

Short communication

Formation and characterization of Cu–Si nanocomposite electrodes for rechargeable Li batteries

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Abstract

We have investigated the structural and electrochemical properties of Cu–Si nanocomposite electrode fabricated by co-sputtering method. Reversible capacity of an amorphous Si electrode is degraded continuously with increasing cycle number up to 40 cycles. However, a Cu–Si nanocomposite electrode, where Cu nano-dots are embedded in an amorphous Si matrix, shows an excellent reversible capacity with a stable value of ca. $400 \mu\text{A h cm}^{-2} \mu\text{m}^{-1}$ up to 40 cycles. The improved reversible capacity of the Cu–Si nanocomposite electrodes is attributed to the enhanced structural stability of the electrodes due to the presence of the Cu nano-dots evenly distributed throughout the Si matrix.

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1. Introduction

Development and fabrication of high-capacity lithium rechargeable batteries are of particular importance for high-power electronic devices. Silicon has been proposed to serve as a possible anode material for replacing the current carbon-based materials (e.g. graphite) because Si itself has higher theoretical capacity (ca. $980 \mu\text{A h cm}^{-2} \mu\text{m}^{-1}$) than that of graphite [1–3]. However, Li insertion into the Si electrode causes structural damages, such as mechanical cracking caused by volume expansion/contraction of Si electrode, thus leading to decrease of cycling performance [2,4]. Consequently, Si alone is still insufficient for the practical use as an anode material of rechargeable Li batteries. Therefore, the prevention or the minimization of the structural changes of the Si electrode during repeated Li insertion and extraction processes is a key issue for the improvement of cycling performance, such as reversible capacity with stable values. In this regards, efforts have been made to improve the cyclability by suppressing the structural

changes in the Si electrodes [5–7]. Recently, the introduction of nano-sized particles in battery systems has been suggested to be one of efficient methods since the physical, electrical and chemical properties of electrode materials can be modified in the presence of nanophases [8–12]. In addition, the use of nanostructured electrodes appeared to strongly affect the reversible capacity of batteries. For example, nano-size Si particles distributed in a carbon matrix exhibited better cycle performance than individual component [6]. Xu and Jain showed that a nanocrystalline ferric oxide cathode could improve Li intercalation capacity and cycling performance. They attributed the enhanced intercalation properties to changes in thermodynamic and kinetic features from those of its microcrystalline counterpart [13]. However, the direct relationship between the structural and electrochemical properties of nanostructured electrodes in a battery system has not been clearly understood so far.

In this work, we have fabricated Cu–Si nanocomposite electrodes, where Cu nano-dots are embedded a Si matrix, by using a co-sputtering system. It is shown that the presence of the Cu nano-dots embedded in an amorphous Si matrix can effectively improve the cycling performance of Li rechargeable batteries.

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2. Experimental

The nanocomposite electrodes of Cu–Si thin films were grown using a RF magnetron sputtering system. Cu foil was used as substrates. The base pressure was less than 5×10^{-6} Torr and a working pressure was 5×10^{-3} Torr for all the electrodes examined. Sputtering was performed under an inert Ar gas atmosphere at 40 SCCM (standard cubic centimeter per minute) at room temperature (RT). Prior to sputtering, any contaminants on the target were removed by pre-sputtering for 30 min. The Cu–Si nanocomposite electrode (220 nm thick) was then deposited for 27 min at RF powers of 60 W (Si target) and 40 W (Cu target). For comparison, a single Si electrode was also prepared at 60 W for 35 min. High-resolution electron microscopy (HREM) bright field images and selected-area electron diffraction (SAED) patterns were obtained using a Phillips CM20T/STEM Electron Microscope at an accelerating voltage of 200 kV. XRD (Rigaku X-ray diffractometer equipped with a Cu K α source) analyses of the as-prepared electrodes were used to examine the structure and crystallinity of the samples. Data were collected over the range of 2θ from 20° to 60° in increments of 0.05° at room temperature. To determine the composition and chemical state of the samples, X-ray photoelectron spectroscopy (XPS) analyses were performed using a VG Scientific (ESCALAB 250) X-ray photoelectron spectrometer, with an Al K α source (1486.6 eV) operated at 15 kV and 150 W, at a base pressure of 2×10^{-9} Torr. Spectra were peak-fitted using bands with a mixed Gaussian–Lorentzian line-shape and a Shirley baseline. The thicknesses and microstructures of the prepared samples were investigated using field emission scanning electron microscopy (FESEM: Hitachi S-4100). To evaluate the electrochemical performance of the nanocomposite electrodes, the electrochemical properties for Li insertion and extraction were examined using a conventional two-electrochemical system. Test cells were fabricated with a working electrode of as-deposited thin-film and a metallic Li anode in an Argon-circulating glove box. A 1.0 M LiPF $_6$ solution in a 1:1 (vol.%) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) was used as the electrolyte. The test cells were aged for 12 h at 25°C after the addition of the electrolyte before electrochemical testing. The cell performance of the nanocomposite electrodes was evaluated by galvanostatically discharging and charging the cell at a constant current density of $20 \mu\text{A cm}^{-2}$ at a cut-off voltage of 0.0–2.0 V (versus Li/Li $^+$) at room temperature using a WBCS 3000 battery tester system (Won-A Tech corp., Korea).

3. Results and discussion

Fig. 1 shows HREM images and SAED patterns obtained from the single Si and Cu–Si nanocomposite electrodes. For the single Si electrode (Fig. 1(a)), the HREM image exhibits uniform speckle contrast and the SAED pattern (shown in the inset) reveals a broad diffuse ring, which represents characteristics of amorphous materials. For the Cu–Si nanocomposite electrodes (Fig. 1(b)), the HREM image shows uniform speckle contrast with dark blobs. The SAED pattern reveals sharp rings consisting of diffracted spots, which is characteristic of crystalline

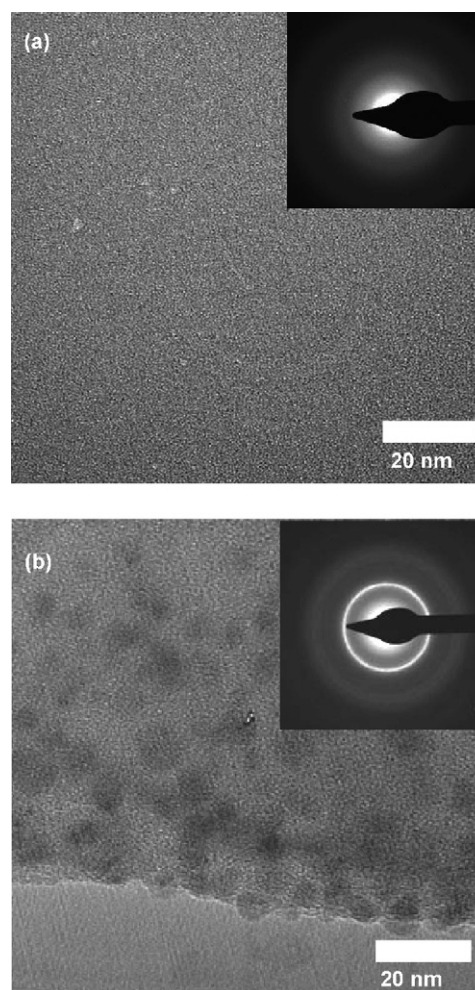


Fig. 1. HREM images and SAED patterns of (a) the single Si and (b) the Cu–Si nanocomposite electrodes.

materials. A comparison of the two samples indicates that the blobs are Cu nano-dots (5–11 nm in size), which are uniformly dispersed throughout the Si matrix.

The structural properties of the samples were further investigated by means of XRD (Fig. 2). The single Si electrode reveals

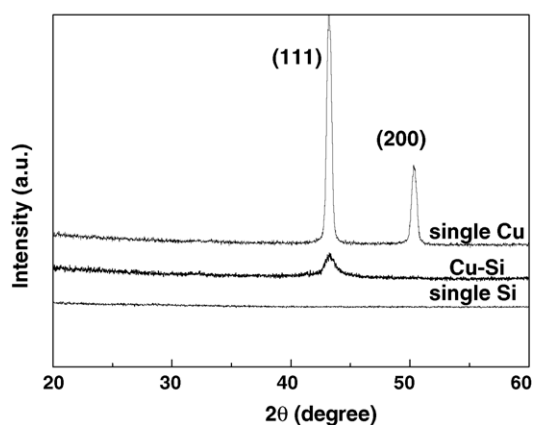


Fig. 2. X-ray diffraction patterns of the metallic Cu film, the Cu–Si nanocomposite electrode, and the Si electrode.

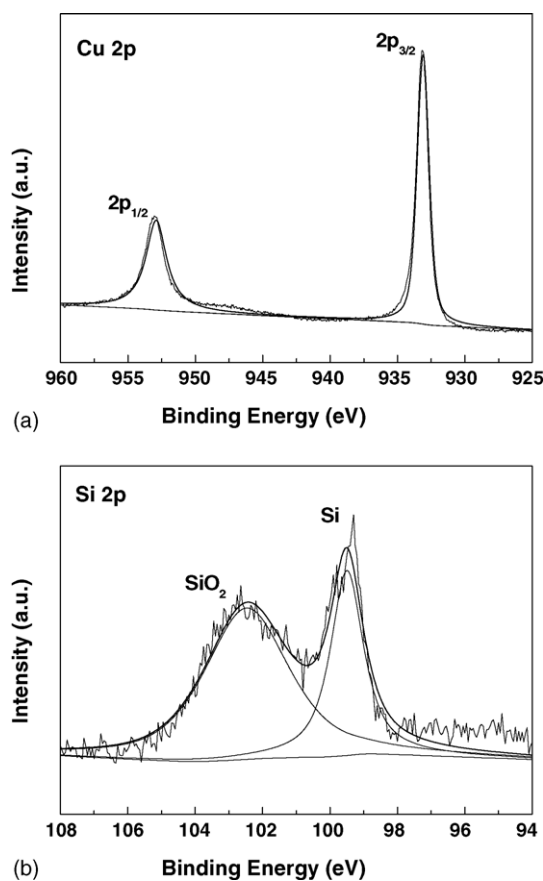


Fig. 3. XPS spectra of (a) the Cu 2p and (b) the Si 2p obtained from the Cu–Si nanocomposite electrodes.

no diffraction peaks, indicating an amorphous structure, whilst a single Cu film, which was sputtered without a Si target, gives crystalline nature ($2\theta = 43.2^\circ$ and 50.3°) [JCPDS 03–1005]. For the Cu–Si electrode sample, there is a broad diffraction peak ($2\theta = 43.2^\circ$). This implies that the Cu nano-dots having FCC structure (space group $Fm\bar{3}m$) are embedded within an amorphous Si matrix. To measure the mean grain (crystallite) size (D) of the Cu nano-dots embedded in the Si matrix, Scherrer equation [14] was used for the (111) plane diffraction peak ($2\theta = 43.2^\circ$):

$$D = \frac{0.9\lambda}{\beta \cos \theta}$$

where D is an average particle size, λ is the X-ray wavelength, β the pure full width of the diffraction line at half its maximum intensity and θ is the Bragg angle. The measurements showed that the Cu nano-dots are about 9 nm in size, which is in good agreement with the HREM result.

To examine the chemical states of Cu and Si, XPS analysis was made of the Cu–Si nanocomposite electrodes. The peak of the C 1s line (284.5 eV) was used as a reference for charge correction. Fig. 3 shows XPS spectra for the Cu 2p (Fig. 3(a)) and the Si 2p (Fig. 3(b)) obtained from the nanocomposite electrodes. The XPS peaks from the Cu $2p_{3/2}$ and $2p_{1/2}$ photoelectrons peaked at 933.0 and 952.8 eV, respectively, are consistent with metallic Cu. In case of the chemical state of Si, XPS spectrum

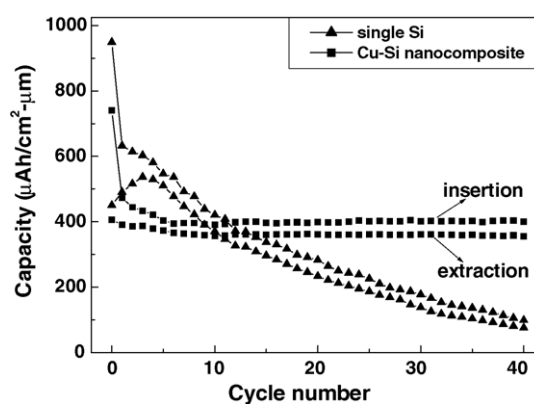


Fig. 4. The cycle number dependence of the insertion and extraction capacities of test cells fabricated with the single Si and Cu–Si nanocomposite electrode up to 40 cycles.

for the Si 2p photoelectrons exhibits two peaks corresponding to the elemental Si at 99.3 eV and the oxidized Si at 103.0 eV. It is believed that the oxidized Si species in the Cu–Si nanocomposite electrode is present as a surface layer, which was formed when the sample was exposed to air before the XPS measurement.

Fig. 4 shows the cycle number dependence of the insertion and extraction capacities of test cells fabricated with the single Si and Cu–Si nanocomposite electrodes. For the single Si electrode, the reversible capacity decreases continuously as the cycle number increases, which is consistent with the result previously observed by Bourderau et al. [15]. For the Cu–Si nanocomposite electrode, however, their reversible capacities decrease with increasing cycle number up to five cycles and then remain almost constant afterwards. The capacities in the first insertion process for the single Si and Cu–Si nanocomposite electrodes are 948.7 and $740.5 \mu\text{A h cm}^{-2} \mu\text{m}^{-1}$, respectively. After 40 cycles, the capacities of the single Si and Cu–Si nanocomposite electrodes drop by 89% and 46% of their initial values, respectively. The presence of the Cu nano-dots embedded in the Si electrode seems to inhibit the degradation of the capacity by enhancing the mechanical stability of the amorphous Si matrix as will be discussed later (Fig. 5), which may allow more sites to be available for the reversible insertion and extraction of Li ions in Li ion batteries. This is in a good agreement with the results previously reported by other groups [9,10,16–18], indicating that the incorporation of nanostructured electrodes into battery systems can significantly improve the electrochemical performance of batteries.

Fig. 5 shows SEM images of the amorphous Si electrode samples without (Fig. 5(a)) and with the Cu nano-dots (Fig. 5(b)) after 10 cycles of Li insertion and extraction processes. The single Si electrode experienced serious cracking and crumbling. However, the Cu–Si nanocomposite electrode remains fairly stable in its morphology. The results show that reversible retention of the single Si electrode is unstable and subject to continuous degradation, whilst the introduction of the Cu nano-dots into the Si matrix plays an effective role in minimising volume change and hence alleviating the cracking and crumbling of the Si electrode, thus leading to the better performance in the reversible capacity for the rechargeable Li batteries.

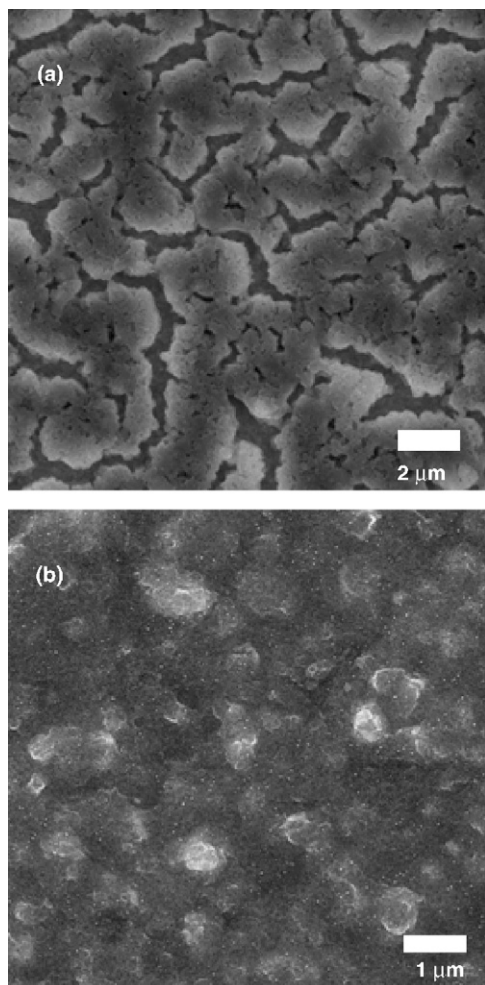


Fig. 5. SEM images of the Si electrodes (a) without and (b) with the Cu nano-dots after 10 cycles.

4. Conclusions

The Cu–Si nanocomposite electrodes, which were prepared using a co-sputtering system, were successfully demonstrated for the test cells of rechargeable Li batteries. The Cu–Si nanocomposite electrodes showed excellent reversible capacity

as compared to the single Si electrode up to 40 cycles. The presence of the Cu nano-dots prevented the decrease of the reversible capacity by stabilizing the amorphous Si electrode. The Cu–Si nanocomposite electrode could be used as one of potential anode materials for realising high-performance rechargeable Li batteries.

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