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Binder-free anode with porous Si/Cu architecture for lithium-ion batteries

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ABSTRACT

Binder-free porous Si/Cu architecture with the unique Cu walls wrapped Si/Cu porous network as lithium-ion battery anode was fabricated by laser remelting, diffusion bonding and dealloying processes. The porous network had enough space to allow for the large expansion of Si during lithation. The Cu walls and Cu skeletons could prevent loss of electrical contact between pulverized Si and current collector. The laser remelting influenced the Cu diffusion behavior during diffusion bonding, and was the most critical process for the fabrication of porous Si/Cu architecture.

The lithium-ion batteries (LIBs) have been widely used in portable electronic devices due to their high energy density and long cycle life [1]. Nevertheless, there are still many critical challenges remaining for high energy/power density applications including ever increasing demand for large capacity and better safety [2,3]. Si anode for LIBs has been intensively investigated to achieve the above goals due to its high lithiation capacity, environmental friendliness, and earth-abundant [4–11]. However, the practical implementation of Si anode is impeded by well-known detrimental pulverization effect and conductivity fading during charge and discharge, which mainly caused by the following two-phase reactions [12].

(1) Crystalline Si ↔ Amorphous Li_xSi (a-Li_xSi)
(2) Amorphous Li_xSi ↔ intermetallic $Li_{15}Si_4$ (i-$Li1_5Si_4$)

The inhomogeneous volume expansion (difference could reach 270%) during the above reactions induces severe stress causing Si pulverization and peeling from the current collector, which results in the conductivity deteriorates continuously [2,3]. Conventionally, the Si anode is obtained by coating a mixed slurry of Si powder, binder and conductive agent onto the current collector. Si powder with fine structure has been considered to be able to accommodate large stress mismatches, and various binders and conductivity agents have been used to enhance the cohesion strength and electrical contact with the current collector [4,5,10,13,14]. Recently, some binder-free anodes have been developed such as physically deposited Si thin film [15,16] and chemically in-situ grown nanorods of Si on the Cu substrate [17], which have shown promising electrochemical performances.

Herein, we demonstrate a binder-free porous Si/Cu architecture with fine Si flakes metallurgically bonded with Cu substrate, which can be realized through laser remelting-diffusion bonding-dealloying hybrid method. The porous Si/Cu architecture prevents pulverized Si losing electrical contact, which therefore renders both strong cohesion and good conductivity. Our data suggests that laser remelting process can modify the microstructure of the initial material, which helps form a unique porous network structure after subsequent diffusion bonding and dealloying processes. By providing a new way for fabrication of binder-free electrode with integrated current collector and active materials, the proposed laser remelting-diffusion bonding-dealloying hybrid method has great potential in the fabrication of energy conversion and storage devices.

The binder-free anode with porous Si/Cu architecture was fabricated through laser remelting, followed with diffusion bonding and dealloying treatment as illustrated in Fig. 1. First, a fiber laser (IPG YLS-6000) with a power of 5.5 kW and a beam diameter of 6 mm scanned over the as-cast AlSi12 (88 wt% Al and 12 wt% Si) alloy plate (100 mm × 50 mm × 10 mm) at the speed of 7 mm/s to form a 3-mm-thick laser remelting layer with fine dendrite microstructure. The laser remelting Al-Si layer was then cut from the substrate with diameter of 8 mm and polished to flat and mirror-like surface with 150 μm thickness for diffusion interface. Next, the 150-μm-thick laser remelting Al-Si layer was metallurgically bonded with Cu substrate through vacuum diffusion bonding process with vacuum level of 10^{-3} Pa (Beijing Jinxiang Aerospace Equipment Co. Ltd. HT-QA-25) to form Al-Si/Cu composite. Under diffusion pressure of 0.5 MPa, the diffusion

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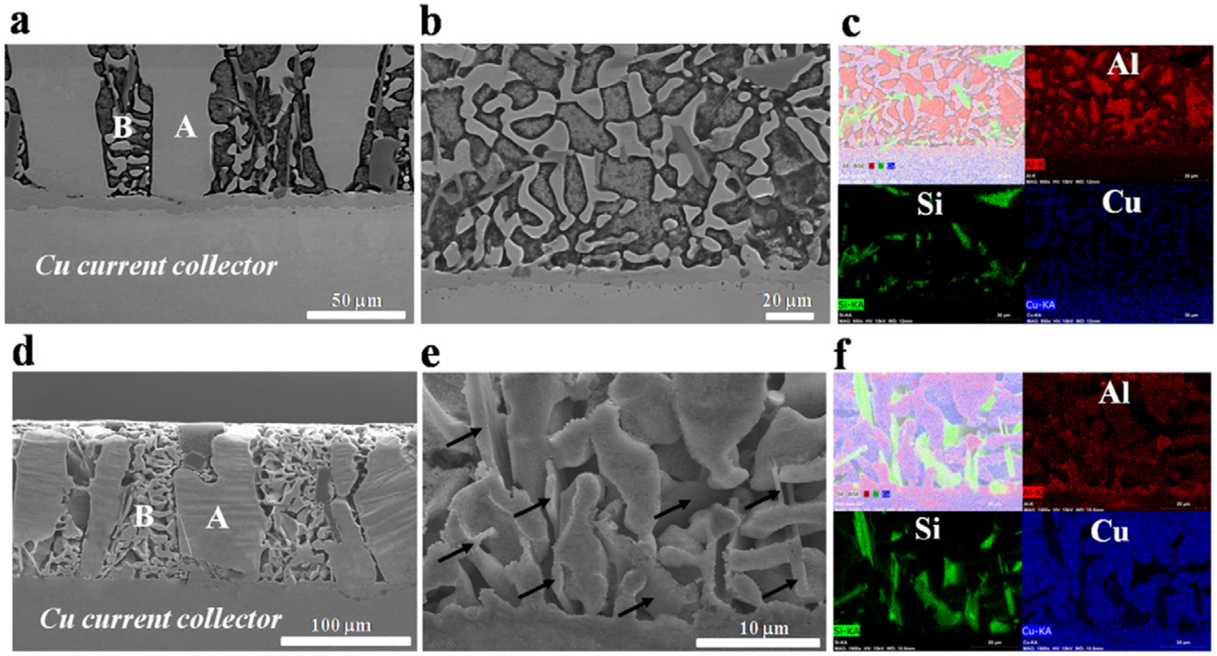

Fig. 1. Microstructure evolution during fabrication: (a)–(c) Al-Si/Cu composite after laser remelting and diffusion bonding. (d)–(f) porous Si/Cu architecture after dealloying.

temperature and holding time were 550 °C and 60 min, respectively. Finally, the diffusion bonded samples were immersed in 3 M HCl solution for 6 h to remove Al, and then immersed in 2 wt% HF solution for 1 h to eliminate the oxides may be generated, leaving a Cu walls wrapped Si/Cu porous network. After each step, the samples were rinsed by deionized water.

The morphology of the samples was examined by a scanning electron microscope (SEM, Hitachi S-3400) equipped with energy dispersive spectrometer (EDS, Lash Detector 5051). To analyze the composition, X-ray diffraction patterns were recorded by an X-ray diffractometer (XRD, Bruker D8 Advance, Cu target). Coin cells (CR2025-type) were assembled in a glove box with the concentrations of moisture and oxygen both below 1 ppm, with Li foils and Celgard 2400 membranes as the counter electrode and the separators. The electrolyte is 1 M LiPF6 in a 50:50 w/w mixture of ethylene carbonate and diethyl carbonate. Cyclic voltammetric (CV) scans (Autolab 302N) were recorded at a scan rate of 0.05 mV/s. Assembled cell was discharged (lithium insertion) by a constant current mode (1 mA/cm^2) to 0.1 V, and charged (lithium extraction) by a constant current mode to 1.5 V followed by a constant voltage mode (until current down to 20%).

Before dealloying process, the Al-Si/Cu composite fabricated through laser remelting and diffusion bonding contained the perpendicular walls (region A) and dendrite microstructures (region B) wrapped by the walls as shown in Fig. 1a. Both regions were mellurgically bonded with below Cu substrate. It is noted that a composition of 34.9 at.% Cu and 65.1 at.% Al were identified by EDS in the region A, indicating the formation of Al_2Cu according to the Al-Cu binary phase diagram. The grey matrix in the region B was α-Al solid solution and the large volume white phase was Al_2Cu (35.2 at.% Cu and 64.8 at.% Al) as shown in Fig. 1b and c. Some flaky phase embedded in the matrix was crystal Si. The results indicated that Cu from the substrate diffused into the laser remelting Al-Si layer during diffusion bonding process.

After dealloying process, the Al atoms were selectively etched, leaving the porous Si/Cu architecture. As shown in Fig. 1d, the porous architecture consisted of walls perpendicular to Cu substrate surface (region A) and porous network (region B) wrapped by the walls. In region A, 96.5 at.% Cu with a little Al was identified, where the Al atoms may be distributed in the Cu solid solution. At a higher magnification (Fig. 1e), microflakes with a few microns in length can be observed in region B. Fig. 1f shows there are two kinds of microflakes in region B: Si microflakes and Cu-based microflakes (Cu95Al4Si1, at.%). The Cu-based microflakes were metallurgically bonded with the Cu current collector and interconnected with each other to form porous skeleton, where Si microflakes were embedded in. It is obvious that the structure features of porous Si/Cu architecture were derived from those of the Al-Si/Cu composite.

Fig. 2a–d show the XRD patterns of the initial as-cast AlSi12 alloy, the laser remelting Al-Si layer, the Al-Si/Cu composite, and the final porous Si/Cu architecture, respectively. The XRD pattern of the initial as-cast AlSi12 alloy can be indexed to Al and Si phase, as indicated in Fig. 2a. Carefully conducted laser remelting treatment did not alter the phases (Fig. 2b). After diffusion bonding, a new phase Al_2Cu appeared in the Al-Si/Cu composite (Fig. 2c) consistent with EDS results, which suggested Cu atoms have diffused into the laser remelting Al-Si layer. Only Si and Cu were left in the final porous Si/Cu architecture after dealloying (Fig. 2d).

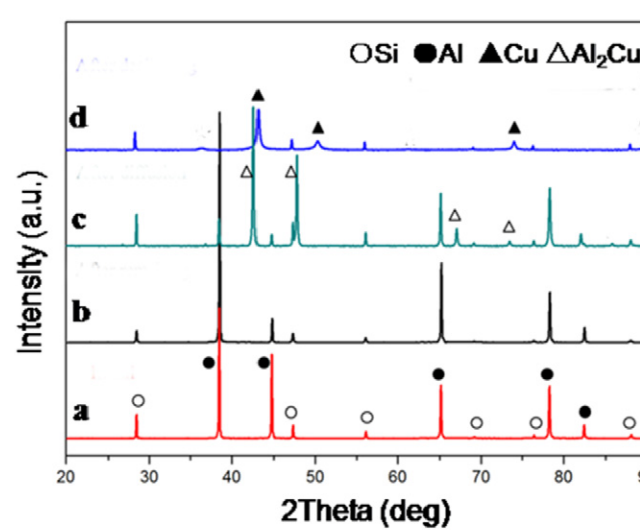

Fig. 2. XRD patterns. (a) Initial as-cast AlSi12 alloy. (b) Laser remelting Al-Si layer. (c) Al-Si/Cu composite. (d) porous Si/Cu architecture.