

Porous Si/Cu6Sn5/C composite containing native oxides as anode material for lithium-ion batteries

Yawen He, Zhongbin Ye, Mohamad Chamas, Moulay Tahar Sougrati, Pierre-Emmanuel Lippens

► To cite this version:

Yawen He, Zhongbin Ye, Mohamad Chamas, Moulay Tahar Sougrati, Pierre-Emmanuel Lippens. Porous Si/Cu6Sn5/C composite containing native oxides as anode material for lithium-ion batteries. Journal of Materials Science: Materials in Electronics, 2022, 33, pp.235-243. 10.1007/s10854-021-07288-1. hal-03415279

HAL Id: hal-03415279 https://hal.science/hal-03415279

Submitted on 4 Nov 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Porous Si/Cu₆Sn₅/C composite containing native oxides as anode material for lithium-ion batteries

Yawen He^{a,b,*}, Ye Zhongbin^a, Mohamad Chamas^a, Moulay Tahar Sougrati^b, Pierre-Emmanuel Lippens^b

^a School of Chemistry and Chemical Engineering, Southwest Petroleum University,

Chengdu 610500, China

^b Institut Charles Gerhardt, UMR 5253 CNRS, Université de Montpellier,

Place Eugène Bataillon, 34095 Montpellier cedex 5, France

*Corresponding author : yawenhe0622@gmail.com

Abstract

Porous Si/Cu₆Sn₅/C composite containing native oxides was prepared via solid state mechanical milling and wet chemical etching. This composite was used as anode material for Li-ion batteries. X-ray diffraction, electron microscopy, ¹¹⁹Sn Mössbauer spectroscopy and X-ray photoelectron spectroscopy show that the composite has a pitaya-like morphology based on porous Si and embedded Cu₆Sn₅ non-porous microparticles with surface native oxides. Both Si and Cu₆Sn₅ are electrochemically active and the activation process during the first charge-discharge cycles improves the nanostructuration of the composite that helps to buffer the volume variations of the Li-Si and Li-Sn alloying reactions. The porous composite delivers a reversible and stable capacity of 900 mAh.g⁻¹ at a galvanostatic current density of 422 mA.g⁻¹ with a retention of 90% for 100 cycles, which is higher than porous Si (53%). The stability during cycling is explained by buffering effects, enhanced electrode conductivity and stable SEI due to the presence of native oxides and the use of FEC-containing electrolyte.

Key words: porous Si composite, anode, passivation

1. Introduction

Silicon is a promising anode material with a high specific capacity (4200 mAh.g⁻¹) for lithium-ion batteries. However, Si suffers from severe problems of volume expansion (~300%) when lithiated. The use of porous or nanosized structures of Si [1] is an efficient way to reduce the effects of volume expansion of electrode materials. Due to the poor intrinsic conductivity of Si [2] and volume expansion during lithiation, carbon coating could enhance the conductivity and buffer Si expansion but the technical process involves wet chemical treatment [3]. To simplify the procedure of synthesis, metals or alloys are preferred to make Si-based composites for lithium-ion battery anodes. Researchers have fabricated different forms of porous Si/Cu [4] composites using Cu as passivation and conductive matrix, leading to good cycling performance. But the synthetic steps are complex. Cu_6Sn_5 shows a theoretical capacity of 600 mAh.g⁻¹ and could be an active matrix delivering extra reversible capacity. The lithiation of Cu_6Sn_5 contributes to the extrusion of Cu [5], which increases the matrix conductivity. The idea of this work is to decrease the Si content in the composite by addition of Cu_6Sn_5 and carbon. In that case, the volume expansion of the electrode could be largely decreased. Meanwhile, Cu_6Sn_5 could provide an extra capacity with the formation of Li_xSn.

One usually distinguishes insertion, alloying and conversion reactions as basic lithiation mechanisms of anode materials for Li-ion batteries. The intercalation materials have usually rather low capacity due to the limited number of lithium that can be inserted into the host structure. For example, the commonly used graphite anode material can only intercalate 1 Li for 6 C between the layers, leading to the capacity of 372 mAh.g⁻¹. Other insertion materials such as titanates provide enhanced safety and fast charge capabilities but also show rather low capacity [6, 7]. Higher capacities can be obtained with conversion [8, 9] or alloying materials that involve more lithium per electroactive element but with strong structural modifications. For example, the alloying materials Si and Sn can reversibly react with up to 4.4 lithium per element to form Li_{4.4}Si (4200 mAh.g⁻¹) and Li_{4.4}Sn (1000 mAh.g⁻¹), respectively, but with strong volume changes of several hundred percent [10]. The alloying reaction of Si particles with lithium gives amorphous Li_xSi [11], and then crystalline $Li_{14}Si_5$ [12]. The η -Cu₆Sn₅ crystalline particles first react with lithium with the formation of the Li₂CuSn phase and extrusion of Cu atoms. Then, there is a twostep process involving the progressive lithiation of Li₂CuSn with Cu extrusion followed by the transformation into Li_{4.4}Sn [5,13–15]. The charge is based on the dealloying reaction of Li_{4.4}Sn and back reaction with Cu for form Li₂CuSn, which is then transformed into Cu_6Sn_5 [14,15]. Moreover, the assynthesized Cu₆Sn₅ was generally reported with oxidized surface in form of SnO₂ [16] that is electrochemically active [17].

In this work, we show that a porous Si/Cu₆Sn₅/C composite can be synthesized by using mechanical milling and wet chemical etching. Chemical etching was used to produce porosity as well as nanostructured Si with embedded Cu₆Sn₅ particles. The composite is described from measurements by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), electron microscopy and ¹¹⁹Sn Mössbauer spectroscopy. Finally, we show that the composite provides a capacity of 900 mAh.g⁻¹ and a better capacity retention during galvanostatic cycling than porous Si.

2. Experimental

Synthesis. Cu_6Sn_5 was prepared via solid state reaction route by using exact stoichiometric ratio of Cu (3 µm, analytical pure 99.99%, Aladdin Co. Ltd) and Sn (5 µm, analytical pure 99.99%, Aldrich) under Ar/H₂ (95/5) flow protection at 350°C for 5 h. Afterwards, $Al_{80}Si_{20}$ (5µm, Hunan 369 Metallurgical Technology Co., Ltd), synthetized Cu_6Sn_5 and carbon (by mass ratio 5:13:2) were mixed into 100 mL pot under Ar atmosphere for 36 h ball milling (balls/powder mass ratio:1/30). Then, 1.0 g of the $Al_{80}Si_{20}/Cu_6Sn_5/C$ composite was immersed in to 2.0 M HCl solution with N₂ flow for 4 h. After filtration, the obtained powder was dried in the oven at 80°C for overnight.

Characterization. The synthesized powder was stored in the Ar-filled glove box. The powder was taken out of the glove-box with the Ar protection setup just before the measurements. X-ray diffraction was carried out by an X-Pert PRO machine (Malvern Panalytical) using under CuK_{α} radiation λ =0.154056 nm. The morphology of the materials was characterized by field emission scanning electron microscopy (SEM, FEI InspectF50, accelerating voltage 200 V-30 kV) and transmission electron microscopy (TEM, FEI Tecnai G2 F30). The ¹¹⁹Sn Mössbauer spectroscopy was used for the identification of the tin phases within the pristine powder. The measurements were performed at 300 K with an absorber thickness of ~25 mg.cm⁻². X-ray photoelectron spectroscopy (XPS) was used with Al K_{α} X-ray source (1486.68 eV) under the voltage of 15 kV and current of 10 mA. The XPS measurements were carried out with a vacuum degree of $5*10^{-10}$ Pa. The binding energy scale was calibrated from the carbon contamination using the C 1s peak at 284.8 eV. N₂-isotherm measurements were performed with 3Flex Micromeritics Instrument Corp. The powder material (~150 mg) was dried at 100°C and degassed at 200°C.

Electrochemistry. The composite was mixed with binder carboxy methylcellulose (CMC, Mw=250,000) and carbon by mass ratio of 70/17/13. The mixture was ball milled for 30 min, casted onto Cu foil and dried in oven under vacuum for 4 hours at 120°C. The loading mass for electrode is approximately 1 mg.cm⁻². Coin cells (type CR2032) were assembled with lithium foil as counter electrode and microporous Whatman separator (GF/A 1820-047) under argon filled glove box. Electrolyte was 1.0 M LiPF₆ in (EC/DEC) + 2 vol% VC + 10 vol% FEC. Galvanostatic electrochemistry cycling tests were performed with voltage cut-off 0.05 - 1.2 V versus Li/Li⁺ (Neware BTS4000) at 25°C. Electrochemical impedance spectroscopy (EIS) measurements were carried out with the SP-50 electrochemical station (Biologic Ins.) and a three-electrode Swagelok cell.

3. Results and Discussion

Figure 1a shows the XRD patterns of the as-synthesized composites before etching: $Al_{80}Si_{20}/Cu_6Sn_5/C$, and after etching: $Si/Cu_6Sn_5/C$. The peaks of $Al_{80}Si_{20}$ can be assigned to Al (*Fm*-3*m*) and Si (*Fd*-3*m*) crystalline phases. As removal of Al by HCl, the broad peak at 28.3° can be assigned to Si (*Fd*-3*m*) with crystallite size of 12 nm as evaluated by the Scherrer's equation. The typical peaks of as-synthesized Cu₆Sn₅ belong to monoclinic phase *C2/c*. The additional peaks at 30.7 and 32.2° are assigned to β Sn. After etching, Al and Sn were dissolved in HCl solution [18]. In Fig. 1b, the composite shows spherical nanostructured particles. The connection, porosity and contact-embedded structure of Si and Cu₆Sn₅ are proved in Fig.1c, 1d and 1e, respectively.

The N₂ isotherm curves and average pore width distribution of the composite are shown in Fig. 2a, giving a surface area of 30 m².g⁻¹ and an average pore size of 15 nm. The decrease of the specific surface area compared to Al₈₀Si₂₀ is due to non-porous Cu₆Sn₅. Simultaneously, the average particle pore width shows a slight change that reflects the pore size of porous Si, which is also consistent with the SEM image. The ¹¹⁹Sn Mössbauer spectra of the composite before and after etching were successfully fitted to two doublets (Fig. 2.b). In both samples, the unresolved doublet at about 2.2 mm.s⁻¹ with a quadrupole splitting of 0.66 mm.s⁻¹ can be assigned to Cu₆Sn₅. The other doublet at approximately 0 mm/s with quadrupole splitting of 0.64 mm.s⁻¹ is attributed to SnO₂ at the surface of tin based particles [19]. The absorption area ratio of η -Cu₆Sn₅/SnO₂ is = 9 before etching and = 2 after etching, which could be due to the etching process [18]. This is also consistent with the oxidation of Sn in H₂O containing HCl solution. By considering that the Lamb-Mössbauer factor of Cu₆Sn₅ relative to SnO₂ is 0.4 at 300 K [20], the Sn atomic ratio in η -Cu₆Sn₅/SnO₂ is 22 before etching and 5 after etching, which confirms the strong oxidation of the tin phases during etching.

The XPS measurements of as-synthesized Cu₆Sn₅ and Si/Cu₆Sn₅/C composite were performed at the same time in the same chamber (Fig. 3). The Cu 2p and Sn 3d spectra of the as-synthesized Cu₆Sn₅ clearly exhibit two main components due to spin-orbit at binding energies (BE): BE = 932.5 eV / 952.5 eV and 485.1 eV / 493.4 eV corresponding to Cu⁰ and Sn⁰, respectively (Fig. 3a). The Sn 3d and O 1s XPS components at BE = 487.0 eV / 495.4 eV (Sn⁴⁺) and 530.7 eV / 532.3 eV, respectively, reflect surface

oxidation due to the exposure of the sample in air. The Cu 2p spectrum of the Si/Cu₆Sn₅/C composite was fitted to a doublet at BE = 934.7 eV / 954.6 eV (Cu²⁺) corresponding to CuO, as confirmed by the satellite peaks at BE = 943 eV / 963 eV due to the unfilled 3d⁹ state in CuO [21], and to a doublet at BE = 932.5 eV / 952.4 eV (Cu⁺) that can be attributed to Cu₂O. The two main peaks of the Sn 3d spectrum at 487.0 eV/ 495.4 eV are due to Sn⁴⁺ in SnO₂ and the two small peaks at 485.1 eV / 493.4 eV to Sn⁰ in Cu₆Sn₅. Thus, both Cu 2p and Sn 3d spectra show the strong oxidation of the surface of the Cu₆Sn₅ particles, in agreement with Mössbauer spectra but not observed by XRD due to the amorphous nature of the oxides. Before etching, the surface oxides or hydroxides were detected because of the absorbed molecules or surface oxidation. After etching, the Sn⁰ is not detectable by XPS, because the ball milling process changed the elemental distribution of Si/Cu/Sn elements as suggested by the SEM-EDS images (the pitaya-like structure) and the surface of Cu₆Sn₅ was oxidized during ball milling and etching process. The surface atomic compositions obtained from the XPS survey spectra are given in Table 1. The observed high relative amount oxygen also reveals the surface oxidation of the particles.

In Fig. 4a, the voltage profile of porous Si in Li half-cell shows a decrease from 1.2 to 0.6 V at the beginning of discharge due to the reduction of native oxides and the formation of a solid electrolyte interphase (SEI) resulting from the electrolyte degradation. The slightly sloppy plateau at about 0.2 V-0.05 V corresponds to the lithiation of Si. The 1st discharge shows a specific capacity of 3000 mAh.g⁻¹, which corresponds to the composition $Li_{3,1}Si$. This is because the voltage cut-off was fixed at 0.05 V vs. Li/Li⁺. In Fig. 4b, the voltage profile of Si/Cu₆Sn₅/C shows the SEI formation and reduction of oxides (CuO, SiO_y, SnO₂) until about 0.5 V, a 1^{st} plateau at about 0.35 V due to the transformation of Cu₆Sn₅ into Li₂CuSn [16,22], and the second plateau at 0.2 V-0.05 V reflecting the continuous lithiation of Li₂CuSn and Si. The CV curve of porous Si shows the typical peaks of the lithiation of Si: 0.01 V and 0.15 V (from the 2nd cycle) and of its delithiation: 0.40 V / 0.53 V (Fig. 4c) [12]. The same peaks are found in the CV curve of Si/Cu₆Sn₅/C while the additional peak at 0.81 V, corresponding to the voltage plateau at the end of charge (Fig. 4b), reflects the delithiation of the Li-Cu-Sn ternary phase (Fig. 4d) [23]. In summary, the electrochemical mechanism for the first discharge of the composite consists of (i) the irreversible reduction of oxides and formation of the SEI leading to a capacity loss of about 300 mAh.g⁻¹, (ii) Cu₆Sn₅ transformation into Li₂CuSn and (iii) alloying reactions of Li_xSi and formation of Li_vSn. During the charge, there are dealloying reactions of Li_xSi and Li_vSn with the formation of amorphous-Si and back-reaction of Li-poor Li_vSn with Cu to form Cu₆Sn₅ at the end of charge.

The comparison of the galvanostatic cycling performance for 100 cycles (C/20 for 3 cycles and then C/3) shows unstable variations and low retention (55%) of the capacity for porous Si while the capacity of Si/Cu₆Sn₅/C composite is more stable with a high retention of 90% (Fig. 5a). This strong capacity fade of porous Si (cycle No. 2-60) could be due to the disconnection of the active particles [24]. To confirm the latter assumption, we evaluated the relative irreversible coulombic efficiency at cycle n: RIC_{DISCONN} = (C_{Cn}-C_{Cn+1})/C_{Cn}, where C_{Cn} and C_{Cn+1} are the charge capacities of the nth and (n+1)th cycles, respectively [25]. In Fig. 5b, the variations of the cumulated RIC_{DISCONN} as a function of cycle number show a strong increase for porous Si that proves the loss of electrical contacts during electrode cycling as discussed previously [25]. The low values and the slight increase of the cumulated RIC_{DISCONN} for the composite reflect better electrical contacts. This result is in line with the observed stable capacity of the composite,

which can be explained by the stability of the electrode film due to the buffering effect and enhanced electronic conductivity of Cu₆Sn₅, Cu and C particles, and to the SEI stabilization owing to the additives (VC, FEC) of the electrolyte [26,27] and active Si [24].

As shown in Fig. 5a, the coulombic efficiency of porous Si increases from 77 to 98 % for the two first cycles and then shows some small variations, in line with capacity fading due to the loss of electrical contacts, as discussed above, or the aggregation of particles during cycling [24]. For the Si/Cu₆Sn₅/C composite, the first discharge consists of the irreversible reduction of native oxides and SEI formation, followed by reversible formation of Li_xSi and Li_ySn active nanoparticles. Such mechanism requires an activation process, of 3 cycles here, for the gradual nanostructuration of the composite as observed previously for other Si-based composites [28]. As a result, there is a strong increase of the coulombic efficiency from 50% to 92% for the two first cycles, then a gradual increase up to 99% for the following 3 cycles and a stabilization at this value until the end of cycling. The Li consumption due to the activation process could be supported by the pre-lithiation techniques for applications in full-cells [29,30]. Compared to other Si-based electrode materials, the present Si composite has a lower but more stable capacity as reflected by the significantly higher capacity retention (Table 2). Finally, the Si/Cu₆Sn₅/C composite shows a stable rate capability (Fig. 5c).

Additional information that explains the performance of the composite was obtained by XRD and electrochemical impedance spectroscopy (EIS). The cycled electrodes at the voltages of 0.2 V and 0.05 V were characterized by XRD. The pattern obtained at 0.2 V exhibits weak peaks at 28.3° due to Si and at $30.5^{\circ}/42.9^{\circ}$ that can be assigned to Cu₆Sn₅ (Fig. 6a). The strong decrease of the peak intensity, compared to the pristine material, confirms the lithiation of these two phases. There is another peak located at 43.3° that could be assigned to Cu nanoparticles. Note that changes in the background intensity below 30° are due Kapton used to maintain the powdered sample during XRD measurements. At the voltage of 0.05 V, no peaks of Si or Cu₆Sn₅ are detected, suggesting the almost full lithiation of all the crystalline phases. The only visible but slight peak at 43.3° reflects the existence of Cu nanoparticles that can improve the electronic properties of the composite. The Nyquist plots of the EIS spectra at the end of the 1st and 25th discharges are shown in Fig. 6b. The spectra were fitted with an equivalent circuit that takes into account the resistances of electrolyte (R_1), SEI (R_2) and charge transfer (R_3) (Fig. 6b). From the 1st to the 25th cycle, the electrolyte resistance is constant $R_1 \approx 4 \Omega$, the SEI resistance decreases from $R_2 = 37$ to 25 Ω and the charge transfer resistance increases from $R_3 = 7$ to 22 Ω . The values of R_2 and R_3 are smaller than reported values in porous Si/Cu based electrodes [35], which confirms the enhanced electronic percolation within the electrode and the improved Li⁺ transportation through the interfaces between the active particles and the electrolyte. This also explains the observed good rate capability of the composite.

4. Conclusion

The porous Si/Cu₆Sn₅/C composite was obtained from $Al_{80}Si_{20}$, Cu₆Sn₅ and C powders by mechanical milling method and wet chemical etching steps for removing Al. This composite shows a porous structure of Si with embedded Cu₆Sn₅ particles. Owing to the porosity and passivation resulting from the etching process, the composite anode shows a reversible capacity of 900 mAh.g⁻¹ for a current of 420 mA.g⁻¹ with a capacity retention of 90% at the 100th cycle, compared with only 53% for porous Si. The better stability is ascribed to Cu, C and Cu₆Sn₅ particles that help to buffer the volume variations

of the Li-Si alloying reactions and enhance the electronic conduction. The passivation from the native oxides and the FEC-containing electrolyte stabilize the SEI and also contribute to the performance of the composite.

Acknowledgements

This work was financially supported by Project of National Natural Science Foundation (NSFC 21650110463), the Southwest Petroleum University key project (KSZ16083) and China scholarship council (CSC) program.

References

1. W. Cao, K. Han, M. Chen, H. Ye, and S. Sang, Electrochim. Acta 320, 134613 (2019).

2. Z. Yi, N. Lin, Y. Zhao, W. Wang, Y. Qian, Y. Zhu, and Y. Qian, Energy Storage Mater. **17**, 93 (2019).

X. T. Cheng Li, Xitao Li, Yan-Zhen Zheng, Jiaojiao Wu, Haiyang Ding, ChemElectroChem 6, 2517
 (2019).

4. L. Cao, T. Huang, Q. Zhang, M. Cui, J. Xu, and R. Xiao, ACS Appl. Mater. Interfaces **12**, 57071 (2020).

5. X. F. Tan, W. Yang, K. Aso, S. Matsumura, S. D. McDonald, and K. Nogita, ACS Appl. Energy Mater. **3**, 141 (2020).

6. T.F. Yi, Y. Xie, Y.R. Zhu, R.S. Zhu, H. Shen, J. Power Sources 222, 448 (2013).

- 7. T.F. Yi, J. Mei, P.P. Peng, S. Luo, Compos. B: Eng. 167, 566 (2019).
- 8. P. Poizot, S. Laruelle, S. Grugeon, L. Dupont, J.M. Tarascon, Nature 407, 496 (2000).
- 9. T.F. Yi, J.P. Qu, X. Lai, X. Han, H. Chang, Y.R. Zhu, Mater. Today Chem. 19, 100407 (2021).
- 10. Y. Jin, B. Zhu, Z. Lu, N. Liu, and J. Zhu, Adv. Energy Mater. 7, 1700715 (2017).
- 11. M. N. Obrovac and L. J. Krause, J. Electrochem. Soc. 154, A103 (2007).
- 12. J. Li and J. R. Dahn, J. Electrochem. Soc. 154, 156 (2007).
- 13. X. L. Wang, W. Q. Han, J. Chen, and J. Graetz, ACS Appl. Mater. Interfaces 2, 1548 (2010).
- 14. D. Larcher, L. Y. Beaulieu, D. D. MacNeil, and J. R. Dahn, J. Electrochem. Soc. 147, 1658 (2000).
- 15. L. Fransson, E. Nordström, K. Edström, L. Häggström, J. T. Vaughey, and M. M. Thackeray, J.

Electrochem. Soc. 149, 736 (2002).

S. Naille, R. Dedryvère, H. Martinez, S. Leroy, P. E. Lippens, J. C. Jumas, and D. Gonbeau, J.
 Power Sources 174, 1086 (2007).

17. A. Y. Kim, J. S. Kim, C. Hudaya, D. Xiao, D. Byun, L. Gu, X. Wei, Y. Yao, R. Yu, and J. K. Lee, Carbon N. Y. **94**, 539 (2015).

Z. Wang, K. Dong, D. Wang, S. Luo, Y. Liu, Q. Wang, Y. Zhang, A. Hao, C. Shi, and N. Zhao, J.
 Power Sources 441, 227191 (2019).

19. B. Gangaja, S. Chandrasekharan, S. Vadukumpully, S. V. Nair, and D. Santhanagopalan, J. Power Sources **340**, 356 (2017).

20. R.C. Reno, M.J. Panunto, J. Electron. Mater. 26, 11 (1997).

21. K. Cao, H. Liu, W. Li, Q. Han, Z. Zhang, and K. Huang, Small 1901775, 1 (2019).

22. X. F. Tan, S. D. McDonald, Q. Gu, Y. Hu, L. Wang, S. Matsumura, T. Nishimura, and K. Nogita, J. Power Sources **415**, 50 (2019).

23. Q. G. Han, Z. Yi, Y. Cheng, Y. Wu, and L. M. Wang, RSC Adv. 6, 15279 (2016).

24. E. Radvanyi, W. Porcher, E. De Vito, A. Montani, S. Franger, and S. Jouanneau Si Larbi, Phys. Chem. Chem. Phys. **16**, 17142 (2014).

25. M. Gauthier, D. Mazouzi, D. Reyter, B. Lestriez, P. Moreau, D. Guyomard, and L. Roué, Energy Environ. Sci. 6, 2145 (2013).

26. T. Jaumann, J. Balach, U. Langklotz, V. Sauchuk, M. Fritsch, A. Michaelis, V. Teltevskij, D.

Mikhailova, S. Oswald, M. Klose, G. Stephani, R. Hauser, J. Eckert, and L. Giebeler, Energy Storage Mater. **6**, 26 (2017).

27. V. Etacheri, O. Haik, Y. Goffer, G. A. Roberts, I. C. Stefan, R. Fasching, and D. Aurbach, Langmuir **28**, 965 (2012).

28. L. Chen, X. Xie, B. Wang, K. Wang, J. Xie, Mater. Sci. Eng. B 131, 186 (2006).

29. Q. Li, X. Liu, X. Han, Y. Xiang, G. Zhong, J. Wang, B. Zheng, J. Zhou, and Y. Yang, ACS Appl. Mater. Interfaces **11**, 14066 (2019).

30. F. Holtstiege, P. Bärmann, R. Nölle, M. Winter, and T. Placke, Batteries 4, 1 (2018).

31. Z. Yi, N. Lin, Y. Zhao, W. Wang, Y. Qian, Y. Zhu, and Y. Qian, Energy Storage Mater. (2018).

32. Y. Yang, X. Qu, L. Zhang, M. Gao, Y. Liu, and H. Pan, ACS Appl. Mater. Interfaces 10, 20591 (2018).

33. B. Rangasamy, J. Y. Hwang, and W. Choi, Carbon N. Y. 77, 1065 (2014).

34. W. An, B. Gao, S. Mei, B. Xiang, J. Fu, L. Wang, Q. Zhang, P. K. Chu, and K. Huo, Nat. Commun.10, 1 (2019).

35. L. Lin, Y. Ma, Q. Xie, L. Wang, Q. Zhang, and D. L. Peng, ACS Nano 11, 6893 (2017).



Fig. 1. (a) XRD patterns of Si/Cu₆Sn₅/C composite before and after (porous composite) etching, (b) SEM images of porous Si/Cu₆Sn₅/C composite, (c) TEM image of porous Si/Cu₆Sn₅/C composite (d) FIB image and (e) corresponding EDS images of porous Si/Cu₆Sn₅/C composite.



Fig. 2. (a) N₂-isotherm curves (inset: pore width distribution) of porous Si/ Cu₆Sn₅/C composite, (b) ¹¹⁹Sn Mössbauer spectra (300K) of Si/ Cu₆Sn₅/C composite before and after etching



Fig. 3. XPS core-level spectra and fitting curves of (a) as-synthesized Cu_6Sn_5 and (b) porous Si/Cu₆Sn₅/C composite



Fig. 4. Voltage curves *vs.* specific capacity of (a) porous Si and (b) porous Si/ Cu_6Sn_5/C composite at C/100. Cyclic voltammetry curves of (c) porous Si and (d) porous Si/ Cu_6Sn_5/C composite at the scan speed of 0.3 mV.s⁻¹.



Fig. 5. Electrochemical performance of porous Si and Si/Cu₆Sn₅/C composite: (a) specific capacity and coulombic efficiency vs.cycle number in galvanostatic regime (C/20 for 3 cycles and cycling at C/3), (b) cumulated RIC_{DISCONN} vs. cycle number, and (c) C-rate capability.



Fig. 6. (a) *Ex-situ* XRD patterns of pristine Si/Cu₆Sn₅/C composite at different voltages during discharge.
(b) Electrochemical impedance spectra of the Si/Cu₆Sn₅/C composite at the end of the 1st and 25th discharge (inset: equivalent circuit with R1: electrolyte resistance; R2: resistance of SEI; R3: resistance of charge transfer).

Atomic (%)	C 1s	Si 2p	Sn 3d	O 1s	Cu 2p
Cu ₆ Sn ₅	61	-	9	26	4
Si/Cu ₆ Sn ₅ /C (after etching)	68	10	1	20	2

Table 1. Atomic composition from XPS survey

 Table 2 Comparison between previously published works on Si-based anode materials for Li-ion batteries and the present results.

Composition	Si precursor and synthetic method	Capacity retention (%)	Formulation (Active material: binder: conductive)	Cycling performance
Ball-milled Si [25]	Si, 1-5 µm powder, high-energy ball milling	60	80:12:8	1500 mAhg ⁻¹ at 50 th cycle, 480 mA g ⁻¹
Si/CNT composite [31]	Al-Si microsphere, wet chemical method and heat	80	70:15:15	1275 mAh g ⁻¹ at 100 th cycle, 200 mA g ⁻¹
Coated Si [32]	Si 2.5 µm powder, pressed ball milling	72	70:20:10	1439 mAh g ⁻¹ at 100 th cycle, 100 mA g ⁻¹
Si/CuO/graphene [33]	Si nano powder, wet chemical method and annealing	~71	Not mention	~1100 mAh g ⁻¹ at 100 th cycle, C/2
Bulk porous Si [34]	metallurgical Si 1-3 μm, 3 steps of heat and wet chemical method	~70	80:10:10	~1250 mAh g ⁻¹ at 100 th cycle, C/2
This work	Al-Si 5 μm powder, 2 steps: low speed ball milling and chemical etching	90	70:17:13	830 mAh g ⁻¹ at 100 th cycle, 420 mA g ⁻¹