Porous Si-Al Composite Anode with Three-Dimensional Macroporous Substrate for Lithium-Ion Batteries

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I. Introduction

Lithium ion batteries (LIBs) are widely used nowadays as a power supply for portable electronic devices. To meet with the ever-increasing demand on specific energy density and safety of the LIBs for diverse applications, including portable electronics, hybrid and electric vehicles, and grid-scale energy storage systems,1-3 the exploitation of new anode materials with improved performances has become the key issue in the development of the smaller, lighter, and longer-lasting LIBs. Among various anode materials, silicon is one of the most promising candidates as an anode material for next generation LIBs due to its high theoretical capacity of 4200 mAh g⁻¹ (~9800 mAh mL⁻¹ for Li₄.₈Si,⁴ ten times that of graphite), low electrochemical potential versus Li/Li⁺ (~0.5 V), abundance, low cost and environmental friendliness.⁵⁻⁷ However, the major problems in utilizing silicon and silicon-based anodes are their poor conductivity and very large volume change (about 310%) during lithium alloying/dealloying (or lithiation/delithiation) process,⁶ which causes the mechanical failure of the active material and thus results in the pulverization and poor cycle performance of the electrode.⁷⁻¹⁰ To improve the conductivity and cyclability of silicon materials, great efforts have been paid on the design of novel nanostructured materials.

Attempts are under way to solve the issue by using composites,¹¹ nano-structured silicon,¹² amorphous silicon,¹³ thin film by vacuum deposition¹⁴ or magnetron sputtering,¹⁵⁻¹⁷, ¹⁸ pillar structure,¹⁹ and so on. Although the remarkable improvements have been achieved by these studies, the cycle performance is still unacceptable in practical applications. Recently, silicon-based electrodes with porous substrates have attracted great interests in both fundamental and applied research. Jiang et al. casted the milled silicon powders into the three-dimensional (3D) copper architecture, which exhibited good cycling performance but unsatisfactory specific capacity.²⁰ The major advantages of such a 3D architecture have been proved: (i) the large open pores allow easy transport of liquid electrolyte; (ii) it is beneficial for fast transferring of lithium ions...
due to short Li⁺ diffusion length or pathway; (iii) the high specific surface area of 3D architecture ensures a large number of active sites for charge-transfer reactions and the active materials are not easy to fall off, thus improving the electrical conductivity; (iv) it provides sufficient space to alleviate the volume change of active materials during lithiation/delithiation, relax the stress/strain, improve the mechanical stability of the electrode structure, and consequently improve cycle-life and coulombic efficiency of the electrode.\(^\text{21}\)

Aluminum exhibits high electrical conductivity, and is active to Li. The theoretic capacity of Al is 2234 mAh g⁻¹ for Al₄Li₋ₓ.\(^\text{22-23}\) Moreover, the two active components (Si and Al) can realize the high capacity of electrode and make the volume change of electrode taking place in a stepwise manner due to their different lithiation potentials, leading to a stable cycling performance.\(^\text{24-25}\)

The addition of Al in silicon and silicon-based anode materials could improve the electrical conductivity (i.e., the addition of Al improves the charge transfer kinetics) and decrease the volume effect of the electrodes.\(^\text{26-27}\)

In this paper, the porous Si-Al composite anodes were fabricated by coating and casting using 3D macroporous copper substrates as current collectors, combined with subsequent heat treatment under various temperatures (including alloying and annealing treatment). The Si and Al microparticles were successfully embedded into 3D macroporous copper substrates. It has demonstrated that the Si-Al composite anode showed the high insertion/extraction capacity, capacity retention, enhanced structural stability and long cycle life, mainly attributed to the optimal heat treatment process and its unique 3D macroporous structure.

2. Experimental section

2.1 Electrode fabrication

Micron-sized silicon powder (Fuzhou Hokin Chemical Technology Co., Ltd., China, \(D_{50} = 1.5 \, \mu m\)) and micron-sized aluminum powder (Hunan Goldhorse Aluminum Industry Co., Ltd., China, \(D_{50} = 1.8 \, \mu m\)) were used as the active materials of preparing the anode. 3D macroporous copper (130 PPI pore size, 100 g m⁻³ surface density, 60 μm thickness, Alantum Advanced Technology Materials Co., Ltd., China) was used as a supporting substrate (i.e. current collector) for electrode fabrication. Firstly, 3D macroporous copper was cleaned with acetone and alcohol followed by drying in vacuum. The slurries were prepared by mixing 75.0 wt.% Si, 15.0 wt.% Al, 8.5 wt.% PAAlLi (Lithium polyacrylate, 10% purity solution), and 1.5 wt.% CMC (sodium carboxymethyl cellulose) in water. The composite electrodes were fabricated by coating and casting slurries onto 3D macroporous copper. Then, they were dried at 80 °C in vacuum for 2 h and compressed under pressure of 5 MPa. Following the compress, the electrodes were alloying treated in a high-vacuum furnace at pressure \(\geq 1 \times 10^{-3}\) Pa. Thereafter, the temperature was reduced to pre-specified levels for annealing treatment. Considering the melt points of Si (1410 °C) and Al (660.4 °C), and the size and thickness of the electrodes, the electrodes were processed at the alloying treatment temperatures of 600, 400, and 200 °C for 120 min and then treated at 150 °C for 60 min. The application of different alloying treatment temperatures resulted in varied microstructure and electrochemical properties of the porous Si-Al composite anodes. The mass loading of porous Si-Al composite anode was obtained by measuring the weight difference of the substrate and electrode. The areal mass loading of the active material is about 5.7 mg per cm² of the anode.

2.2 Characterization

The structure and morphologies of the substrate and porous Si-Al composite anodes without/with heat treatment were observed by scanning electron microscopy (SEM, FEI Quanta 200, USA). The chemical compositions of porous Si-Al composite anode were examined using SEM-equipped energy dispersive X-ray analysis (EDX, AMETEK Apollo XP, USA). The phase structures of porous Si-Al composite anodes were analyzed by X-ray diffraction (XRD, Bruker D8 Advance, Germany) with Cu Kα radiation in the scanning range of 20–85°.

2.3 Electrochemical evaluation of the porous Si-Al composite

To evaluate the electrochemical properties of the porous Si-Al composite anodes, the 2430-type half-cells (2 cm² in area) containing the porous Si-Al composite anode, separator, electrolyte and lithium foil as the counter electrode were assembled in Ar (99.995%)-filled glove box (Vacuum Atmospheres, Mikrouna, Universal 1220/1000, <10 ppm O₂ and H₂O). The electrolyte used in the experiments was 1 mol L⁻¹ LiPF₆ dissolved in a 1:1:1 (v/v) mixture of ethylene carbonate (EC), dimethyl carbonate (DMC) and ethyl methyl carbonate (EMC) with 1 wt% vinylene carbonate (VC) additive. The crimped coin cells were removed from the glove box and

Figure 1. SEM image showing the 3D structure of macroporous copper substrate.
allowed to equilibrate for 12 h prior to galvanostatic cycling. At room temperature, all galvanostatic charge/discharge tests were performed at a constant current density of 100 mA g⁻¹ (0.1C rate) using an Arbin battery test system (Arbin, BT 2000-8A) up to 100 cycles. The cells were discharged from the initial open-circuit voltage to 0.005 V versus Li⁺/Li, and cycled between 0.005 and 2.0 V after the first charge.

3. Results and discussion

Figure 1 shows SEM image of 3D structure for macroporous copper substrate. Obviously, copper substrate is 3D interconnected macroporous reticular structure. Furthermore, the 3D macroporous copper has a large specific surface area. The surface morphologies of porous Si-Al composite anodes without heat treatment were analyzed by SEM and are shown in Figure 2. These porous Si-Al composite anodes showed a rough surface because the surface profile of the substrate. The active materials cover the substrate and have a dense structure without any gaps and cracks. Therefore, it can be concluded that the Si-Al composite anodes have a porous structure in macroscopic view, while having a relatively dense structure in microscopic view. The EDX analysis shows that the Si/Al composition ratio is about 5 : 1. Figure 3 shows the surface morphologies of porous Si-Al composite anodes with heat treatment (a and b: 200 °C × 2 h + 150 °C × 1 h; c and d: 400 °C × 2 h + 150 °C × 1 h; e and f: 600 °C × 2 h + 150 °C × 1 h). It is evidently found that the heat treatment at different temperatures has a great effect on the morphology of the anode materials. For the anodes treated at 200 or 400 °C, the morphologies of the resulting materials

![Figure 1](image1)

![Figure 2](image2)

![Figure 3](image3)
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have no significant change compared to that for the original one (Figure 3 a–d). However, for the porous Si-Al composite anode heat treated at $600 \, ^\circ\text{C} \times 2 \, \text{h} + 150 \, ^\circ\text{C} \times 1 \, \text{h}$, the morphology is significantly different from those treated at lower temperatures (Figure 3e). From the magnified image (Figure 3f), a lot of bigger crystalline particles were found in the porous Si composite. It indicates that the crystals grow fast with the increase in the heat treatment temperature. Thus, the difference in the morphology and surface particle size of porous Si-Al composite anodes heat treated at various temperatures will strongly affect the electrochemical performance of the final anode materials.

Figure 4 shows the typical XRD patterns of the porous Si-Al composite anodes with 3D macroporous copper substrate. The XRD result illustrates that the diffraction peaks in porous Si-Al composite anode without heat treatment are mainly attributed to the crystalline silicon, aluminium and copper. The diffraction peaks of crystalline $\text{Al}_5\text{Si}$ (PDF# 65-8554) in the porous Si-Al composite anode heat treated at $200 \, ^\circ\text{C} \times 2 \, \text{h} + 150 \, ^\circ\text{C} \times 1 \, \text{h}$ is very weak, and the peaks of crystalline $\text{Al}_5\text{Si}$ and Al almost overlap together. The porous Si-Al composite anode heat treated at $400 \, ^\circ\text{C} \times 2 \, \text{h} + 150 \, ^\circ\text{C} \times 1 \, \text{h}$ possibly consists of large amount of crystalline $\text{Al}_5\text{Si}$ (PDF# 65-8554), $\text{Cu}_3\text{Si}$ (PDF# 65-9054) and a few crystalline $\text{Cu}_3\text{Si}$ (PDF# 51-0916), determined by the XPS analysis. Furthermore, the peaks of crystalline $\text{Cu}_3\text{Si}$ and Cu almost overlap together. With increasing the temperature, the diffraction peaks of crystalline $\text{Al}_5\text{Si}$ (PDF# 65-8554), $\text{Cu}_3\text{Si}$ (PDF# 65-9054) and $\text{Cu}_3\text{Si}$ (PDF# 51-0916) in the porous Si-Al composite anode heat treated at $600 \, ^\circ\text{C} \times 2 \, \text{h} + 150 \, ^\circ\text{C} \times 1 \, \text{h}$ are relatively intense and sharp, indicating that larger sizes of the crystalline grains. Thus the amount of alloys increases, while the amount of active materials decreases with increasing the treat temperature. These resultant alloyed particles should be attributed to the atom diffusion during the heat treatment. Comparing the porous Si-Al composite anode heat treated at $600 \, ^\circ\text{C} \times 2 \, \text{h} + 150 \, ^\circ\text{C} \times 1 \, \text{h}$ and the porous Si-Al composite anode heat treated at $400 \, ^\circ\text{C} \times 2 \, \text{h} + 150 \, ^\circ\text{C} \times 1 \, \text{h}$, the former has a shaper peak than the latter, showing that the crystallinity degree and crystalline grains size of the former are larger than these for the latter.

Figure 5 shows the cycle performance of porous Si-Al composite anodes without/with heat treatment. For the porous Si-Al composite anode without heat treatment, the first extraction capacity and initial coulombic efficiency are 2225 mAh g$^{-1}$ and 86.5%, respectively. And the reversible capacities retain 46.9% of the second extraction capacity after 100 cycles. For the porous Si-Al composite anode heat treated at $200 \, ^\circ\text{C} \times 2 \, \text{h} + 150 \, ^\circ\text{C} \times 1 \, \text{h}$, the first extraction capacity and initial coulombic efficiency are 2175 mAh g$^{-1}$ and 89.0%, respectively. And the reversible capacities retain 65.4% of the second extraction capacity after 100 cycles. For the porous Si-Al composite anode heat treated at $400 \, ^\circ\text{C} \times 2 \, \text{h} + 150 \, ^\circ\text{C} \times 1 \, \text{h}$, the first extraction capacity and initial coulombic efficiency are 2134 mAh g$^{-1}$ and 90.5%, respectively. And the reversible capacities retain 84.0% of the second extraction capacity after 100 cycles. For the Si-Al composite anode heat treated at $600 \, ^\circ\text{C} \times 2 \, \text{h} + 150 \, ^\circ\text{C} \times 1 \, \text{h}$, the first extraction capacity and initial

![Figure 4. Typical XRD patterns of porous Si-Al composite anodes with three-dimensional macroporous substrate. (a) without heat treatment, (b) $200 \, ^\circ\text{C} \times 2 \, \text{h} + 150 \, ^\circ\text{C} \times 1 \, \text{h}$, (c) $400 \, ^\circ\text{C} \times 2 \, \text{h} + 150 \, ^\circ\text{C} \times 1 \, \text{h}$, and (d) $600 \, ^\circ\text{C} \times 2 \, \text{h} + 150 \, ^\circ\text{C} \times 1 \, \text{h}$.](image)

![Figure 5. Extraction-insertion capacity and coulombic efficiency as a function of cycle number for the porous Si-Al composite anodes with three-dimensional macroporous substrate.](image)


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coulombic efficiency are 2110 mAh g⁻¹ and 89.8%, respectively. And the reversible capacities retain 64.3% of the second extraction capacity after 100 cycles. The irreversible capacity and low coulombic efficiency of the first cycle are ascribed to the reductive decomposition of the electrolyte solution and the subsequent formation of a solid electrolyte interphase (SEI) layer on the surface of composite electrode.⁸ In addition, the irreversible loss for the first cycle should be ascribed to the delamination during the first charge of a small portion of the composite. The fractured edge in the composition was formed during the electrode punching. At the second and sequential cycles, the irreversible capacities decrease, namely, coulombic efficiencies increase significantly. This means that after the first cycle, the microstructures of porous Si-Al composite anodes become stable. In contrast, the porous Si-Al composite anode heat treated at 400 °C × 2 h + 150 °C × 1 h exhibited the best cycle performance among these composite anodes, providing a rechargeable capacity of 1761 mAh g⁻¹ after 100 cycles (Figure 5a). It can be found that the coulombic efficiency of the porous Si-Al composite heat treated at 400 °C × 2 h + 150 °C × 1 h increases rapidly with increasing cycles and maintains a relatively stable value in the subsequent cycles (Figure 5b), indicating the highest charge and discharge efficiency among these porous Si-Al composite anodes. This is attributed to the formation of the alloy, improving the system performance. However, with the temperature increasing, the amount of alloys increase (i.e. the amount of active materials decrease), resulting in the decrease of the capacity. Furthermore, the crystallinity degree and crystalline grains size of the porous Si-Al composite heat treated at 600 °C × 2 h + 150 °C × 1 h are larger than these of the porous Si-Al composite heat treated at 400 °C × 2 h + 150 °C × 1 h, so the electrochemical performance of the former is evidently worse than that of the latter.

The charge-discharge curves of the porous Si-Al composite without/with heat treatment are presented in Figure 6. It shows that there is a plateau at about 0.25 V vs. Li⁺/Li during the first lithiation process for the porous Si-Al composite without heat treatment (Figure 6a), while this plateau occurs at about 0.45 V vs. Li⁺/Li during the first lithiation process for the porous Si-Al composite anodes heat treated at various temperatures (Figure 6 b-d). The reason of the difference is that the porous Si-Al composite without heat treatment does not have any alloy phase. For the porous Si-Al composite anodes without/with heat treatment, the second and following charge curves differed from the first one, suggesting the existence of the drastic, lithium-driven, structural or textural modifications.⁹ Hamon et al. reported that for Al, there was a plateau at about 0.26 V vs. Li⁺/Li during the lithiation process and at 0.50 V vs. Li⁺/Li during the delithiation process, respectively.²² However, because the content of Al is relatively low (only 16.7% accounting for the total amount of active materials), the lithiation/delithiation plateaus of Al is not very obvious in the present research. Also, because the lithiation/delithiation plateaus of Si and Al is very close, so there may be overlapped. Comparing the charge-discharge curves of porous Si-Al composite anodes, the capacity fade of porous Si-Al composite without heat treatment is the fastest and largest (Figure 6a). With increasing temperature of heat treatment, the capacity fade firstly becomes small (Figure 6 b-c), and then becomes large (Figure 6d). However, the capacity fade of the porous Si-Al composite heat treated at 400 °C × 2 h + 150 °C × 1 h is the slowest and smallest among these composites anodes. It is evident that the heat treatment under appropriate conditions (400 °C × 2 h + 150 °C × 1 h) has improved significantly the charge-discharge performance of the porous Si-Al composite electrode, which may be attributed to the formation of two kinds of Cu-Si alloys between active material and 3D macroporous copper substrate, and an Al-Si alloy between active materials during the heat treatment. Thus the heat-treated samples show the improved cycling performance compared to the porous Si-Al composite anode without heat treatment.

The above results suggest the enhanced structural stability and superior electrochemical properties of porous Si-Al composite anodes, which can be mainly attributed to heat treatment under appropriate conditions. Silicon, aluminum and copper diffuse into the interfaces by heat treatment. Al-Si alloy was possibly formed within the interfaces of the active materials, while Cu-Si and Cu-Si alloys were produced at the interfaces of the active materials and macroporous copper current collector. These alloys have decreased the swelling amount of the active materials during the discharge-charge process. It is considered that these alloys may also decrease the reactivity of the active materials at the same time. The stress at the interfaces by the swelling of the active materials decreases, and the separation of the active materials from the interface are suppressed.³⁰ The mechanical stability of porous Si-Al composite anodes assisted by the appropriate heat treatment guarantees their excellent cyclability. The adhesion between the Si-Al composite and the
3D macroporous copper was strengthened by heat treatment under appropriate conditions (400 °C × 2 h + 150 °C × 1 h). Meanwhile, it has assumed that this is originated from the interface binding force between the porous Si-Al composite and the 3D macroporous copper current collector, the stress during discharge can be released partly to prevent the active materials from pulverizing and delaminating from the 3D macroporous copper current collector.

4. Conclusions

Porous Si-Al composite anodes were fabricated by coating and casting using 3D macroporous copper substrates as current collectors as well as subsequent heat treatment at various temperatures (including alloying and annealing treatment). It has demonstrated that the porous Si-Al composite anode showed high insertion/extraction capacity, capacity retention, enhanced structural stability and long cycle life which can be mainly attributed to the optimal heat treatment process. For the porous Si-Al composite heat treated at 400 °C × 2 h + 150 °C × 1 h, the first extraction capacity and initial coulombic efficiency are 2134 mAh g⁻¹ and 90.5%, respectively. And the reversible capacities retain 84.0% of the second extraction capacity after 100 cycles.

Future work will focus on studying the composition of porous Si-Al composite anodes. The uniform distribution of Si and Al particles in the 3D macroporous copper will also be studied. It is envisaged that by optimizing the parameters, such as Si and Al grain sizes, crystallite structure, composition, pore size and porosity of the macroporous substrate, both the capacity and reversibility of these materials can be further improved. It is expected that the porous Si-Al composite anode with 3D macroporous substrate will be improved for practical application in the near future.

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