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Designing self-standing silicon-copper composite helices as anodes for lithium ion batteries

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A B S T R A C T

In this study, we have fabricated helical thin films to be used as an anode material in lithium ion batteries (LIB). The thin films having various Cu–Si atomic ratios (30–70%, 20–80%, and 10–90%) are prepared by using ion-assisted glancing angle co-deposition.

Cu plays a crucial role in holding the electrode together, minimizing overall capacity loss and enabling faster electron transfer thus, improving the electrochemical performances of the electrodes. Increasing the Cu/Si atomic ratio affects the structure of the helices and their alignment. Implementing ion assisted deposition at the beginning of the film deposition helps to improve film adhesion. The Si-20 at.% Cu anode delivers 1885 mAh g^{-1} initially with 98% coulombic efficiency and retains 77% of the capacity after 100 cycles at 100 mA g^{-1}.

1. Introduction

Lithium-ion batteries (LIBs) are the most promising energy storage system for medical, portable electronic devices (cell phones, laptops, and digital cameras) and power sources for future electric and hybrid vehicles [1–4]. Nowadays, increase in the energy density of the current commercial lithium-ion batteries (LIBs) is highly required. The performance of LIBs depends on the active materials employed for Li storage in electrodes. The main requirements for active materials are high Li^+ diffusion coefficient, high electronic conductivity, safety, low cost, environmental compatibility and high reversible capacity for long cycle life [2–8].

Graphite has been mostly used as an anode material in LIBs. However, its theoretical capacity (372 mAh g^{-1}) is not high enough to satisfy high energy density requirements for advanced applications. Therefore, to improve the energy and power densities of LIBs, the use of alternative materials such as silicon (Si), tin (Sn), magnesium (Mg), and antimony (Sb) has been investigated [9–12].

Silicon has a theoretical capacity of 3579 mAh g^{-1} (at room temperature) and has a moderate working potential (0.4 V vs Li/Li^+) that promotes the safe use of the battery by avoiding lithium deposition in cycling. However, Si anodes face several challenges in becoming a commercially viable electrode. First, Si undergoes a high volume expansion (around 300%) during lithiation process resulting in an immense stress (as high as 1 GPa) generation [13,14]. Such high pressure causes pulverization, cracking, and delamination from current collector thus, a failure in the early stages of cycling. Second, in lithiation when voltages go below the reduction potential of the electrolyte, a passive film (so called solid-electrolyte interphase (SEI)) is formed at the electrode/electrolyte interfaces. This SEI which mostly contains organic and inorganic products prevents the direct reaction of active materials with the electrolyte [15]. Finally, the low electrical conductivity of Si material decreases the efficiency during cycling [13,16].

Recently, compositional and/or morphological improvements have been proposed to overcome the disadvantages of Si anodes by increasing the electrical conductivity and mechanical stability. In this sense, they have suggested to form Si-M alloys where M stands for ductile and electrochemically inactive metals (versus Li^+) or disperse Si particles in an inactive buffer matrix [17–19]. So far, in literature Cu has been used as an inactive but beneficial electrode additive in various forms [20–22]. Its presence in Si based anodes provides new electron pathways, reducing polarization and inhibiting the agglomeration of Si particles in cycling. Being ductile Cu also buffers the stress that occurs upon cycling [23]. In addition, Cu-containing particles, such as Cu_3Si intermetallics enhance reversibility in galvanostatic test [23,24]. Moreover, Cu increases the

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adhesion of the anode to the current collector (Cu) leading to a longer cycle life with good capacity retention.

Even though some of the obstacles in front of Si anodes can be eliminated by using Cu, the huge volumetric expansion of the Si electrode upon cycling remains an issue. Thus, the possibility of using structured electrodes such as solid nanowires, hollow spheres and tubes have been studied [25,26]. Among them, yolk-shell structured Si electrodes [27], crystalline–amorphous core–-shell Si based nanowires [28] and double walled Si-SiO_x nanotubes [29] have been particularly analyzed as possible new generation negative electrodes. The results show that the high aspect ratio of the nanostructures provides short Li^+ diffusion path, which decreases polarization and makes electron transfer along the nanostructures faster. Plus, the free spaces among the nanostructures provide more rooms in the electrode to avoid fracture following the volumetric changes, yielding a longer cycle life.

To date, template-directed electroplating, chemical vapor deposition, direct chemical etching, and nanolithography have all been used to form structured composite electrodes [30–32]. However, long processing time, restricted aspect ratios of the nanostructures, safety concerns, difficulties in controlling morphology, and limited choices of materials to form nanostructures have led investigators to look for alternative production techniques [33,34]. Among others, glancing angle deposition (GLAD) becomes remarkable because of its significant advantages: GLAD enables researchers to fabricate 3D nanostructures using various precursors. Plus, it is possible to both control the alignment of the nanostructures and their interfacial properties in GLAD method [35–37]. Moreover, this process avoids the hazard of working with flammable, explosive, or carcinogenic metal nanoparticles, and permits direct deposition of nanostructures on the current collector eliminating the need for binders or additives. The latter ensures direct transport of electrons from electrode to current collector and fast Li+ diffusion through the small diameters of nanostructures. In the GLAD process, deposition flux impacts at a substrate with an angle of (α) >70° while rotating the substrate with two programmable stepper motors: one adjusts α, and the other controls the azimuthal rotation (Φ) of the substrate with respect to normal [38,39].

Various structures from zigzag to helices can be produced by GLAD. Helices, like “micro-springs,” are believed to be more resistant to normal stress, which is expected to improve the cyclability of the electrode versus Li. So far, metallic helices are produced for different purposes [39–41]. To date, composite SiCu helices formed by ion assistance (IA) method have not been produced and tested as anodes in LIBs.

In this study, first in literature, we produced different Cu containing (30, 20, and 10 at.%). composite SiCu thin films with helical morphology. We believed that the incorporation of Cu into Si would change the structure as well as the morphology of the helices due to the difference in the atomic mobility of Cu compared to Si. Herein, ion assistance was used particularly to promote the film adhesion.

First time, the change in the morphology and the structure of the SiCu composite helices regarding the different Cu contents were determined by scanning electron microscopy (SEM), and X-ray diffraction (XRD) methods. The electrochemical performances of the anodes were examined in galvanostatic tests. Electrochemical impedance spectroscopy was also applied after the 1st and 30th cycles at 0.2 V.

2. Experimental procedures

The experimental setup used in this study was given in Fig. 1. During the GLAD evaporation stage, two quartz-crystal microbalances (QCMs) were used independently to monitor the deposition rates and thicknesses of Cu and Si, separately.

Four kinds of substrates were used: a Cu foil (≥99.99% purity, 1.5-mm thickness) for electrochemical analysis, as Cu is too ductile a Si wafer for cross-sectional SEM, a stainless steel disk (15.5-mm diameter and 1.5-mm thickness) for compositional and a glass disk with amorphous structure (Tedpella) for structural analyses. During the deposition, the samples were initially sputtered for 8 min using 900 eV Ar+ from a Kaufman ion source at a gas feeding rate of 8 sccm. The incident angle of Ar^+ to substrate normal was about 35° and the pressure in the chamber was 0.01 Pa. Once the substrates surfaces were cleaned, the shutters were opened and the deposition was started. At the beginning of each deposition, the ion energy was reduced to 250 eV and IA-GLAD was initiated (at 250 V and 23 mA) for 3 min to produce adherent films. Next, the Ar flow and ion gun were turned off, while the evaporation continued. The deposition current was 30 mA (beam). The discharge and accelerator voltages were 40 V and 100 V, respectively. The oxygen pressure was fixed around 8×10^{-5} Pa throughout the deposition.

To form helices, we fixed the substrate position so that the incident flux angle (α) was 80° with respect to the substrate normal. An azimuthal rotational speed was 0.2 rpm. For each experiment the film thicknesses was fixed to 600 nm as read from the sum of the values noted on the QCMs of Si and Cu.

Three SiCu samples were prepared with 30, 20, and 10 at. % Cu. The surface morphologies and the thicknesses of the “pristine” samples (i.e., no charging or discharging) were determined with field-emission SEM (JEOL JSM 7000F and JEOL 5410). The phases present in the pristine samples were determined by XRD (Philips PW3710 System) with a 2θ range of 10–90° in steps of 0.05° (with CuKα at 40 kV and 30 mA). The sample compositions were determined by EDS (Oxford) analysis (Table 1). The film weight was determined with a microbalance (My Weigh iBalance 101) before and after the deposition. The amount of active material was calculated by multiplying the total coating mass with the active material weight percentage determined in the EDS analyses (see Table 1).

For electrochemical testing, cells were assembled as 2032 coin cells in an Ar-filled glove box (Mbraun, Labmaster). The SiCu helices containing films were used as test electrodes, pure Li foils (≥99.99 at. %) as counter electrodes, and a porous polypropylene film (Celgard 2400) as a separator. The electrolyte was Merck quality. It was 1 M $LiPF_6$ dissolved in ethylene carbonate (EC) and dimethyl carbonate (DMC) in a 1:1 weight ratio. To improve the stability of the solid-electrolyte interphase (SEI) on the electrode, 10% vol. fluoroethylene carbonate (FEC) was added into the electrolyte [42]. The cells were tested at room temperature with 100 mA g^{-1} rate (areal mass loading is approximately 0.2 mg/cm^2), and operated at a voltage range of 0.2 V–1.2 V versus Li/Li^+. The cells were opened and disassembled after the 3rd, 30th, and 100th cycle. Next, the electrodes were washed with DMC and naturally dried in the glove box prior to surface examination.

Furthermore, an HS-3E test cell (Hohsen Corp., Japan) was constructed to accomplish cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The three-electrode configuration used for these tests was described in our previous work [43].

Cyclic voltammetry was performed for the 1st, 2nd, and 30th cycles in the range of 0.2 V–1.2 V (vs. Li/Li^+) at a scan rate 0.03 mV s^{-1}. Also, EIS analyses were done to measure the impedance of the electrode after 1st and 30th cycles in the frequency range of 10 mHz–10 kHz with 10 mV (rms) at 0.2 V (Gamry PCI4/750) discharge potential. To get the impedance of the samples at 0.2 V, the cell was discharged to 0.2 V, then, a certain amount of time was allowed for potential relaxation at open circuit voltage (OCV) (until the OCV potential drift was less than 0.5 mV h^{-1}).