

Supporting information

An amorphous Si material with sponge-like structure as anode for Li-ion and Na-ion batteries

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Experimental section

Chemicals

All the reagents used here are of analytical grade without further purification. Magnesium powder was purchased from Sinopharm Chemical Reagent Co. Ltd. Silicon tetrachloride was purchased from Aladdin.

Synthesis of the sponge-like porous amorphous silicon

In a typical procedure, 1.5g magnesium powder was loaded in a stainless steel autoclave (volume 20 mL), subsequently, 3 mL silicon tetrachloride was added into the autoclave. The above procedure is conducted in a glove-box filled with N₂. Then, the autoclave was sealed immediately and heated in an electric stove with a heating ramp rate of 5 °C min⁻¹ and maintained at 380 °C for 20 h. After cooling to room temperature naturally, the precipitate was collected and washed with 0.1M hydrochloric acid, distilled water, and ethanol. The obtained sample was immersed in diluted ethanol-based hydrofluoric acid (HF) solution for 10 min. Finally, the product was dried in vacuum at 50 °C for 10 h for further characterization.

Characterization

The products were characterized by X-ray powder diffraction (Philips X' Pert Super diffract meter with Cu K α radiation ($\lambda=1.54178$ Å)). Raman spectroscopy was conducted with a JYLABRAM-HR Confocal Laser Micro-Raman spectrometer at 514.5 nm. X-ray photoelectron spectroscopy (XPS) data were recorded on an ESCA-Lab MKII X-ray photoelectron spectrometer. The morphologies were characterized by using a field-emission scanning electron microscope (SEM, JEOL-JSM-6700F) and transmission electron microscope (TEM, Hitachi H7650). High resolution transmission electron microscopy (HRTEM) images were acquired on a JEOL-2010

transmission electron microscope with an accelerating voltage of 200 kV. The Brunauer-Emmett-Teller (BET) surface area and HK-plot pore distribution were measured using a BEL SORP-max machine, BEL, Japan.

Electrochemical measurements

The electrochemical properties of the as-prepared sponge-like porous amorphous silicon were evaluated through coin-type half cells (2016 R-type) which were assembled under an argon-filled glove box (H_2O , $O_2 < 1$ ppm). In the lithium ion batteries, metallic Li sheet was used as counter and reference electrode. 1 M $LiPF_6$ in a mixture of ethylene carbonate/ dimethylcarbonate (EC/DMC; 1:1 by volume) was served as the electrolyte (Zhuhai Smoothway Electronic Materials Co., Ltd (China)). In the sodium ion batteries, metallic Na sheet was used as counter and reference electrode. 1 M $NaPF_6$ in a mixture of ethylene carbonate/ dimethylcarbonate (EC/DMC; 1:1 by volume) was served as the electrolyte (Zhuhai Smoothway Electronic Materials Co., Ltd (China)). For preparing working electrode, the slurry mixed with as-prepared active material, carbon black (super P) and sodium alginate (SA) binder in a weight ratio of 6:2:2 in water solvent was pasted onto a Cu foil and then dried in a vacuum oven at 80 °C for 10 h. The active material density of each electrode was determined to be about 0.8 mg cm^{-2} . Galvanostatic measurements were conducted using a LAND-CT2001A instrument with a fixed voltage range of 0.005–1.5 V (vs. Li/Li^+) for lithium ion batteries and a fixed voltage range of 0.01–3.0 V (vs. Na/Na^+) for sodium ion batteries at room temperature. Electrochemical impedance spectroscopy (EIS) was performed on electrochemical workstation (CHI660D), with an alternating current (AC) voltage of 5 mV in the frequency range from 100 kHz to 0.1 Hz.

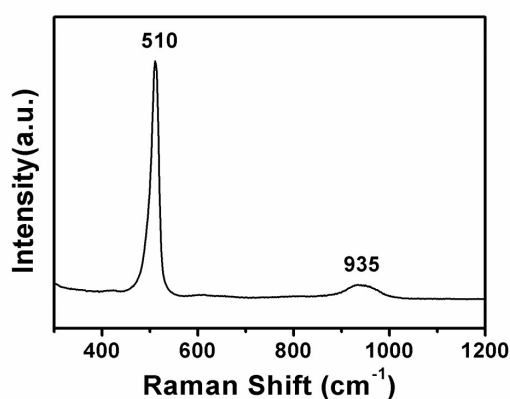


Fig. S1 Raman spectrum of the Si nanocrystallites.

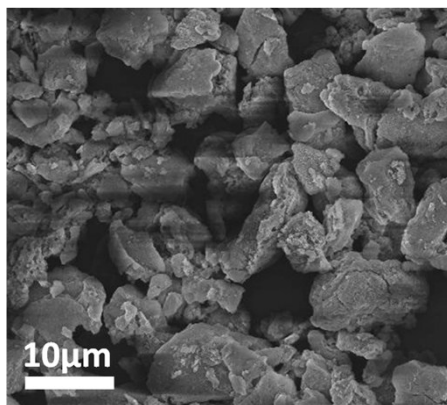


Fig. S2 The low-magnification SEM image of the prepared amorphous Si sample

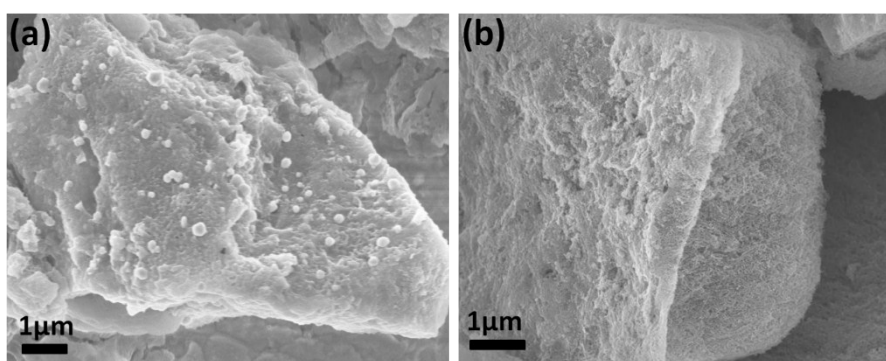


Fig. S3 SEM images of (a) the sample right out of the autoclave, and (b) the sample after the first wash with HCl, water and ethanol

As shown in Fig. S3, the surface of the crude product shows no obvious pores. After washing with HCl, water and ethanol, the sample shows a sponge-like pore structure, which is similar to the final product, indicating that the pores have already formed.

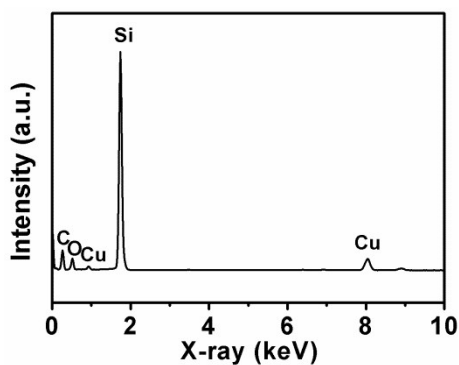


Fig. S4 EDX spectrum of the prepared amorphous Si sample

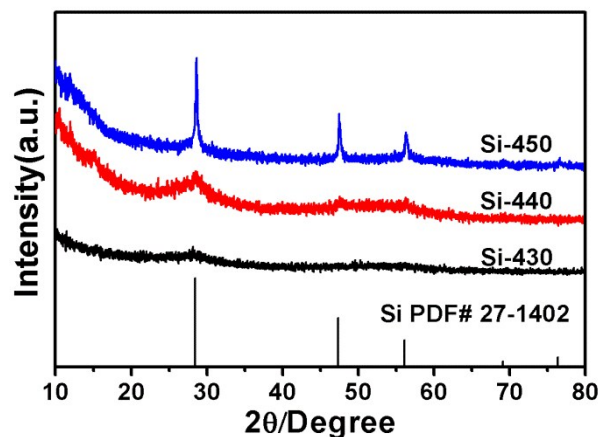


Fig. S5 XRD patterns of the as-prepared samples obtained at 430 °C, 440 °C, and 450 °C

In the reaction system, the temperature has a critical effect on the formation of amorphous silicon. To understand the reaction process at different temperatures, a series of related experiments were carried out. Fig. S5 shows the XRD patterns of the as-prepared samples obtained at 430 °C, 440 °C, and 450 °C, denote as Si-430, Si-440, and Si-450, respectively. In the pattern of the Si-430, no obvious diffraction peaks can be observed, indicating the amorphous form of sample. With the temperature rise, a weak peak of 28.67 ° in the pattern of Si-440 shows the crystallization of part of Si. When the temperature rises to 450 °C, three strong diffraction peaks of 28.65, 47.48, and 56.27 ° can be indexed to the lattice planes of (111), (220) and (311) of cubic Si (JCPDS No. 27-1402), indicating that the well-crystallized Si is obtained at 450 °C.

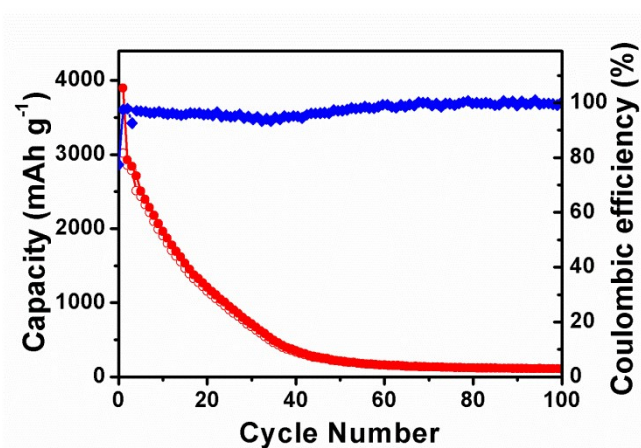


Fig. S6 The long term cycling properties of the commercial silicon electrode at 3.6 A g⁻¹.

With massive volume expansion, the 200 mesh commercial silicon anode undergoes rapid capacity fading upon cycling, and only 95 mAh g⁻¹ can be maintained after 100 cycles at 3.6 A g⁻¹.

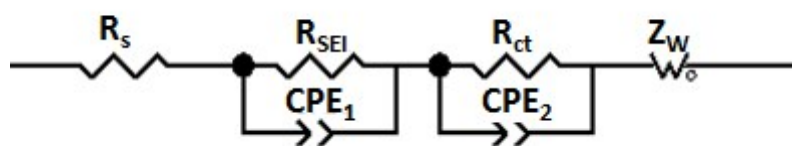


Fig. S7 Equivalent circuit used to model the impedance spectra.

Table S1. Simulated Kinetic Parameter for the Cell of the Sponge-like Porous Amorphous Silicon and Commercial Silicon Electrodes in the fresh state.

Sample	$R_s(\Omega)$	$R_{ct}(\Omega)$	$Z_W(\Omega)$
Amorphous Si	0.52	132.8	1.857
Commercial Si	2.64	286.5	148.2

Table S2. Simulated Kinetic Parameter for the Cell of the Sponge-like Porous Amorphous Silicon and Commercial Silicon Electrodes after cycle in different states.

Sample	States	$R_s(\Omega)$	$R_{SEI}(\Omega)$	$R_{ct}(\Omega)$	CPE_1	CPE_2
Amorphous Si	1st cycle at 0.36 A g⁻¹	4.987	53.88	79.36	3.481×10^{-6}	5.319×10^{-4}
Commercial Si	1st cycle at 0.36 A g⁻¹	5.439	55.43	128.4	3.643×10^{-6}	6.036×10^{-4}
Amorphous Si	10th cycle at 1 A g⁻¹	3.835	43.82	58.06	5.411×10^{-6}	3.253×10^{-4}
Commercial Si	10th cycle at 1 A g⁻¹	7.643	160.0	78.30	3.346×10^{-6}	3.752×10^{-4}
Amorphous Si	10th cycle at 10 A g⁻¹	3.637	37.42	84.92	7.409×10^{-6}	2.818×10^{-4}
Commercial Si	10th cycle at 10 A g⁻¹	4.625	68.33	272.0	4.353×10^{-6}	6.773×10^{-4}