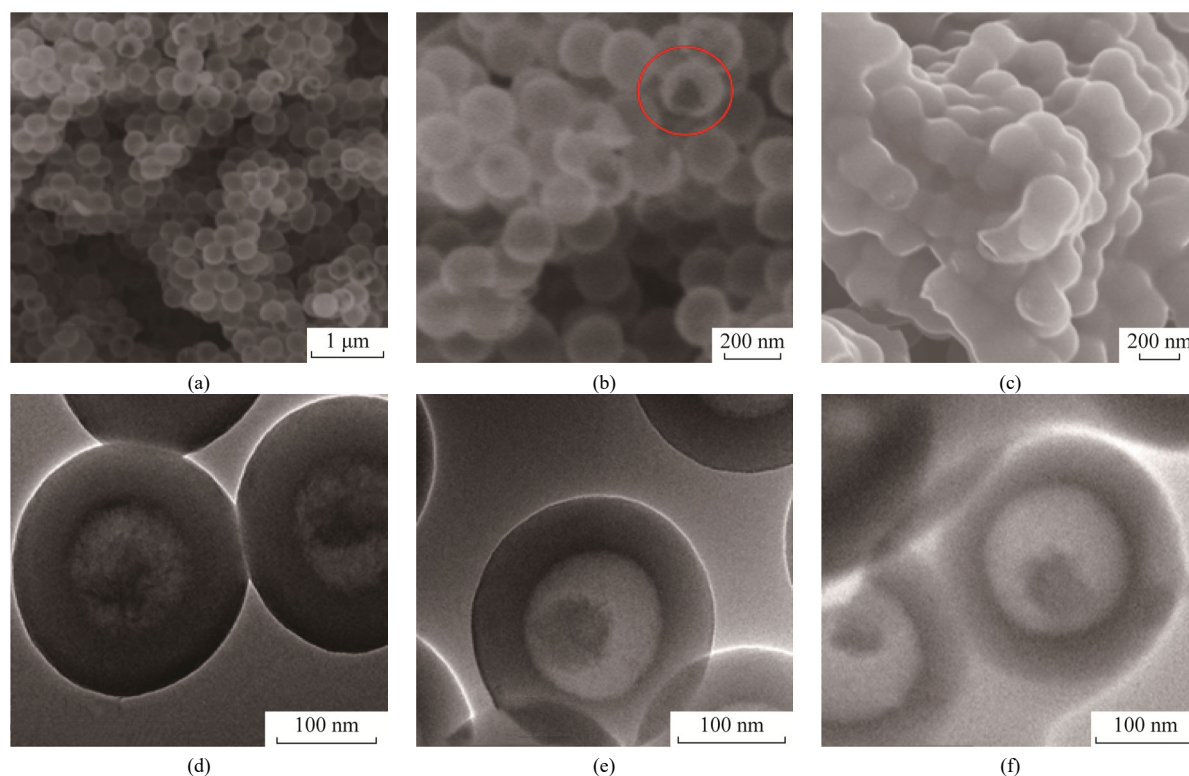


Fig. 1 (a, b) SEM and (d, e) TEM images of YS-PMOs ; (c) SEM and (f) TEM images of $\text{YS}@C$

$\text{P}@C$ and its intermediates are amorphous (Fig. 3). As shown in Fig. 3a, all samples exhibit amorphous diffraction peaks. A large broad peak at 20°–30° is the 002 peak of carbon, whereas a weak broad peak at 40°–45° is the 100 peak of carbon. $\text{P}@C$ shows two Raman peaks at 1340 cm^{-1} and 1600 cm^{-1} , assigned to amorphous carbon (Fig. 3b). The peaks in the D- and G-

band peaks can be used to characterize the degree of graphitization of carbon materials. Calculations show that the graphitization degrees (I_D/I_G) of $\text{YS}@C$ and $\text{P}@C$ are 0.93 and 0.97, respectively. These values may be attributed to the carbon in $\text{P}@C$ originating from BTEB and TEOS, with the contribution from BTEB arising from its phenyl groups. Carbon atoms on the

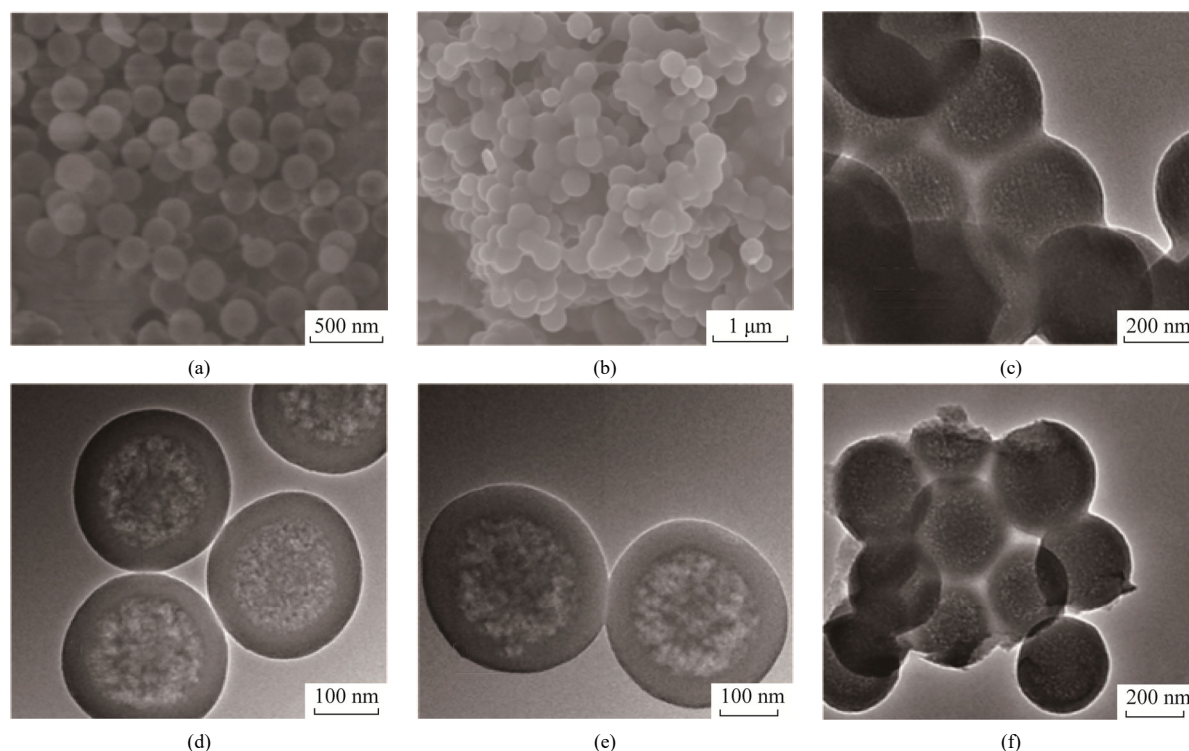


Fig. 2 (a, b) SEM and (d, e) TEM images of P-PMO; (c) SEM and (f) TEM images of P@C

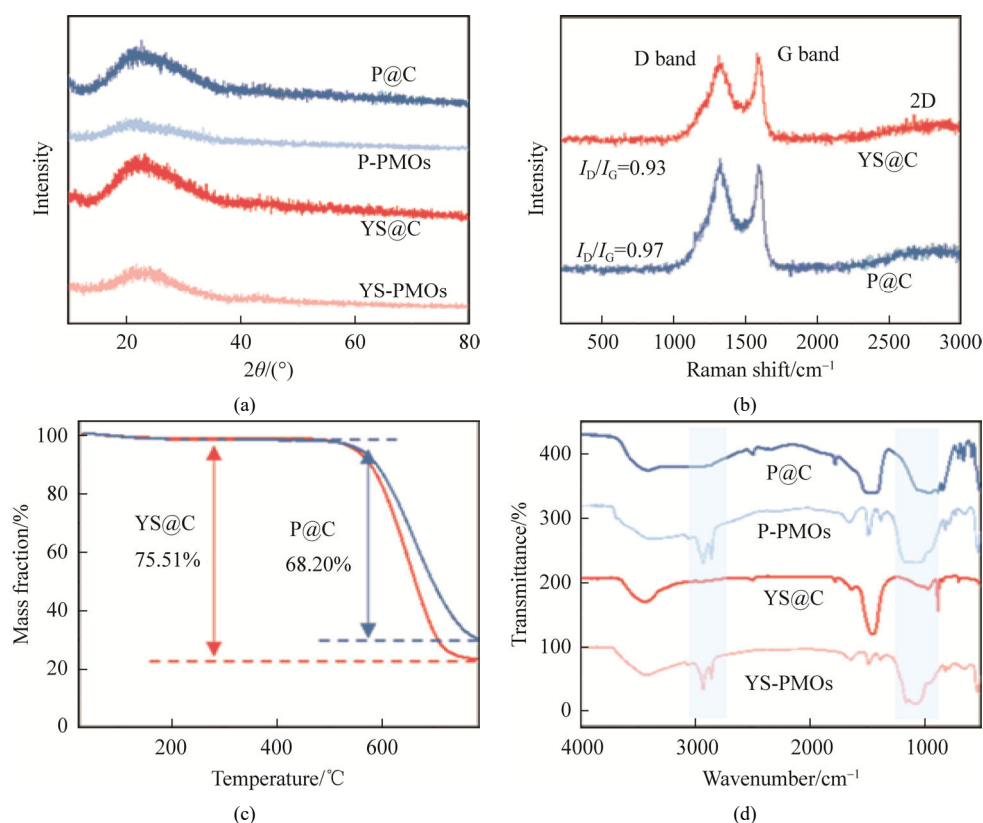


Fig. 3 (a) X-ray diffraction patterns, (b) Raman spectra, (c) thermogravimetric curves, and (d) infrared spectra of YS@C and P@C

phenyl group exhibit sp^2 hybridization, which is conducive to the formation of graphite during carbonization. At the same time, SiO_2 produced *via* the hydrolysis of TEOS is lost during etching, increasing the degree of graphitization. The carbon contents of

YS@C and P@C were measured *via* thermogravimetric analysis (Fig. 3c). The carbon contents of YS@C and P@C are 75.51% and 68.2%, respectively. Carbon in P@C originates from two sources: the outermost coating of RF and siloxane (styrene). The higher carbon

content of YS@C may be attributed to the lower proportion of SiO₂ compared with P@C. Fourier transform infrared spectroscopy revealed (Fig. 3d) that the characteristic peaks of organic matter observed in PMOs (3000 cm⁻¹ and 1000 cm⁻¹) are absent in YS@C and P@C, indicating the removal of hydrogen from organic functional groups during high-temperature carbonization.

Furthermore, we conducted nitrogen adsorption–desorption tests to investigate the surface conditions of YS@C and P@C (Fig. 4a). Both materials exhibit type-IV isotherms, with H4-type hysteresis loops,

suggesting the presence of irregular slit-shaped mesopores and macropores. The specific surface areas of YS@C and P@C are 17.041 m²·g⁻¹ and 27.458 m²·g⁻¹, respectively. The analysis of mesopores using the Barret–Joyner–Halenda model (Fig. 4b) showed that the average pore sizes of YS@C and P@C are 2.371 nm and 2.561 nm, respectively. The pore size distribution of YS@C is denser in the range of 2–4 nm.

X-ray photoelectron spectroscopy (XPS) was conducted to analyze the elemental composition and chemical state of YS@C and P@C. The measured spectra in Fig. 5a indicate that these two samples

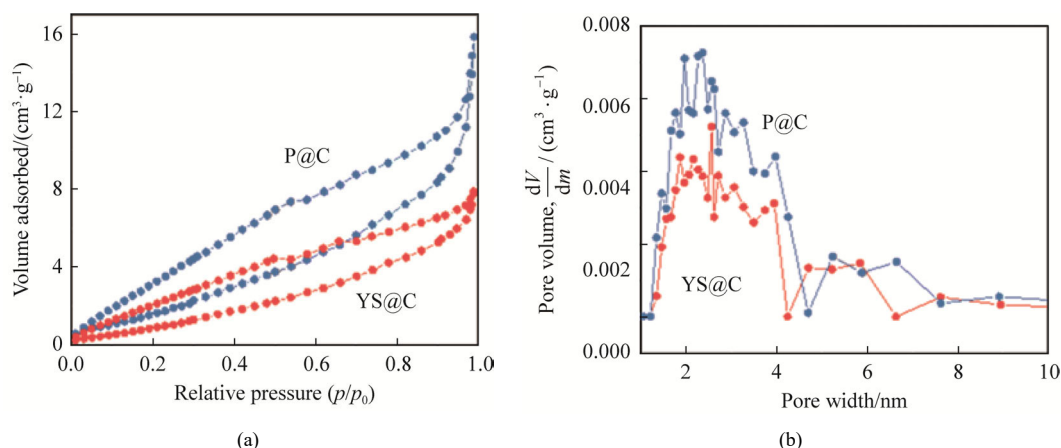


Fig. 4 (a) N₂ adsorption–desorption curves and (b) pore size distributions for YS@C and P@C

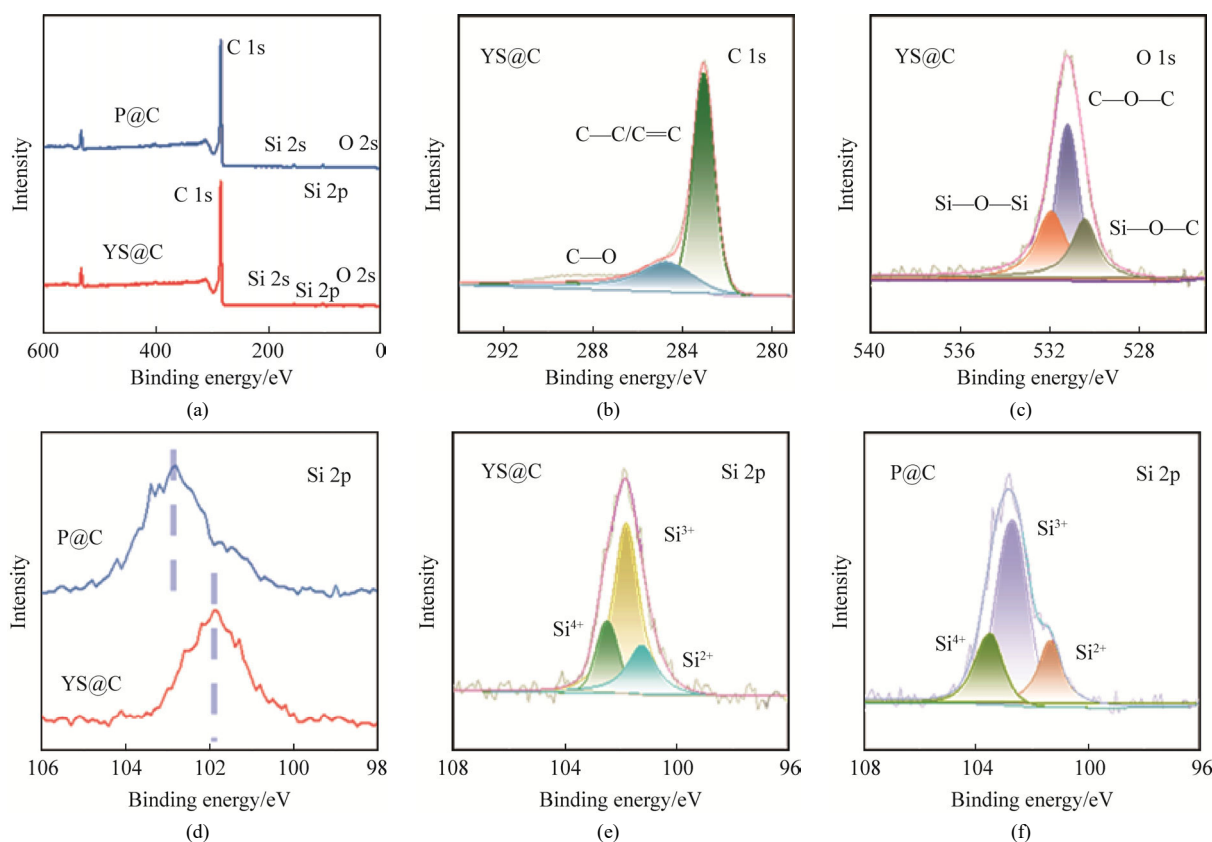


Fig. 5 (a) XPS spectra of YS@C and P@C, (b) C 1s and (c) O 1s high-resolution XPS spectra of YS@C, (d) Si 2p spectra of YS@C and P@C, and Si 2p high-resolution XPS spectra of (e) YS@C and (f) P@C

primarily comprise carbon, oxygen, and silicon. The high-resolution C 1s spectrum in Fig. 5b shows two deconvoluted peaks at approximately 283 eV and 284 eV, corresponding to the C=C/C—C and C—O bonds. The O 1s spectrum in Fig. 5c exhibits three deconvoluted peaks at 533.6, 532.5 eV, and 531.4 eV, attributed to O from Si—O—Si, C—O—C, and Si—O—C bonds, respectively. The comparison of Si 2p spectra between YS@C and P@C is shown in Fig. 5d. The lower binding energy of the Si 2p peak in YS@C indicates a lower average valence state of silicon. Most of the inorganic SiO₂ in YS-PMOs is etched away by sodium carbonate, and the generated silicon mainly originates from polysiloxane (R—SiO_{1.5}). In contrast, only a small portion of SiO₂ is etched in P-PMOs, resulting in a slightly higher average valence state of silicon. The further fitting of the Si 2p peak is shown in Fig. 5e. According to literature, the three deconvoluted peaks at 103.4, 102.3 eV, and 101.4 eV correspond to Si⁴⁺, Si³⁺, and Si²⁺. Based on the areas of these peaks, the percentage contents of Si⁴⁺, Si³⁺, and Si²⁺ are 31.69%, 36.93%, and 31.38%, respectively. The average valence state of silicon in YS@C is 2.796 9. Based on the fitting results of the Si 2p peak (Fig. 5f), the content of silicon in different valence states in P@C was calculated (Table 1). The average valence state of silicon in P@C is 2.999 2.

Furthermore, YS@C and P@C were assembled into half-cells to study their electrochemical properties. Initially, the lithiation of P@C was examined (Fig. 6). The reduction peak at approximately 1.5 V during the first lithiation was attributed to the irreversible reaction between SiO_x and Li, resulting in the formation of Li₂O,

lithium silicate, and crystalline silicon. Subsequently, the generated crystalline silicon underwent an alloying reaction with Li at around 0.1 V, forming the Li_xSi alloy. The peak observed at approximately 0.5 V corresponds to the decomposition of the electrolyte and the formation of an SEI film. After the first cycle, crystalline silicon transformed into amorphous silicon. Consequently, in the second cycle, the newly observed reduction peak at around 0.38 V indicates the lithiation of amorphous silicon. Furthermore, CV curves from the 2nd to the 4th cycles show good overlap, suggesting the good reversibility and stability of the electrode. In contrast, the peaks of P@C at 1.5 V and 0.6 V are smoother, indicating a milder and less intense electrolyte reduction and SEI formation. This difference may be attributed to the medium-to-high carbon content of YS@C, which can catalyze electrolyte decomposition and accelerate side reactions, thus making the peak at 0.5 V in the CV curve more pronounced.

Fig. 7 shows the behavior of the YS@C and P@C electrodes during the first five cycles of constant-current charge/discharge at 0.1 A·g⁻¹. The initial charge and discharge specific capacities of YS@C are 587.61 mA·h·g⁻¹ and 1054.39 mA·h·g⁻¹, respectively, corresponding to an initial Coulombic efficiency of 55%. P@C exhibits lower initial Coulombic efficiency (only 49%) because of its larger specific surface area, resulting in more side reactions.

Fig. 8a shows a comparison of the rate performance of YS@C and P@C at different current densities. The specific capacity of YS@C is higher than that of P@C at 0.1, 0.2, 0.5, 1.0 C, and 2.0 C, with values of 659, 582, 471, 392 mA·h·g⁻¹, and 289 mA·h·g⁻¹,

Table 1 Relative contents of Si²⁺, Si³⁺, and Si⁴⁺ obtained by fitting the Si 2p XPS peaks to calculate the average valence states of Si ions

Sample	Relative content of the Si component			Average valence state of Si
	Si ²⁺	Si ³⁺	Si ⁴⁺	
YS@C	0.316 9	0.369 3	0.313 8	2.796 9
P@C	0.316 1	0.368 6	0.315 3	2.999 2

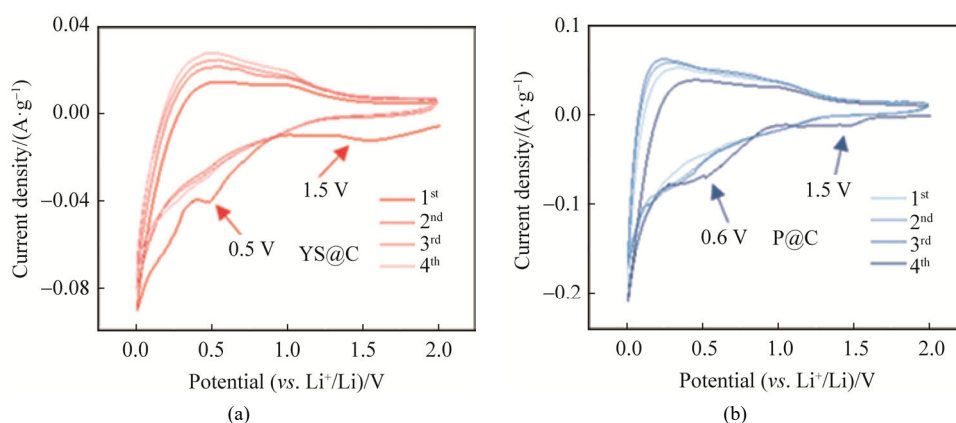


Fig. 6 CV curves in the first four cycles for the (a) YS@C and (b) P@C electrodes

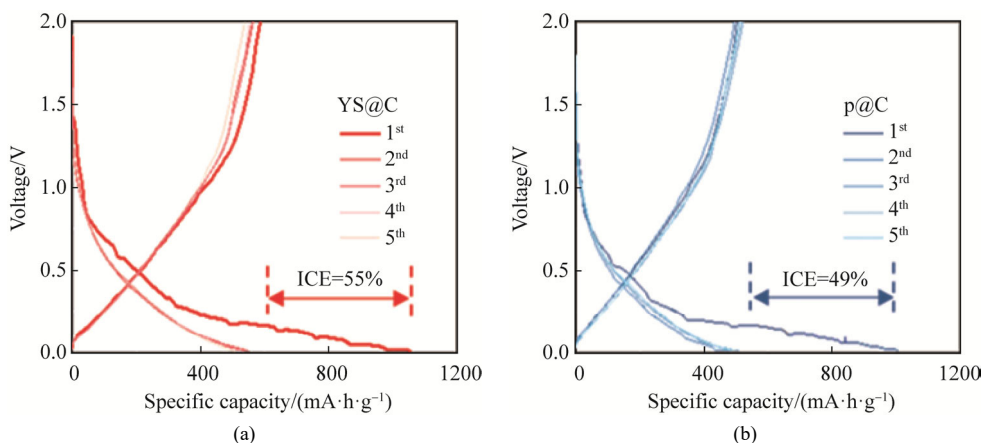


Fig. 7 Constant-current charge/discharge curves in the first five cycles for the (a) YS@C and (b) P@C electrodes at $0.1 \text{ A} \cdot \text{g}^{-1}$

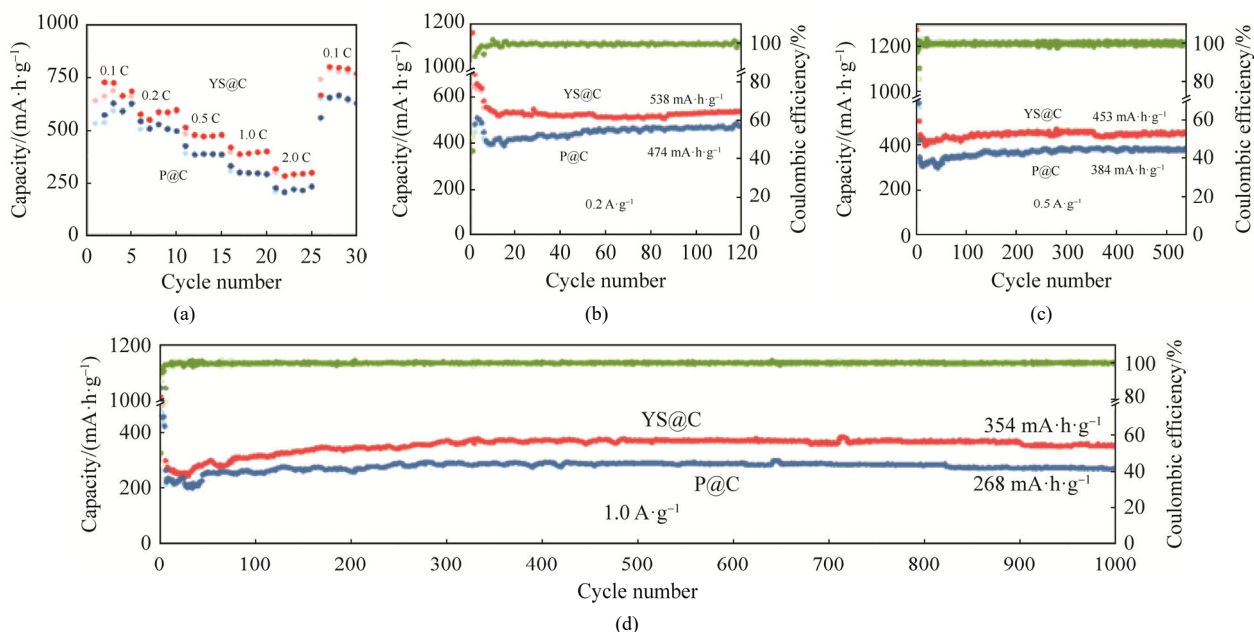


Fig. 8 (a) Rate performance and (b, c, d) cycling performance of the YS@C and P@C electrodes

respectively. After five charge–discharge cycles at current densities of 0.1, 0.2, 0.5, 1.0 C, and 2.0 C, the specific capacity of YS@C at $0.1 \text{ A} \cdot \text{g}^{-1}$ is higher than that in the initial cycle at the same current density. This is because YS@C reacts with Li^+ mainly on its outer carbon layer at the beginning of the cycle, resulting in capacity reduction. Moreover, after cycling, the active substances in the inner layer begin to participate in the reaction, leading to a slight increase in capacity. The data from subsequent long cycling confirm that the specific capacity increases after a certain number of cycles. Fig. 8b presents a comparison of the cyclic performance of YS@C and P@C at a current density of $0.2 \text{ A} \cdot \text{g}^{-1}$. After 120 cycles, the discharge specific capacity of YS@C is as high as $538 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$, whereas that of P@C is only $474 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$, which is approximately $64 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$ lower than that of YS@C. At a current density of $0.5 \text{ A} \cdot \text{g}^{-1}$ (Fig. 8c), both materials can still stably cycle 550 times, showing

specific capacities of $453 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$ and $384 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$, respectively. More importantly, YS@C exhibits ultrastable long-term cycling stability under fast charging and discharging conditions. Next, the samples were activated five times at a current density of $0.1 \text{ A} \cdot \text{g}^{-1}$ and then cycled at a high current density of $1.0 \text{ A} \cdot \text{g}^{-1}$. Even after 1000 cycles (Fig. 8d), YS@C still maintains a high specific capacity of $354 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$. Starting from the 6th cycle, the Coulombic efficiency of YS@C consistently remains above 99%. The excellent electrochemical performance of YS@C can be attributed to the following factors: 1) YS@C has a high content of YS-PMO-derived siloxanes ($\text{SiO}_{1.5}$) and a low content of inorganic SiO_2 , resulting in a high specific capacity; 2) the void space in the yolk–shell structure effectively alleviates the volume expansion of SiOC during charge and discharge, improving the cycling stability of the electrode; 3) the shell composed of SiO_x and amorphous carbon reduces the contact

between the active material and the electrolyte, thereby minimizing side reactions; 4) amorphous carbon in the shell improves the overall conductivity of the active material, and the rigid SiO_x layer enhances the overall mechanical strength of the material, thereby improving the structural stability of the electrode material. In short, the unique gradient composition and structure, from the core to the shell, endow YS@C with excellent electrochemical performance.

The relationship between diffusion and charge transfer in the two electrode materials was investigated using the electrostatic intermittent titration technique (GITT; Fig. 9). As shown in Fig. 9c, the Li^+ diffusion coefficient of the YS@C anode is slightly higher than that of the P@C anode. This is attributed to the unique multilevel structure of YS@C, which can accelerate the

migration of Li^+ and enhance conductivity, indicating the faster transport capability of YS@C.

The CV curves of the two electrodes were measured at different scanning rates and analyzed. The lithium-ion kinetics are shown in Fig. 10a–Fig. 10d. As shown in Fig. 10c, the contribution of the pseudocapacitance-controlled lithium storage gradually increases with scanning rate. At a scanning rate of $2.0 \text{ mV}\cdot\text{s}^{-1}$, the contribution of pseudocapacitance reaches 82.2%. At high scanning rates, the pseudocapacitive control mechanism enables the rapid insertion of lithium ions. The pronounced pseudocapacitive properties of YS@C are closely related to its yolk-shell structure. The presence of gaps in YS@C shortens the diffusion distance of Li^+ , allowing Li^+ to quickly embed or deintercalate between

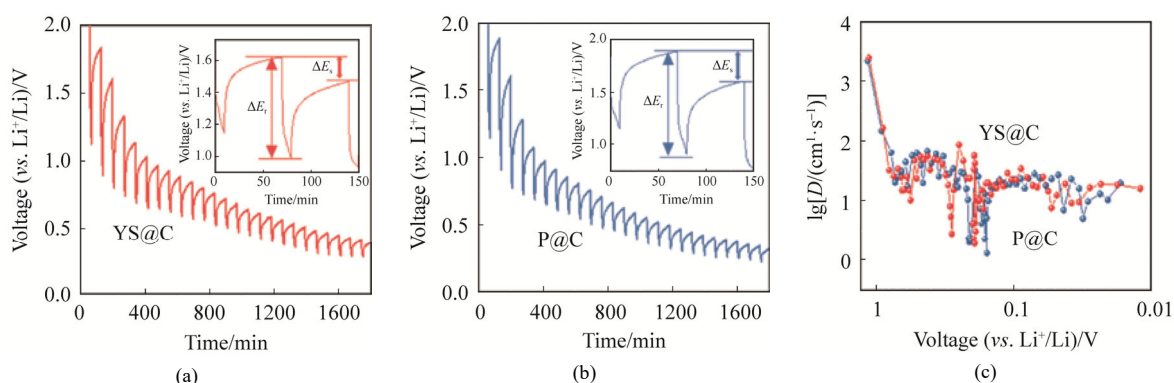


Fig. 9 GITT curves for (a) YS@C and (b) P@C, and (c) Li^+ diffusion coefficients calculated based on GITT data

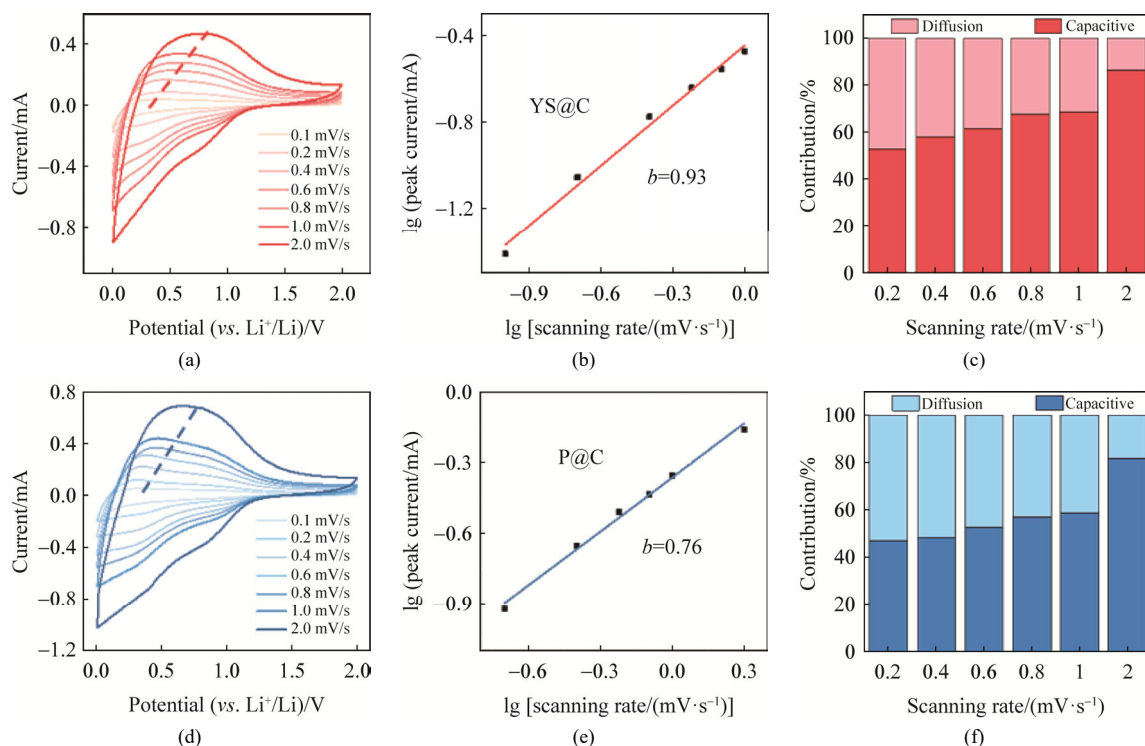


Fig. 10 CV curves for the (a) YS@C and (d) P@C anodes at scanning rates of $0.1\text{--}2.0 \text{ mV}\cdot\text{s}^{-1}$ and (b, e) corresponding linear relationships between the peak current and scanning rate. (c, f) Summary of nondiffusion-limited current contributions at different scan rates

the shell and nucleus. Moreover, the pseudocapacitive contribution rate for P@C at different scanning rates is generally lower than that for YS@C (Fig. 10f). The pseudocapacitive contribution rate for P@C is relatively low mainly because of its limited internal void space, which increases the bulk diffusion distance of Li^+ .

The results of electrochemical impedance spectroscopy also indicate the better electrochemical performance of YS@C (Fig. 11). As electrodes are activated through charging and discharging, the semicircle radius of P@C decreases with increasing number of cycles. At any stage of the cycle, the radii of the semicircles for YS@C are smaller than those for

P@C, indicating the lower interfacial impedance and higher conductivity of YS@C.

To compare the integrity of the YS@C electrode before and after cycling with that of the P@C electrode, SEM was used to examine the morphological changes in the electrodes after 300 cycles. Both electrodes exhibit a smooth morphology prior to cycling (Fig. 12a and Fig. 12b). However, after 300 cycles, the P@C electrode shows structural degradation and visible cracks (Fig. 12c). In contrast, the YS@C electrode (Fig. 12d), with its unique yolk-shell structure, preserves its structural integrity after cycling because of accommodating the volume expansion of SiO_x within the intermediate void space.

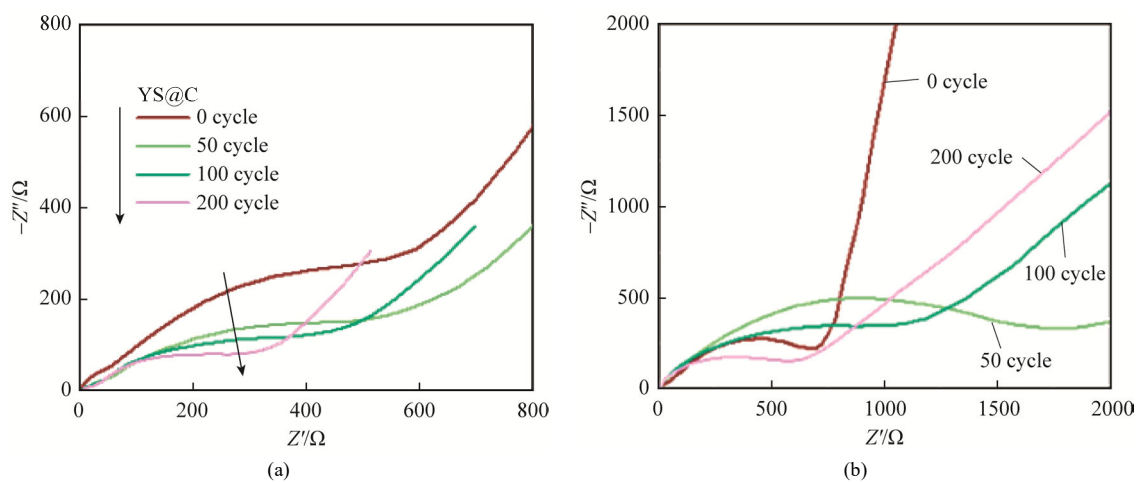


Fig. 11 Nyquist plots of the (a) YS@C and (b) P@C anodes

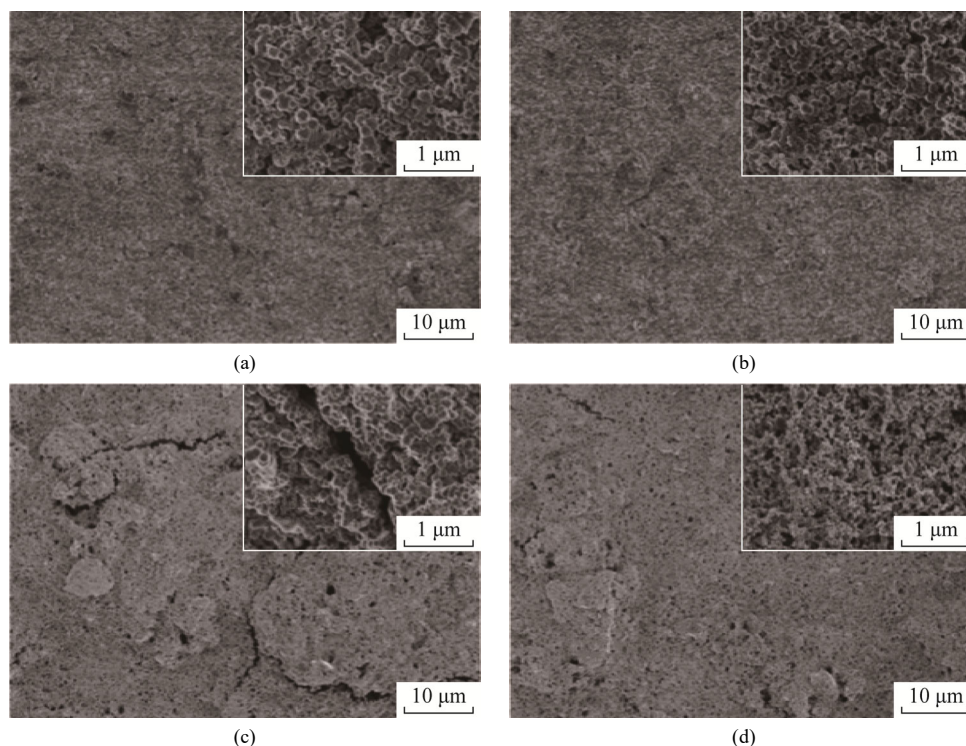


Fig. 12 SEM images of the (a) P@C and (b) YS@C electrodes before cycling; SEM images of the (c) P@C and (d) YS@C electrodes after 300 cycles

4 Conclusions

Egg yolk-shell-structured and porous SiOC anode materials (denoted as YS@C and P@C, respectively) are prepared using simple chemical selective etching. Compared to P@C, YS@C has a core with a high specific capacity and an intermediate void space that effectively alleviates the volume expansion of SiO_x , considerably shortening the diffusion distance of Li^+ to the core. The shell, composed of amorphous carbon and SiO_2 , minimizes side reactions, improves the kinetics of lithium insertion and extraction from the active material, and enhances the structural stability of electrode materials. This gradient composition and structure endow YS@C with excellent electrochemical and kinetic performance, particularly outstanding cycling stability, rate performance, and high pseudocapacitance. YS@C maintains a high specific capacity ($453 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$) throughout 550 charge-discharge cycles at a high current density of $0.5 \text{ A}\cdot\text{g}^{-1}$. Even at a high current density of $1 \text{ A}\cdot\text{g}^{-1}$, it stably cycled for 1000 cycles with a specific capacity of $354 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$. The preparation of YS@C in this study provides valuable guidance for the design and synthesis of other advanced materials with a gradient composition and structure.

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作者贡献声明:

陈垒: 论文构思, 设计研究思路实验方案与研究方法, 统筹划分研究任务内容

叶巧巧: 材料制备, 撰写初稿, 分析数据并且推导结论

韩成轩: 使用软件, 根据实验数据绘制图表

蒲敏捷: 电化学性能测试, 绘制图表

冯怡雯: 材料物理化学性能表征测试, 绘制图表

郑甜甜: 软件使用、验证、绘制图表

杨建平: 提供资源、获取资助, 审阅与修订

Preparation of Egg Yolk-Shell/Porous Silicon Oxycarbide Anode Materials *via* Mild Alkaline Etching

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Extended Abstract

Introduction Lithium-ion batteries (LIBs) with a high energy density are critical for advancing electric vehicles and renewable energy storage systems. Silicon oxycarbide (SiOC) anode materials emerge as promising candidates due to their high cycling stability,

suitable operating potential, low cost, and environmental compatibility. Unlike conventional silicon anodes that suffer from severe volume expansion (*i.e.*, >300%), SiOC materials benefit from the uniform distribution of silicon and carbon in an atomic scale, forming protective Li_2O and lithium silicate layers during initial lithiation that mitigate volume changes. However, a practical implementation of SiOC anodes remains challenging due to their intrinsically low electronic/ionic conductivity and significant volumetric changes during cycling, leading to electrode pulverization, loss of electrical contact, and excessive solid-electrolyte interphase (SEI) growth. In this study, a novel synthesis strategy was proposed to create SiOC anodes with engineered yolk-shell and porous architectures that could simultaneously optimize structural stability, ionic/electronic transport, and interfacial properties.

Methods This work employed a meticulously controlled sol–gel process followed by selective etching under mild alkaline conditions to fabricate SiOC anode materials with distinctive architectures. A yolk–shell structured material (YS@C) was prepared by a sequential addition approach *via* incorporating 1,4-bis(triethoxysilyl)benzene (BTEB) to form the core, and then adding tetraethoxysilane (TEOS) to create the shell. For the porous material (P@C), BTEB and TEOS were introduced simultaneously. The structures both underwent selective etching with a 2.4 mol/L Na_2CO_3 solution, removing portions of the inorganic silica, while preserving the organic–inorganic hybrid framework. Subsequently, resorcinol-formaldehyde resin was coated onto the etched structures and carbonized in 10% H_2/Ar atmosphere at 800 °C to form conductive carbon layers. The structural and chemical properties were determined by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), and BET surface area analysis. The electrochemical performance was evaluated through cyclic voltammetry, galvanostatic charge-discharge testing, rate capability analysis, long-term cycling, and impedance spectroscopy, respectively.

Results and discussion The mild alkaline etching strategy produces monodisperse YS@C particles (with the sizes of 250–270 nm) featuring a distinctive yolk–shell structure with an intermediate void space, and P@C particles (with the sizes of 320–350 nm) with uniformly distribute internal pores. The structural analyses reveals amorphous characteristics with carbon contents of 75.51% for YS@C and 68.2% for P@C. The specific surface areas measured are 17.041 m^2/g for YS@C and 27.458 m^2/g for P@C, with the average pore sizes of 2.371 nm and 2.561 nm, respectively. The XPS analysis demonstrates different silicon valence states, with the average values of 2.796 9 for YS@C and 2.999 2 for P@C, indicating varying degrees of silicon oxidation that affect the electrochemical behavior.

In electrochemical testing, YS@C delivers the superior performance with an initial Coulombic efficiency of 55%, compared to 49% for P@C. Most significantly, YS@C maintains an exceptional cycling stability with specific capacities of 453 $\text{mA}\cdot\text{h}\cdot\text{g}^{-1}$ after 550 cycles at 0.5 A/g and 361 $\text{mA}\cdot\text{h}\cdot\text{g}^{-1}$ after 1000 cycles at 1 A/g, with the Coulombic efficiency consistently of > 99% after the sixth cycle. The kinetic analyses reveals the superior Li^+ diffusion coefficient and remarkable pseudocapacitive contribution of YS@C (*i.e.*, 82.2% at 2.0 mV/s) due to its shortened ion diffusion pathways. The post-cycling SEM examination confirms the structural integrity after 300 cycles of YS@C, while P@C exhibits significant cracking and degradation.

Conclusions This research demonstrated that the gradient composition and hierarchical architecture of YS@C, featuring a high-capacity siloxane-rich core, intermediate void space, and protective carbon/SiOx shell, could collectively address the fundamental limitations of SiOC anode materials. The internal void space effectively accommodated volume expansion during lithiation/delithiation, while the carbon-rich shell enhanced conductivity and minimized detrimental side reactions with the electrolyte. The mild alkaline etching approach presented could offer a gentle yet effective method for engineering complex architectures without damaging the organic components critical for performance. The exceptional electrochemical performance of YS@C, particularly its unprecedented cycling stability at high current densities, could establish a benchmark for SiOC-based anodes.

This work could advance the development of high-performance lithium-ion battery anodes and provide valuable design principles for engineering gradient-structured materials for various energy storage applications. Future research could focus on scaling this synthesis approach and exploring its applicability to other conversion/alloying-type electrode materials requiring volume change accommodation.

Keywords selective etching method; silicon-oxygen-carbon-based anode; high energy density battery; carbon coating; sol–gel method