**Modified SiO hierarchical structure materials with improved initial coulombic efficiency for advanced lithium-ion battery anodes†**

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Silicon-based anode materials are indispensable components in developing high energy density lithium-ion batteries, yet their practical application still faces great challenges, such as large volume change during the lithiation and delithiation process that causes the pulverization of silicon particles, and continuous formation and reformation of the solid electrolyte interfaces (SEI) which results in a low initial coulombic efficiency. As an endeavor to address these problems, in this study, Si/SiO/Li2SiO3@C structures were prepared via a facile method using SiO, pitch powder and Li2CO3/PVA solution followed by annealing treatment. The Si/SiO/Li2SiO3@C composite shows a great improvement in lithium storage where a high discharge capacity of 1645.47 mA h g⁻¹ was delivered with the 1st C.E. of 69.05% at 100 mA g⁻¹. These results indicate that the designed method of integrating prelithiation and carbon coating for SiO and the as-prepared macro scale Si/SiO/Li2SiO3@C structures are practical for implementation in lithium-ion battery technology.

So far, various methods have been proposed and employed to modify Si-based materials in order to improve their lithium storage performance. For example, constructing core/shell structure nanoparticles/nanowires where Si acts as core materials and SiO/SiO2 serves as shell layers have been realized through solution methods or physical/chemical vapor deposition. Such one-dimensional core/shell nanostructure allows the delivery of high capacity and maintains high capacity retention. Polymer coating on Si-based materials has also led to significant improvement in specific capacity and cycling performance because of the prevention of Si particles aggregation as well as accommodation of their volume expansion. Fabrication of various Si-based composite materials, e.g. Si-carbon nanotubes, metal fibril mat-supported silicon anode, etc. is also demonstrated for high performance lithium storage. In addition, surface coating with carbon or metal layer on Si-based materials to avoid direct contact between Si/SiO and electrolytes is also proved to be effective in promoting stable solid electrolyte interphase (SEI) and increasing the electric conductivity to maximize the overall electrochemical performance.

Compared with the huge volume change of pure Si during lithiation, the volume expansion issue of SiO is less severe than that of Si, thus SiO is currently more preferable in integrating into EVs batteries anodes. However, SiO encounters several drawbacks. One is the low intrinsic electrical conductivity, which lowers the electrochemical activity; another is the low initial coulombic efficiency (1st C.E.) because the oxygen component in SiO can irreversibly consume some Li during the

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**Introduction**

During the last five decades, exacerbating air pollution together with the concerns of severe fossil fuel depletion have drawn public awareness of accelerating the electrification of our transportation systems. The ever-increasing demand for electric buses (E-bus) and electric vehicles (EVs) has thus stimulated the development of high performance lithium ion batteries (LIBs). However, graphite, the primary anode material, which has a theoretical capacity of 372.22 mA h g⁻¹, cannot satisfy the high energy density requirement of the EVs and is not usually considered as an anode material in these types of LIBs, e.g. 300 W h kg⁻¹ battery packs. Among the various types of candidate anodes proposed for LIBs, Si-based materials have high theoretical capacities, e.g. Si with a capacity of 4211.52 mA h g⁻¹ (Li1.4Si) or 3589.28 mA h g⁻¹ (Li1.75Si) and silicon monoxide (SiO) of 2322.15 mA h g⁻¹, which have attracted intensive research efforts in both academic and industrial area. However, Si-based materials still suffer from huge volume expansion and pulverization issues, which inevitably lead to the rapid failure of the battery.

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† Electronic supplementary information (ESI) available: The XRD pattern of the solute from the wash supernatant, the morphology of the Si/SiO/Li2SiO3@C composites after acid treatment, charge and discharge profiles of three samples at 50 µA. The electrochemical performance of BTR material and Si/SiO/Li2SiO3@C composite. See DOI: 10.1039/c9ra00778d
first cycle.\textsuperscript{30,31} These consumed Li need to be compensated so that the 1st C.E. of the anode could be close to those of cathodes before it is widely used.\textsuperscript{32,33} Benefit from the investigation of Si anodes, great advancement has been achieved in solving the pulverization of SiO.\textsuperscript{34–36} Recently, some research attention is directly paid to solving the low 1st C.E. problem. Their attempts mainly focus on converting the O atoms in the SiO to a buffer layer like SiAl\textsubscript{0.2}O\textsubscript{37} or lithium silicates\textsuperscript{38} during materials synthesis stage, but no significant progress has been available. Furthermore, the nanosized LIBs electrode materials provided in these studies is not yet practical for industrial application. It is of extremely urgent and meaningful to develop an effective and efficient method to tackle these issues so as to pave the way for the practical implementation of SiO.

In this work, a novel method was developed to prepare carbon-coated prelithiated micron-sized SiO anode materials for lithium storage, which is displayed in Fig. 1. Hierarchical free-standing SiO–Li\textsubscript{2}CO\textsubscript{3}/PVA sponges were first prepared through solution method, followed by annealing in N\textsubscript{2} flow to generate macroscale Si/SiO/Li\textsubscript{2}SiO\textsubscript{3}@C hierarchical structures. Such composites combining the advantages of carbon-coating and prelithiation are desirable in lithium storage. When tested as lithium-ion battery anode, a high capacity of 1645.47 mA h g\textsuperscript{−1} was obtained with a high 1st C.E. of 69.05% compared to 12.29% of the pristine SiO-based anode at 100 mA g\textsuperscript{−1}. Rate capability testing shows that when 100, 200, 500, 1000 and 2000 mA g\textsuperscript{−1} current densities were applied, the delivered capacities are 748.59, 609.68, 487.13, 311.52 and 197.80 mA h g\textsuperscript{−1}, respectively.

**Methods**

**Materials preparation**

In a typical synthesis, 10.0 g polyvinyl alcohol (average M\textsubscript{w}: 31 000, Sigma Aldrich, 99.9%) were first dissolved in 180 g 80 °C DI water to form a transparent solution through continuous stirring, after which 18.0 g lithium carbonate (Li\textsubscript{2}CO\textsubscript{3}, Sigma Aldrich, 99.9%) was added to form the PVA–Li\textsubscript{2}CO\textsubscript{3} solution. To prepare the SiO–Li\textsubscript{2}CO\textsubscript{3}/PVA sponge, 2.62 g silicon monoxide (SiO, Sigma Aldrich, 99.9%, D\textsubscript{50} = 5.07 μm) were mixed with 50 mL PVA–Li\textsubscript{2}CO\textsubscript{3} solution under stirring for 10 min, then 10 mL alcohol (Sigma Aldrich, 99.5%) where 0.8 g pitch powder was previously dissolved was rapidly dropped into the above mixture solution to form the SiO–Li\textsubscript{2}CO\textsubscript{3}–Pitch–PVA sponge. The final mole ratio of SiO : Li\textsubscript{2}CO\textsubscript{3} in the sponge was adjusted to be 8 : 1. The obtained sponges were then kept in a 100 °C vacuum oven for 3 hours to evaporate the remained water and alcohol. The dry sponges were then transferred into a tube furnace and annealed at 1000 °C under nitrogen flow for 6 hours to form the Si/SiO/Li\textsubscript{2}SiO\textsubscript{3}@C structures. The Si/SiO/Li\textsubscript{2}SiO\textsubscript{3}@C structures were further treated by 2.0 M HNO\textsubscript{3} for 60 minutes to remove some of the Li\textsubscript{2}SiO\textsubscript{3} as well as introduce some pore structures. Carbon-coated SiO (SiO@C) were also prepared through carbonation of the sponge obtained from a mixture of pristine SiO–PVA solution and ethanol-pitch powder solution.

**Physical characterization**

The morphologies of the pristine SiO, SiO@C and Si/SiO/Li\textsubscript{2}SiO\textsubscript{3}@C were visualized using field-emission electron microscopy (FESEM, FEI, Nova NanoSEM 450 operated at 1 kV). The phases of these samples were identified using X-ray diffraction (XRD, Rigaku SmartLab 3 kW, 40 kV) with Cu Kα irradiation.

**Electrochemical evaluation**

For the preparation of working electrodes, 80 wt% active materials, 10 wt% super P carbon and 10 wt% LA133 binder (5 wt% in H\textsubscript{2}O, purchased from Chengdu Indigo Power Sources Co., Ltd) were mixed with DI water and stirred to form a slurry. The black slurry thus obtained was coated on Cu foil by an automated doctor blade and followed by drying under a vacuum environment at 90 °C for 12 h to remove the solvent. The dry electrodes were calendared and the total material loading was ~6 mg cm\textsuperscript{−2}. The electrodes were assembled into CR2016 coin cell in an argon-filled glove box configuration with lithium.

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**Fig. 1**  Schematic synthesis procedures of the Si/SiO/Li\textsubscript{2}SiO\textsubscript{3}@C composites.
metal foil as the counter/reference electrode, polypropylene separator (Celgard 2400), and electrolyte solution obtained by dissolving 1 M LiPF₆ and 5% FEC in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (EC/DMC, 1:1, v/v). The charge/discharge tests were performed using a NEW-ARE battery tester in a voltage window of 0.005–1.5 V. Cyclic voltammetry characterization (0.005 V to OCV) were performed using an electrochemical workstation (Solartron analytical equipment, 1287 Electrochemical Interface). EIS measurement was carried out on the same equipment as CV with a frequency ranging from 100 kHz to 0.01 Hz (1260 Impedance/Gain-Phase Analyzer). Before the EIS tests, the coin cells were fully discharged and then charged to 50% SOC.

Results and discussion

Fig. 1 illustrates the synthesis procedure of the Si/SiO/Li₂SiO₃@C composites where more details are available in the experiment section.

The XRD patterns of the pristine SiO, carbon coated-SiO (SiO@C) and Si/SiO/Li₂SiO₃@C are displayed in Fig. 2. For the pristine SiO, a broad peak around 20–30° was observed, corresponding to the amorphous nature of SiO, which has been revealed to be composed of silicon nanocrystals, SiO₂ and amorphous SiOₓ (0 < x < 2) interfaces. SiO@C exhibits two peaks, where the broad peak around 20–30° was SiO and the peak at 28.5° belongs to nanosized Si generated from the disproportion of SiO during the carbonization process. Diffraction patterns corresponding to Li₂SiO₃ (PDF no. 29-0828), nano-sized Si (PDF no. 27-1402) and the remained SiO are displayed in Fig. 3. As shown in Fig. 3a, the peak at 28.5° is connected porous Si/SiO/Li₂SiO₃@C composites are desirable high performance lithium storage application where the porous structures provide not only free space for volume expansion accommodation but also efficient channels for Li⁺ diffusion.

The electrochemical properties of the pristine SiO, SiO@C and Si/SiO/Li₂SiO₃@C composites were investigated in half-cell batteries. The CV responses of the coin-cells using these anode materials are shown in Fig. 4. Different CV responses are observed from the three types of coin cells. For the pristine SiO (Fig. 4a), in the first cycle, the broad peak ranging from 0.2–0.5 V and the shape peak followed at around 0.05–0.2 V can be attributed to the conversion and lithiation process corresponding to the lithiation of Si and irreversible formation of Li₂SiO₃. During the anodic scan, peaks at around 0.6 V correspond to the delithiation of Li–Si alloys. In the following cycles, the lithiation and delithiation peaks all slightly shift to the lower potential, which demonstrates the dominant process is the lithiation and delithiation of Si as SiO was converted into Si and Li₂SiO₃ during the first cycle. It is noted that the anodic peak in the 2nd cycle is the strongest, suggesting an activation process and in the 3rd cycle, its amplitude weakens, indicating a stable state is achieved or a possible degradation may have occurred, as pristine SiO is fragile upon cycling. The CV profiles of SiO@C are far more complicate compared with that of SiO and are exhibited in Fig. 4b. In the first cathodic scan, a broad peak centered at around 0.65 V appears which is related to the formation of the solid-electrolyte interface (SEI) layer. In the 2nd and 3rd cycle, this peak shifts to around 1.0 V and the intensity is weaker. The lithiation peaks below 0.2 V turn broader and their intensities increase as cycle number increases, which is contrary to that of pristine SiO. These results suggest a different SEI formation mechanism as well as a gradual utilization of SiO after carbon coating. The anodic scan also show a gradual increase of peak intensities upon cycling and the peaks slightly shift to the higher potential. For the Si/SiO/Li₂SiO₃@C, similar CV responses as SiO@C are observed where broader cathodic and anodic peaks compared with SiO@C are centered at around 0.1 and 0.2 V, respectively, as shown in Fig. 4c.
Fig. 5a shows the first charge and discharge curves of the coin-cells using the above mentioned anode materials at a current density of 100 mA g\(^{-1}\). The discharge voltage of pristine SiO is 0.1–0.2 V higher than those of SiO@C and Si/SiO/Li\(_2\)SiO\(_3\)@C composites. It may be caused by the differences in reaction kinetics and hindrance where in pristine SiO, SiO directly contacted with electrolyte, while in the later two cases, carbon layers surrounded the particles resulting in different SEI structures. Another reason is the disproportion of SiO during the carbonization process in the SiO@C and Si/SiO/Li\(_2\)SiO\(_3\)@C composites and the different discharge–charge curves between nano-sized Si and micron-sized SiO.\(^{41,42}\) The charge and discharge curves of SiO@C and Si/SiO/Li\(_2\)SiO\(_3\)@C composites almost overlay with each other except for the end of charge and discharge, which indicates similar conversion and alloying reactions with different degrees of sluggish in kinetics. For the pristine SiO, the initial discharge and charge capacity are 1787.89 and 219.88 mA h g\(^{-1}\) respectively, in which the 1\(^{st}\) C.E. is as low as 12.29%. It is also noted that the delivered capacities rapidly fade for pristine SiO and at the 5\(^{th}\) cycle, dropping to only 95.03 and 89.28 mA h g\(^{-1}\), which evidently show that pristine SiO is not suitable to be applied in practical battery cells (Fig. 5b). When SiO was coated with 5% of carbon (SiO@C), the initial discharge and charge capacities increase to 1759.46 and 1021.02 mA h g\(^{-1}\) with a 1\(^{st}\) C.E. of 58.03%, which is a significant improvement compared with that of pristine SiO. The mechanisms under such improvements in specific capacities and 1\(^{st}\) C.E. can be attributed to both the enhancement of
electric conductivity and prevention of direct contact of SiO with the electrolyte to avoid SEI formation on SiO by the introduction of the exterior carbon layer. Although improved 1st cycle performance was achieved, the delivered capacities at the following cycles behave similarly as the pristine SiO (Fig. 5b). As some SiO particles underwent huge volume expansion and cracked during discharge, these particles were not recovered during the following delithiation process and the interior lithiation parts were further electronically isolated due to the shrinkage of the delithiation portion, which inevitably exacerbates the capacity fading of these two kinds of materials. The delivered capacities of the Si/SiO/Li2SiO3@C composites in the 1st cycle are 1645.47 and 1136.18 mA h g⁻¹, corresponding to a 1st C.E. of 69.05%. The 2nd and 3rd cycle charge capacities are stable at around 800 mA h g⁻¹. The rate performance of the Si/SiO/Li2SiO3@C composites was also investigated. At the current density of 100, 200, 500, 1000 and 2000 mA g⁻¹, the delivered capacities at the corresponding 10th cycle are 748.59, 609.68, 487.13, 311.52 and 197.80 mA h g⁻¹, respectively. When the current density was switched to 200 mA g⁻¹, the capacities restore to 601.10 mA h g⁻¹, which demonstrates a good rate capability of the Si/SiO/Li2SiO3@C composites. It is also noted that for SiO@C and Si/SiO/Li2SiO3@C composites, $R_{3//CPE2}$ both appear. The carbon coating (and possibly Li2SiO3 in the Si/SiO/Li2SiO3) may be responsible for this as it generates another interface between the carbon layers and the active materials of SiO or Si/SiO/Li2SiO3. To further elucidate these phenomena, coin cells of the three different anode materials were charged and discharged at 50 μA. Under such small current, the polarizations, especially kinetic aspects, which occurred during the charge and discharge processes in the coin-cells, can be minimized. From Fig. S3,† we can observe that when comparing the
discharge and charge profiles (specific capacities < 100 mA h g\(^{-1}\)), the discharge potential of pristine SiO is 0.3–0.4 V higher than those of SiO@C and Si/SiO/Li\(_2\)SiO\(_3\)@C composites, which delivers the largest resistance polarization. The SiO@C sample shows the lowest overpotential and at the beginning of the discharge, a typical voltage hysteresis can be observed, revealing a gradual activation of the SiO materials that is protected by the carbon coating layer. The charge and discharge curves of Si/SiO/Li\(_2\)SiO\(_3\)@C composites fall within the other two samples which indicates the improved conductivity of electrons or increase of lithium ions transfer hindrance from carbon coating or introduction of lithium silicates which optimizes the ionic conductivity and enhance the resistance to volume expansion, leading to an overall cycle stability.

**Conclusions**

In summary, we have developed a facile method to construct the hierarchical Si/SiO/Li\(_2\)SiO\(_3\)@C composites for advanced LIBs anodes. The as-prepared composites not only have a high 1\(^{st}\) C.E. of 69.05% but also show improved cycling stability. Benefited from the partial prelithiation of SiO and carbon coating, the Si/SiO/Li\(_2\)SiO\(_3\)@C anode has a superior electrochemical performance, with a prolonged cycle performance of 78.46% capacity retention over 35 cycles at 100 mA g\(^{-1}\) and an excellent rate property of 197.8 mA h g\(^{-1}\) at a high current density of 2000 mA h g\(^{-1}\). Such a design not only mitigates the volume expansion issue but also facilitates electron transport and guarantees structural robustness which pave the way for fabricate durable Si-based anode materials for lithium storage.

**Conflicts of interest**

There are no conflicts to declare.

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