

Contents lists available at ScienceDirect

Journal of Power Sources



journal homepage: www.elsevier.com/locate/jpowsour

Controlling siloxene oxidization to tailor SiO_x anodes for high performance lithium ion batteries



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HIGHLIGHTS

G R A P H I C A L A B S T R A C T

- We propose a facile method to realize the regulation of oxygen content in SiO_x.
- Experiments and theoretical calculations shed light on the oxidization mechanism.
- Nominal O/Si ratio of SiO_x rapidly increases to 1.5 and then rises with minor slope.
- SiO_{1.47} shows the optimal properties in terms of Li-ion and electric conductivity.

ARTICLE INFO

Keywords: Siloxene Silicon suboxides Oxygen content Anode Lithium-ion batteries



ABSTRACT

Silicon suboxides (SiO_x, 0 < x < 2) have been shown commercial prospect in lithium-ion batteries because of relative high capacity and mild volume expansion. However, few methods are available to prepare oxygentunable SiO_x. Herein, we introduce a bottom up strategy to realize the consecutively regulation of oxygen content in SiO_x via stepwise oxidizing silicane/siloxene precursor. Experimental results show that x value rapidly increases up to 1.5 and then rises extremely to 2.0 with minor slope. Furthermore, theory calculations indicate oxygen is preferentially inserted into Si–Si bonds to form buckled Si–O–Si limited to SiO_{1.5}H with higher driving force than the following Si–OH formation which is well consistent with the experimental results. Virtually, nominal SiO_x is substantially the mixture of Si, SiO_{1.5}, SiO, SiO_{1.5} and SiO₂ with SiO_{1.5} as the predominate component. Among the representative SiO_x samples, SiO_{1.47} exhibits the optimal electrochemical performance with reversible capacity of around 700 mAh g⁻¹ and almost 100% capacity retention at 0.5C (1C = 1500 mA g⁻¹) after 300 cycles because of higher Li-ions diffusivity and less fracture. In addition, 95.4% capacity retention is achieved after 100 cycles at 0.2C in full-cell system.

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https://doi.org/10.1016/j.jpowsour.2019.05.071

Received 12 March 2019; Received in revised form 27 April 2019; Accepted 19 May 2019 Available online 28 May 2019 0378-7753/© 2019 Elsevier B.V. All rights reserved.

1. Introduction

Nowadays, silicon suboxides $(SiO_x, 0 < x < 2)$ anodes are particularly prospective because of their trade off capacity and volume expansion compared with Si [1,2]. Because generated irreversible Li₂O and various lithium silicates (mostly Li₄SiO₄) reduce the specific capacity and in turn act as buffer components to boost the cycling stability [3–5]. With respect to x, a smaller value would result in higher reversible capacity and initial Coulombic efficiency, whereas dramatically capacity fading. Previous studies revealed that SiO_x with x value around 1.0 delivered capacity more than 1000 mAh g⁻¹ but unsatisfactory cycle lifespan. However, SiO_{1.63} with ~40 wt% coating-carbon content manifested 625 mAh g⁻¹ at 500 mA g⁻¹ and negligible capacity degradation after 400 cycles [6]. When x value is close to 2, for example, SiO_{1.93} exhibited inferior reactivity with lithium [7,8]. Consequently, insight into the effect of oxygen content on the electrochemical performance in diverse SiO_x needs to be urgently developed.

At ambient atmosphere, SiO₂ is the only thermodynamics equilibrium crystal phase based on Si-O (oxygen) binary phase diagram [9]. Accordingly, it is impracticable to prepare homogeneous silicon suboxides (SiO_x, 0 < x < 2) via oxidizing elemental Si. In addition, any carbothermal or magnesiothermal reduction of SiO₂ just forms elemental Si instead of substoichiometric silicon suboxides. So far, extensive efforts have been devoted to exploit various routes to generate SiO_x materials, oxidizing Si with slight oxide layer [10,11] or making mild oxygen defects on surface of SiO₂ [6,8,12,13]. Apparently, the core-shell structural SiOx materials exhibit a nominal O/Si atom ratio near 0 or 2. For example, SiO_x ($0 \le x \le 0.37$) were lately prepared by mechanical milling Si under controllable Ar/air atmosphere [14]. Moreover, hydrogen silsesquioxane (HSiO_{1.5})_n was demonstrated to form amorphous $SiO_{1.5}$ after thermal processing [15,16]. State-of-the-art commercial available SiO displays amorphous structure and uniform components which is produced by sublimating and quenching of specific proportion of Si and SiO2 mixture over 5000 °C [17]. As well, this method was carried out to prepare amorphous SiO_x with x in the range of 0.83-1.21 [18]. Though some specific SiO_x have been successfully prepared and investigated, it still need to exploit facile approaches to tune the oxygen content in a wide range as well as in control.

Siloxene as the emerging material was prepared and used into energy storage devices [19-21] Here, we develop a novel strategy to controllably tune oxygen content in SiO_x with the adjustable x value from 0 to 2 in theory derived from silicane. In fact, self-prepared siloxene (O/Si ratio approximate 1.0 after heat-treatment), is used as precursor to tune the oxygen content of SiOx based on the gradually oxidization of siloxene. Our investigation suggests a new perspective to synthesize SiO_x and simultaneously achieve the adjustment of oxygen content. Moreover, the as-prepared materials give a chance to further understand the structural models of elusive silicon-oxygen clusters which are controversial and inconclusive. Experimental characterizations and complementary theoretical calculations are carried out to reveal the thermodynamics and kinetics toward the silicane/siloxene oxidization processing and recognize the intermediate products. As proof-of-concept, SiO_x with four typical x values, namely $SiO_{1.01}$, $SiO_{1.25}$, $SiO_{1.47}$ and $SiO_{1.78}$, are prepared to study their lithium ions storage performance in detail.

2. Experimental section

2.1. Materials synthesis

CaSi₂ (Cā30 wt%, Sinopharm Chemical Reagent Co., Ltd.) was first purified by 2 mol L⁻¹ NaOH (Aladdin, 97%) aqueous solution to remove Si impurity but not FeSi₂ confirmed by our previous report [22]. After freeze drying, siloxene was generated by exfoliating as-obtained CaSi₂ using 5 mol L⁻¹ HCl (Aladdin, \geq 98%) with the assistance of water bath ultrasound for 12 h using sealed plastic beaker under air atmosphere. The product was received by centrifuging and washing with water until the rinsed water pH became neutral. Then, siloxene precursor was received after freeze drying process. Subsequently, oxidizing siloxene was conducted via two typical routes, pure H₂O and 50%RH air atmosphere, respectively. Siloxene with various oxidation extent were prepared by stirring 0.3 g siloxene precursor in 100 ml Milli-Q water (18 MΩ cm) under 300 rpm or exposing siloxene at 50%RH air atmosphere with different times. The obtained resultants were heated at 350 °C for 1 h and transferred to amorphous silicon oxides (a-SiO_x). To obtain SiO_x anode materials, a-SiO_x was first heated at 900 °C with the ramp rate of 10 °C min⁻¹ under the flowing of 200 sccm Ar, and then subjected to CVD coating at 900 °C for 1 h with additional 200 sccm C₂H₄ followed by naturally cooling down.

2.2. Materials characterizations

Particle size distribution was detected by laser particle analyzer (Microtrac S3500). X-ray powder diffraction (XRD) was carried out on Bruker D8 Advance with Cu K α radiation ($\lambda = 1.5418$ Å) operated at 40 kV and 40 mA. Scanning electron microscope (Hitachi S4800) was used to characterize the morphology. The TGA analysis was tested by PerkinElmer Pyris Diamond under an air atmosphere from 25 to 1000 °C at a heating rate of 10 °C min⁻¹. Raman spectra (Raman, Renishaw inVia Reflex) were collected from 200 to 1200 cm⁻¹ with a He–Ne laser at the wavelength of 785 nm. The Fourier transformed infrared spectra (FTIR, Nicolet 6700) were collected from 400 to 4000 cm⁻¹. X-ray photoelectron spectroscopy (XPS, Axis Ultra DLD) measurements were performed using Al Ka monochromatic beam (1486.6 eV). All spectra were calibrated using C 1s peak (284.6 eV) from conductive tape. X-ray fluorescence (XRF, Bruker S8 tiger) was used to assess the mass content of Si in SiO_x which could be used to calculate the corresponding O/Si atomic ratio. More details are shown in Supplementary Materials.

2.3. Electrochemical measurements

The negative electrodes were prepared by casting slurries on Cu foil with active materials, conducting agent (Super-P), styrene butadiene rubber (SBR) and carboxymethyl cellulose (CMC, Mw = 5000000) at a mass ratio of 80:10:7:3. The slurry were dried at 80 °C for 8 h in air followed by 4 h in vacuum at 120 °C (Büchi glass oven B-585). The positive electrodes consisted of LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ (NCA, BTR New Energy Material Ltd.), carbon black (super P), and polyvinylidene fluoride (PVDF) with a weight ratio of 90:5:5 in N-methyl pyrrolidone (NMP). The slurry was casted onto aluminum foil and dried at 80 °C for 24 h under vacuum. Cells were assembled within Ar-filled glove box (Mbraun, H₂O level <0.1 ppm and O₂ level <0.1 ppm) using Celgard 2400 as separator. 1 M LiPF₆ dissolved in EC/DEC = 1:1 by volume with 5 wt% FEC was used as electrolyte additive. All the electrolyte and additives are obtained from Zhangjiagang Guotai-Huarong New Chemical Materials Co., Ltd.

For the half-cell, Li foil (6 mm in thickness) was used as both reference and counter electrode. The galvanostatic charge-discharge was performed using Land CT 2100A battery-test system between 0.005 and 1.5 V versus Li/Li⁺ at constant current (CC) mode. Cyclic voltammetry (CV) measurements were performed between 0.005 and 2.5 V at specified rate and electrochemical impedance spectroscopy (EIS) in the frequency of 10^{-1} - 10^{5} Hz with an ac voltage 10 mV were recorded by electrochemical workstation (Solartron 1470E) using CR2032-type coin cells. The lithium-ion diffusion coefficients were determined by GITT method. More details were shown in Supplementary Materials.

In the full-cell configuration, pre-lithiated SiO_x and NCA were used as anode and cathode, respectively. A self-discharge mechanism was used to prelithiate SiO_x anode in which SiO_x electrode was directly contacted with Li foil in the presence of electrolyte under the pressure of 150 g. The cells were charged in the potential range of 2.5–4.3 V at



Fig. 1. Bottom-up strategy to prepare miscellaneous silicon suboxides. Si $(O_x V_{\ddot{O}4-x})$ tetrahedrons were constructed in SiO_x solid. If no O atom, we suppose there will be an oxygen vacancy $(V_{\ddot{O}})$ between Si–Si bonds. Images a-e are associated with O/Si ratio of 0, 0.5, 1.0, 1.5 and 2.0, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

 $0.05C~(1C=200~mA~g_{NCA}^{-1})$ under constant current followed by constant voltage (CCCV) mode with the cut-off current in the CV period being 0.005C and discharged at 0.05C under CC mode. In the subsequent cycles, the cells were charged at 0.2C under CCCV mode with the cut-off current in the CV period being 0.02C and discharged at 0.2C under CC mode. The n/p ratio defined by the capacity ratio of anode and cathode was 1.13.

2.4. DFT-based theoretical calculations

All of the calculations were performed using the Density-Functional Theory (DFT) with the exchange-correlation functional treated in the spin-polarized Generalized Gradient Approximation (GGA) as parameterized by Perdew-Burke-Ernzerhof (PBE) [23,24] with the projected augmented wave (PAW) method [25] as implemented in the Vienna Ab initio Simulation Package (VASP) [26-28]. The standard version of the PAW potentials for Si, H and O were supplied with VASP. The valence electrons for Si, H and O atoms were treated with 3s²3p², 1s¹ and 2s²2p⁴. Convergence with respect to both energy cutoff and k-point mesh was tested. As a result of the convergence, an energy cutoff of 600 eV was chosen to ensure that the total energies were converged within 1.0 meV/fu. A k-point mesh of $(11 \times 11 \times 11)$ and $(4 \times 4 \times 1)$ in the Monkhorst-Pack sampling scheme including the gamma point were used for bulk and sheet structure, respectively. Spin polarization was taken into account and the Methfessel-Paxton method was employed to determine electron occupancies with a smearing width of 0.1 eV in all cases. The vdW (van der Waals)-DF exchange-correlation functional was used for surface structures. During geometry optimization, atomic positions and lattice parameters were relaxed until the force on each atom below the limit of 10^{-2} eV/Å using the Gaussian smearing method [29] with a smearing parameter of 0.1 eV. For bulk Si, the predicted lattice parameter is 5.467 Å, which agrees well with the available experimental data [30] of 5.431 Å, confirming the choice of the parameters for DFT calculations.

For the calculation of silicane to siloxene oxidation, 2×2 supercells of silicane sheet was used, and a vacuum thickness of 20 Å separating the



Fig. 2. Experimental evidences about siloxene oxidation mechanism to tailor SiO_x. (a) Digital photos about siloxene slurry (left) and powder (right). (b) O/Si atomic ratio strongly depends on the oxidizing time though two different oxidation operations, pure water and 50RH% air. (c) Raman spectra record the structural evolution processes of siloxene. (d) FTIR further confirm the structural transformation of siloxene during H₂O oxidation. (e) Illustrations show that Si-Si bonds in the Si₆ plane are gradually replaced by Si-O bonds and Si-H bonds out of Si6 plane are gradually substituted by Si-OH bonds. (f) SEM image of silicon suboxide annealed at 350 °C for 1 h. The inset shows the magnifying planner depth about 300 nm. Components configuration in thickness illustrated at the right side. (g,h) XPS used to identify the surface (g) and ca. 20 nm (h) in depth after Ar-ion etching of silicon suboxide. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)



Fig. 3. DFT calculations uncover siloxene oxidation mechanism. (a,b) Calculated reaction driving force of siloxene oxidation in H₂O (a) and O₂ (b). (c) Calculated energy vs lattice parameter (relative to Si_6H_6) for the siloxene SiO_yH with y = 0.5, 1.0, 1.5 and 2.0. The positions of O atoms in the siloxene are located in the Si-Si bond or in the Si–H bond. $z = N_{Si-OH}/(N_{Si-H} +$ N_{Si-OH}) presents the ratio of O atoms located in the Si–H bond, where $N_{\mathrm{Si}^-\mathrm{H}}$ and $N_{\mathrm{Si}^-\mathrm{OH}}$ are the number of Si-H bond and Si-OH bond in the siloxene, respectively. All possible configuration structures with O atom at different position were considered in the calculation. (d-f) The most stable structures of SiH (d), SiO1.5H (e) and SiO_{2.5}H (f), respectively.

layers was included in the direction perpendicular to the silicene plane.

3. Results and discussion

3.1. Design of oxygen-tunable SiO_x

As we can see, Si atomic coordination number is identical in Si and SiO₂ crystal, corresponding to four Si-Si and Si-O bonds, respectively. Here, we suppose oxygen vacancy exists in Si-Si bond (Fig. 1). Consequently, all the Si atoms are tetrahedral coordination with O atom or oxygen vacancy (Vö). When oxygen gradually introduced into Si-Si bonds, the component will evolve from Si to SiO_{0.5}, SiO_{1.5} and SiO₂ step by step. To achieve this assumption, we believe that several guidelines should be considered. First, a proper precursor only including Si and H should be found. It could be used to generate Si after annealing. Second, the original precursor could be gradually oxidized to form Si-OH or Si-O-Si bonds, which would transformed into silicon oxide when undergoing heat-treatment. Foremost, the oxidation rates should be controllable. Based on these considerations, layer polysilane (Si₆H₆) is a suitable starting material. Si₆H₆ can be prepared from calcium disilicide (CaSi₂), in which the Si₆ rings are interconnected in the lateral dimension and meanwhile Si atom is saturated with hydrogen in the vertical direction [31]. Research results confirmed that fresh sixfold Si rings were capable of dissociation O₂, with O atoms penetrating and forming Si-O-Si bridges when exposing to air within 3 min[32,33]. Additionally, hydrogen gas bubbling was observed when rinsing in water indicated Si-H bonds were substituted by Si-OH bonds and siloxene Si₆H_x (OH)_{6-x} was generated [34]. Recently, we prepared novel siloxene with oxygen inserted Si6 rings terminated with H and OH ligands by delamination of CaSi2 in dilute aqueous HCl under ambient atmosphere[22]. The as-obtained siloxene is relatively chemical stable at ambient air for one week with the O/Si ratio around 1.0 after annealing at Ar atmosphere. If all the Si-Si and Si-H bonds in Si₆H₆ are converted into Si-O-Si and Si-OH bonds, respectively. The resultant materials would turn into SiO2 after annealing process. Therefore, successive oxidation starting from Si₆H₆ to Si₆O₉(OH)₆ could be realized the consecutive increasing about oxygen concentration from Si to SiO₂ in theory.

3.2. Unveiling siloxene oxidation mechanism

Generally, fresh Si_6H_6 is subject to oxide spontaneously and form siloxene in the case of trace water or oxygen. Actually, we employ as-

prepared siloxene as raw materials in the experiment. As shown in Fig. 2a, primarily, we synthesized large-scale light-yellow suspension and followed by freeze drying procedure to obtain siloxene powders which was developed by ourselves [22]. Several kinds of siloxene with different degrees of oxidation have been prepared in pure water and 50%RH air. X-ray fluorescence (XRF) was used to determine the O/Si atomic ratio of SiO_x derived from siloxene (more details seen in Note S1 and Fig. S1). When reacting with water, the O/Si ratios rapidly grow from 1.01 to ca. 1.5 and then the rising slope becomes gentle until O/Si ratio is up to 2.0 if reaction time is enough (Fig. 2b). By contrast, it shows sluggish oxidation dynamics when oxidizing at moist air. Clearly, XRF results suggest that we have achieved to tailor silicon suboxides SiO_x with x among 1.0 to 2.0.

To reveal the oxidation pathway about as-obtained siloxene reacting with H₂O, ex-situ Raman spectra and Fourier transformed infrared spectra (FTIR) were applied. As shown in Fig. 2c, the appearance of Si–O–Si and Si–OH vibrations at 498 and 730 cm⁻¹ in pristine siloxene indicate oxygen inserts into planar Si–Si bonds and partial Si–H is substituted by Si–OH, respectively. As the reaction time increasing to 16 days, overwhelming majority of Si–H bonds are converted into Si–OH which was confirmed by the disappearance of Si–H bond. After that, the absorption intensity of peak ~386 cm⁻¹ assigned to Si–Si vibration gradually weaken indicates more and more oxygen atoms have incorporated in Si₆ rings and forming Si–O–Si bonds. In addition, terminated hydroxy groups in the direction perpendicular to the layer undergo dehydration condensation reaction and Si–O vibrations centered at 332 and 908 cm⁻¹ emerge.

The chemical bonds evolution of siloxene was further identified by FTIR as a function of reaction time (Fig. 2d). The results agree well with but more sufficient than Raman data. The gradually disappearance of Si–Si stretching in Si₆ plane (522 cm⁻¹) combined with the gradually increasing peak intensity at ca. 453 cm⁻¹ assigned to Si–O–Si bending from lateral direction demonstrate oxygen atoms are continuously embedded into Si6 rings. The gradually disappearance of Si-H bending (648 cm^{-1}) combined with the gradually increasing peak intensity at ca. 885 cm⁻¹ assigned to Si–OH demonstrate terminal hydrogen is replaced by hydroxy step by step. It is noteworthy that Si-OH absorption band decreases and Si–O–Si vibration (790 cm⁻¹) clearly appears when the reaction time extends to 30 days. Remarkably, hydroxy groups between the adjacent siloxene layers are subjected to undergo condensation reaction which coincides with Raman results. Intriguingly, it reveals that infrared absorption band will be red-shift as the increasing of oxygen content in the Si skeleton backbone (Fig. 2e). The signature ranging from

2050 to 2350 cm^{-1} could be effective to distinguish the absorption bands among (Si₃)Si-, (Si₂O)Si-, (SiO₂)Si- and (O₃)Si- which are terminated with H or OH and labeled as 1, 2, 3 and 4 shown in Fig. 2e [31]. Though there are four kinds of individual coordination type of Si, FTIR confirms diverse coordination types coexist in the home-made siloxene samples. The main difference is the content of (Si₃)Si- decreases until its characteristic peak completely disappears, as well as higher oxygen content coordination type exhibits more content as the oxidizing time extension. To further insight into oxidation process, etching assisted XPS was used to detect the silicon valence state along the thickness direction of single amorphous silicon oxide sheet as shown in Fig. 2f. The spectra of Si 2p in SiO_x are composed of a broad peak at 103 eV and shoulder peaks (Fig. 2g,h and Figs. S2 and 3). The deconvolution of Si 2p shows the existence of five possible oxidation states, Si⁰, Si⁺, Si²⁺, Si³⁺ and Si⁴⁺. Obviously, the dominated chemical valence of Si is +3, which takes up a large portion more than 50%. After 2 min etching at 4 kV, the average chemical valence decreases to +2.62, while the surface is +2.74, which manifests siloxene sheet is gradually oxidized from surface to center. When further extending etching time, the Si 2p spectra are almost identical (Fig. S3), which could be concluded that siloxene shows uniformly oxidizing processes with only ca. 20 nm in depth exhibiting higher degree of oxidation.

To verify the oxidation process from silicane to siloxene and possible mechanism, the thermodynamics toward siloxene oxidation were investigated by density functional theory (DFT) calculations. Silicane sheet (SiH, as shown in Fig. 3d) with a single-layer structure, exhibits buckled arrangement in which the adjacent row of Si atoms creased along the zigzag direction, and the adjacent Si atom are saturated with H atom along the opposite directions. A unit cell includes two Si atoms and two H atoms, and the lattice parameter is 3.866 Å, where the bond length of Si–Si is 2.346 Å and the bond angle is 110.97°. The distance between two nearest neighbor Si atoms projected on the axis perpendicular to the plane is 0.722 Å. The optimized atomic structure agrees with previous theoretical work [35]. The cohesive energy of the silicane sheet was calculated and the value is -3.36 eV per atom, indicating the silicane sheet is stable in thermodynamic.

As calculated, there are five distinct configurations for SiO_{0.5}H siloxene discussed in Fig. S4. To compare the relative stability, the total energies vs lattice parameter was shown in Fig. 3c. The total energy decreases as the reducing of z value (z means $N_{Si^-OH}/(N_{Si^-H} + N_{Si^-OH})$ in $SiO_{0.5}H$. Obviously, the configuration of z = 0.0 with the meta-position in SiO_{0.5}H displays the lowest energy, indicting all of O atoms inserted into Si–Si bonds with the meta-position is the most stable configuration. Therefore, during the silicane oxidation to SiO_{0.5}H process, all of O atoms are firstly inserted into Si-Si bonds with the meta-position. Consequently, the configuration (z = 0.0 with Meta) is adopted as the structure model of SiO_{0.5}H (Fig. S4e). The lattice parameter is elongated to 4.329 Å, because of the formation of Si-O-Si connections. The buckled height between the two neighboring Si atoms of the SiO_{0.5}H sheets increase to 0.965 Å from 0.722 Å (SiH), indicating the plane of the SiO_{0.5}H sheet becomes more puckered, in which the bent Si–O–Si connections are alternated up and down along the O atoms inserted direction. The cohesive energy of SiO_{0.5}H sheet is $-4.03\,\text{eV}$ per atom, which is larger than that of SiH (-3.36 eV per atom), indicating that SiO_{0.5}H sheet is more energetically favourable and stable than silicane.

Similarly, we obtained the stable structure model toward different siloxenes of SiOH, SiO_{1.5}H, SiO₂H and SiO_{2.5}H by considering all possible configurations and then comparing the calculated total energy. As shown in Fig. 3c, for SiOH, the configuration of z = 0.0 (meta) has the lowest energy, indicting the structure with all of O atoms inserted into Si–Si bonds with the meta-position is the most stable configuration. The energy of z = 1.0 is ~ 1.0 eV/f. u. higher than that of z = 0.0. Therefore, SiOH (z = 0.0 with Meta) is adopted as the structure model of SiOH siloxene as shown in Fig. S5a. Analogously, for SiO_{1.5}H, the configuration with all of O atoms inserted into Si–Si bonds and all of Si–Si bonds transferred into Si–O–Si bonds is the most stable structure, which is



Fig. 4. Structure and morphology of siloxene and annealed silicon suboxides with various oxygen content. (a) XRD patterns of siloxene. (b) XRD patterns of SiO_x@C. The x value is 1.01, 1.25, 1.47 and 1.78 corresponding to sample A, B, C and D, respectively. (c–f) SEM images of SiO_x@C, x = 1.01 (c), x = 1.25 (d), x = 1.47 (e) and x = 1.78 (f), respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

chose as the structure model of SiO_{1.5}H siloxene as shown in Fig. 3e. The lattice parameter is further elongated to 5.026 Å. The buckled height between the two neighboring Si atoms of SiO_{1.5}H sheet is further increased to 1.092 Å, indicating the plane of SiO_{1.5}H sheet is more puckered than that of SiO_{0.5}H and SiOH. When further oxidization to SiO₂H and SiO_{2.5}H sequentially, the O atoms start to insert into Si–H bonds derived from the structure of SiO_{1.5}H, and the lattice parameter remains unchanged (Fig. 3c), and the structure models are shown in Fig. S5b and Fig. 3f, respectively.

In order to explore the oxidation mechanism of silicane to siloxene, we considered the oxidization reaction of silicane (SiH) with water (H_2O) or oxygen (O_2) molecules. The two oxidization reactions can be written as

$SiH + yH_2O \rightarrow SiO_yH + y/2H_2$	(1))
		-

$$SiH + y/2O_2 \rightarrow SiO_yH$$
 (2)

The reaction driving force of siloxene oxidization with $\mathrm{H}_2\mathrm{O}$ or O_2 can be calculated as

$$\Delta E_{\rm r}({\rm H}_{2}{\rm O}) = E({\rm SiO_vH}) + y/2E({\rm H}_{2}) - E({\rm SiH}) - yE({\rm H}_{2}{\rm O})$$
(3)

$$\Delta E_{\rm r}({\rm O}_2) = E({\rm SiO}_{\rm y}{\rm H}) - E({\rm SiH}) - y/2E({\rm O}_2) \tag{4}$$

where *E* (SiO_yH) and *E* (SiH) is the total energy of the SiO_yH siloxene and silicane sheet, respectively; *E* (H₂O), *E* (H₂) and *E* (O₂) is the total energy of an isolated H₂O, H₂ and O₂ molecule, respectively. Following this definition, as shown in Fig. 3a, ΔE_r (H₂O) of SiO_{0.5}H is obtained as -0.40 eV/f. u., indicating that the transformation from silicane to SiO_{0.5}H siloxene by H₂O oxidation is an exothermic reaction. The reaction driving force of siloxene oxidation in H₂O is initially increased



Fig. 5. Electrochemical performances of SiOx@C with various oxygen content. (a) CV curves at the 3rd cycle for various silicon suboxides from 2.5 to 0.005 V at 0.1 mV s⁻¹. Note that threefold current density of sample D is applied for comparison. (b) The first charge-discharge curves of four SiOx@C samples measured at $0.1C/0.1C(150 \text{ mA g}^{-1})$. (c) Reversible capacity comparison when measured at different C-rates $(1C = 1500 \text{ mA g}^{-1})$. (d) Reversible capacity retention measured at 0.5C with initial four cycles activated at 0.1C and following two cycles at 0.2C. The SiO_x@C mass loadings are 1.12, 1.00, 1.12 and 0.67 mg cm^{-2} with respect to sample A, B, C and D, respectively. (e) Coulombic efficiencies are defined to reflect the lithium-ion loss at each cycle. (Inset) Magnified view of the Coulombic efficiencies at each cycle unveils the imperceptible differences. (f) EIS plot of prelithiated electrode and the inset shows its delithiation curve at 0.05C. (g, h) The initial galvanostatic chargedischarge profile of the pre-Li SiO_{1.47}@C-LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ full cell at 0.05C (1C = 200 mA g_{NCA}^{-1}) (g) and its cycling performance at 0.2C recorded 2.5-4.3 V (h), along with the at Coulombic efficiencies. The n/p ratio based on capacities of both electrodes is 1.13. The anode electrode mass loading is 1.8 mg cm $^{-2}$.

and then decreased with the y from 0.0 to 2.5, and it reaches the maximum of -1.24 eV/f. u. at y = 1.5, indicating the oxidation in H₂O from SiOH to SiO_{1.5}H is more efficient than other siloxene states in thermodynamic. It can explain the experiment observation that the O/Si ratios are rapidly grown from 1.01 to ca. 1.5 and then the rising slope becomes smaller until O/Si ratio up to 2.0 when reaction with H₂O. Because O atoms are first inserted into Si–Si bonds from SiOH to SiO_{1.5}H and then inserted into Si–H bonds after SiO_{1.5}H during the oxidation process. In addition, the reaction driving force of siloxene oxidation by O₂ is larger than that by H₂O, but the tendency of siloxene oxidation by O₂ from silicane to SiO_{2.5}H is the same as H₂O. In experiment, due to the using of air not pure O₂, the oxidation rate may be controlled by the diffusion of O₂ in air to silicane surface, thus it shows sluggish oxidation dynamics when oxidizing in air.

3.3. Structure and morphology of SiO_x

As the proof of concept, several typical SiO_x were prepared to study the relationship between oxygen concentration and electrochemical performance. The raw materials exhibit significant peaks assigned to (100) and (001) plane of siloxene, a visible SiO₂ diffraction peak at $2\theta = 26.6^{\circ}$ and FeSi₂ impurity as shown in Fig. 4a. After oxidizing in water, siloxene structure was destroyed and amorphous SiO_x was generated. Original siloxene (a) and oxidized siloxene (b, c and d) undergone annealing and disproportionating at Ar atmosphere and subsequent carbon deposition using C₂H₄. XRD patterns confirm remarkable amorphous carbon and silicon (Fig. 4b). XRF combined with TGA (Fig. S6) measurements detected the accurate O/Si ratio and carbon content. Four typical samples A (SiO_{1.01}), B (SiO_{1.25}), C (SiO_{1.47}) and D (SiO_{1.78}) exhibit comparative carbon content of 41.1%, 43.1%, 45.5% and 36.0% in weight, respectively. Microscopic morphologies demonstrate that a series of flake SiO_x adhere together and form micrometer-scale secondary particles (Fig. 4c–f). Particle size distribution further indicates D50 of sample A, B, C and D is 25.2, 16.6, 10.6 and 13.5 μ m, respectively (Fig. S7).

3.4. Electrochemical performances of SiO_x

Cyclic voltammogram of SiO_x@C electrodes were shown in Fig. 5a and Fig. S8. The magnitude of oxidation current density decreases as the oxygen concentration increasing, and then remarkable peak at 0.25 V assigned to carbon was appeared in SiO178@C because capacity contribution from carbon increases with the enhancing of oxygen content. As shown in Fig. 5b, A, B, C and D electrodes deliver reversible capacity of 1054.0, 875.4, 774.7 and 328.5 mAh g^{-1} and initial Coulombic efficiency of 75.5%, 69.5%, 67.2% and 53.2% at 0.1C $(1C = 1500 \text{ mA g}^{-1})$, respectively. Higher oxygen content leads to smaller reversible capacity and lower initial Coulombic efficiency, and more importantly larger polarization. To confirm the lithium ion migration kinetics, SiO_x@C electrodes were tested at higher current density as shown in Fig. 5c. SiO_x@C with larger x value shows superior rate capability. Nevertheless, SiO1.78@C abnormally exhibits higher capacity at 0.2C than 0.1C. On the one hand, more irreversible byproducts such as Li₂O and Li-silicates would be generated for SiO_x@C with higher x value, which of course results in lower initial Coulombic efficiency and even involving the following several cycles as shown in Fig. S9. On the other hand, sluggish kinetics results in lower reversible capacity and larger polarization. Therefore, it is reasonable to R. Fu et al.



Fig. 6. Kinetic analysis of SiO_x@C anodes. (a,b) EIS measurements of fresh Li-SiO_x@C half cell (a) and after 50 cycles at 0.5C (b). (c) Li diffusion coefficient of SiO1.47@C as a function of state of charge. The cells were performed at 0.1C for the first two cycles and then 0.5C ($1C = 1500 \text{ mA g}^{-1}$). The GITT procedures consisted of galvanostatic discharge-charge pulses 15 min each followed by relaxation for 4 h. (d) Li diffusion coefficient during the delithiating operation after 300 cycles. (e–h) Surface images of electrodes undergoing 200 cycles at 0.5C assigned to SiO_{1.01}@C (e), SiO_{1.25}@C (f), SiO_{1.47}@C (g) and SiO_{1.78}@C (h), respectively.

understand capacity climbing phenomenon up to 500 cycles with a limited capacity of 450 mAh g^{-1} for SiO_{1.78}@C as shown in Fig. S10. In Fig. 5d, SiO_{1.01}@C and SiO_{1.25}@C deliver 850 and 780 mAh g⁻¹ at 0.5C, respectively, which is higher than 700 mAh g^{-1} in SiO_{1.47}@C. While, the capacity exhibits rapidly decay over 100 cycles. By contrast, SiO_{1.47}@C clearly shows improved cyclic stability with negligible capacity loss upon 300 cycles. Almost identical voltage-capacity profiles and redox peaks at different cycles explains its outstanding stability (Fig. S11). Nevertheless, SiO_{1.78}@C shows successive capacity growth among 500 cycles. The ascending capacity ratio is 37.1% which strikingly exceed the value < 10% in the other samples (Fig. S12). Therefore, SiO_x@C with O/Si atomic ratio more than 1.5 consumes more time to activate the whole electrode and lead to dramatic capacity improvement. Actually, drastic capacity rising brings about a huge challenge to match the cathode in full cell design. In addition, Coulombic efficiency (CE) could be used to take account for the reversibility about lithium ion inserting into and then extracting from active materials as shown in Fig. 5e. The CEs statistical result for SiO1.47@C electrode indicates 84.0% CE values more than 99.8% (Fig. S13). In generally, higher CEs give rise to less lithium loss and then bring about superior cycling stability [36]. Consequently, we choose SiO_{1.47}@C as a case to carry out a full cell test in paring with advanced LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ (NCA) cathode (Fig. S14). Before that, we apply self-discharge mechanism which has been

demonstrated to be a powerful method to improve the initial CE of SiO_{1.47}@C. The initial CE increases to 89.6% (Fig. S15) because of pre-generation solid electrolyte interface (SEI) and reversible components with capacity of 137 mAh g⁻¹ as shown in Fig. 5f. When testing at 0.05C ($IC = 200 \text{ mA g}_{NCA}^{-1}$), the prelithiated SiO_{1.47}@C-NCA full cell exhibits a reversible capacity of 191.4 mAh g $_{NCA}^{-1}$ corresponding to 1.27 mAh cm⁻², and decent cycle stability such as 95.4% retention of original capacity after 100 cycles (Fig. 5g and h). Even at a high mass loading of 2.3 mg cm⁻², the full cell prototype still shows 85.9% capacity retention (Fig. S16). To our best knowledge, micrometer-sized SiO_{1.47}@C prepared here exhibits excellent cycling performance in both half-cell and full-cell configurations when compared with the reported results considering similar evaluating conditions (Table S1). In a word, SiO_x with the optimal stoichiometry is SiO_{1.47}.

3.5. Kinetics analysis of SiO_x

To unravel the electrochemical regulation of $SiO_x@C$, electrical conductivity and lithium ions diffusivity were further identified by EIS and GITT characterization as shown in Fig. 6. EIS results indicate the charge transfer resistance (R_{ct}) for fresh electrode is positive correlation to the oxygen content (Fig. 6a). Nevertheless, R_{ct} significantly decrease after 50 cycles and the smallest value is shown in SiO_{1.47}@C electrode

(Fig. 6b). To further understand the kinetic aspects of Li-ion transportation, we extracted the diffusion coefficient as a function of the depth of charge/discharge based on credible GITT method (Note S2 and Figs. S17–19). The Li diffusion coefficient (D_{Li}) is calculated and shown in Fig. 6c,d and Fig. S20. Majority of DLi is ranged from 10^{-10} -10^{-11} cm² s⁻¹. When focusing on the charging section, it is not difficult to find that DLi almost keeps stable in SiO1.47@C while others are falling off as the cycling going on. After the 300 cycles, the highest D_{Li} belonging to SiO_{1.47}@C electrode means the best lithium ions transportation which is well consistent with abovementioned electrochemical performance (Figure 6d). Apparently, more oxygen content results in larger R_{ct} (poorer electrical conductivity). Meanwhile, more oxygen content means less Li-ions migration (lower capacity, as shown in Fig. 5b) which would lead to less volume variation (less fracture, as shown in Fig. 6e-h) and consequently better structure integrity (superior Li-ion diffusivity). So, electron and Li-ion mobility are mutually exclusive properties in SiOx electrode. When the oxygen content exceeding a critical point, for example $SiO_{1,47}$, more inactive matrix Li₂O and Li-silicate are generated and then results in sluggish Li-ions movement. Because Li-ions diffusion coefficient of LivSi is at least 2 orders of magnitude higher than that of inactive matrix [3]. So, there will be an optimal oxygen content in considering cyclic stability and rate capability. Herein, SiO1.47@C shows the optimal electrochemical performance due to the synergistic effect between electric conductivity and Li-ion diffusivity.

4. Conclusions

In summary, we have established an innovative and facile approach to tune the oxygen content of SiO_x with x ranging from 0 to 2 in theory and 1-2 in experimental here as a case. Highly active silicane delaminated from layered CaSi2 are apt to form siloxene when exposing at O2 and H₂O atmosphere. Diverse siloxene which only contain Si, O and H elementals are explored as precursor to synthesize SiOx with controllable oxygen content via stepwise oxidizing original siloxene which exhibits the O/Si ratio around 1.0 after heat treatment. Experiments combined with theoretical calculations shed light on the oxidization mechanism, especially oxygen atoms are predominately inclined to incorporate into Si-Si bonds and generate Si-O-Si bridges in siloxene up to form SiO_{1.5}H with higher driving force. Subsequently, oxygen will continue to insert into Si-H bonds to form Si-OH with relative lower driving force. After annealing, nominal SiO_v mixture will be received because Si^0 , Si^+ , Si^{2+} , Si^{3+} and Si^{4+} coexist in SiO_x , but Si^{3+} is the main valence state. Then, four typical samples SiO1.01, SiO1.25 and SiO1.47 and SiO_{1.78} are investigated to evaluate their electrochemical properties. Given in capacity and cycle-stability, SiO_{1.47} exhibits the optimal electrochemical performances because of the synergistic effect of electrical conductivity and Li-ion diffusivity. Furthermore, a prototype full-cell device is assembled with NCA as cathode. Consequently, we have successfully exploited a new route to controllably tune the oxygen content of SiO_x (1 < x < 2) and demonstrated that SiO_x with x approximate 1.5 exhibits the optimum electrochemical performances for lithium-ions storage.

Acknowledgements

The authors would like to acknowledge the financial supports from

the National Natural Science Foundation of China (Grant No. 51872305) and the National Key Research and Development Program of China (Grant No. 2016YFB0100100). We thank Prof. Y. Xia (NIMTE, China) for constructive discussions.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jpowsour.2019.05.071.

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