

Short communication

Amorphous Si film anode coupled with LiCoO₂ cathode in Li-ion cell

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Abstract

An amorphous silicon film with an average thickness of up to 2 μm was deposited on copper foil by direct-circuit (dc) magnetron sputtering and coupled with commercial LiCoO₂ cathode to fabricate cells. Their cycle performance and high rate capability at room temperature have been investigated. In the voltage range 2.5–3.9 V at the current density of 0.2C (0.11 mA cm⁻²), the lithiation and delithiation capacity of this cell was first increased to 0.55 mAh cm⁻² within 80 cycles and maintained stable during the following cycles. After 300 cycles its capacity still retained 0.54 mAh cm⁻². High-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) image indicated that the sputtered film could keep an amorphous structure although the volume expansion ratio during the lithiation and delithiation was still up to 300% after 300 cycles observed from scanning electron microscopy (SEM) image. This recovered amorphous structure was believed to be beneficial for the improvement of the cycle life of the cell. Rate performance showed that the cells had a promising high rate capability. At 30C, its lithiation/delithiation capacity remained 25% of that at 0.2C.

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1. Introduction

Rapid developments of portable electronic devices strongly stimulate the demands for lightweight and compact lithium-ion batteries with higher capacity and power density. Although carbon-based materials are still the accepted anodes used in commercial batteries, intense research is currently ongoing to identify higher capacity anode materials for the next generation of lithium-ion batteries. Si reveals a promising potential to be used in these batteries due to its theoretical gravimetric capacity of nearly 4200 mAh g⁻¹, which corresponds to a fully lithiated state of Li₂₂Si₅. Although this value is very favorable when compared to that of the graphite, which is only 372 mAh g⁻¹ (LiC₆), it cannot be retained over prolonged cycles. Reasons of capacity loss are generally ascribed to the volume expansion (up to 297%) and microstructure change

which lead to undesirable crumbling and mechanical degradation during the electrochemical lithiation and delithiation [1].

Many attempts have been made and proven to be effective on reducing the deleterious effects of decrepitation of Si anodes. Graetz et al. [2] reported an amorphous Si film anode with 100 nm thickness deposited by physical vapor deposition gave a capacity of 2000 mAh g⁻¹ over 50 cycles. Moon et al. [3] prepared a 200 nm thick Si film by radio-frequency (rf) magnetron sputtering, which gave a capacity around 3000 mAh g⁻¹ up to 70 cycles. Maranchi et al. [4] employed rf magnetron sputtering to prepare 250 nm and 1 μm thick amorphous Si film electrodes. Preliminary cycling data showed promising results with the 250 nm thick films exhibiting reversible capacities of 3500 mAh g⁻¹ for 30 cycles with no obvious signs of failure, while the 1 μm thick films exhibited much fast capacity fade. Lee et al. [5] enhanced the gravimetric capacity of 500 nm thick Si film deposited on rough Cu current collector by rf magnetron sputtering with the capacity up to 1500 mAh g⁻¹ after 30 cycles. Thin Si films deposited on Ni foil by vacuum deposition showed

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similar electrochemical properties reported by Takamura et al. [6–8]. The 50 nm thick Si film deposited on a Ni foil gave a fluctuated capacity of 2000 mAh g⁻¹ at 30C, while the performance of thicker films (over than 300 nm) became poor [8]. Dahn and Hatchard [1] considered the film thickness had a negative effect on the cycle performance of Si film anode, which was coincided with the Obrovac's result [9].

Although much improvement has been made by the above researchers, Si films prepared by different methods are too thin to commercially use. When increasing the thickness, the capacity of the Si film anodes could hardly keep stable at desired values [4,8,10]. Thus, it becomes the crucial problem for commercial produce when increasing the thickness of films without damage to cycle stability. A great improvement on the Si thin-film electrode was reported by Sakai's group [11], which presented a possibility for the application of micrometer-scale Si film anodes in the secondary Li-ion batteries. They found that the 2 μm thick film anode by electron-beam deposition delivered a capacity of 3400 mAh g⁻¹ after 50 cycles and gradually decreased to 2550 mAh g⁻¹ after 200 cycles.

The attractive behavior of Si anode pushed researchers for its practical use in the Li-ion cell. Sakai and co-workers [11] assembled LiCoO₂/Si cells by selecting 4 μm or 6 μm thick Si films as anodes, showing a stable capacity of 1.5 mAh cm⁻² within 200 cycles. Lee et al. [12] fabricated a LiMn₂O₄/Si thin-film battery, which yielded a reversible capacity of about 0.016 mAh cm⁻² μm after 100 cycles. Jung et al. [13] made a cell by coupled a 50 nm thick Si film anode with a LiMn₂O₄ cathode, exhibiting good cyclic durability up to 400 cycles except a low capacity of 300 mAh g⁻¹. They [11,13] assumed the improvement of the cyclic performance was due to the limited depth of lithiation in the Si anode. However, its mechanism is still not clear.

On the focus of preparing Si anodes with the thickness of more than 1 μm for practical applications, amorphous Si films were sputtered on Cu foils by magnetron sputtering and coupled with commercial LiCoO₂ cathodes to form full Li-ion batteries to investigate their cyclic performance and high rate capability in this present work.

2. Experimental

Si films were sputtered on rough Cu foils by dc magnetron sputtering with Si wafer as targets using a GDM-300BII high vacuum sputtering equipment [14]. The chamber reached a base pressure of 1.0×10^{-3} Pa, and maintains 2.0 Pa of Ar gas during sputtering. An expected Si film was obtained with a direct-circuit (dc) power supply of 30 W for 3 h.

The film thickness of the as-prepared film was observed from scanning electron microscope (SEM, JEOL JSM-6700F) image. The surface morphology analysis was determined by SEM (JEOL JSM-6700F) and high-resolution transmission electron microscope (HRTEM, FEI Tecnai20).

Circular sheets were punched from the as-prepared Si film and dried at 80 °C under vacuum for 24 h prior to fabricat-

ing the cells. A commercial LiCoO₂ cathode, which capacity was much more than that of the Si anode, was used as a counter electrode. The electrochemical properties of the cells were examined using 2025 coin cells, which were sealed in a glove box with 1 M LiPF₆ in EC/DMC (ethylene carbonate/dimethyl carbonate, v/v% = 1:1) solution as the electrolyte and a Celgard-2300 membrane as the separator. Rate capability of the cells was evaluated by cycling at 0.2C, 1C, 5C, 10C, 20C and 30C between 2.5 and 3.9 V with a 10 min rest period between each cycle, respectively. Here, the C is based on the practically obtained specific capacity. Before every new rate, the cell was discharged to 2.5 V at 0.2C. The cyclic performance was carried out by charging and discharging between 2.5 and 3.9 V at 0.2C. All the charge and discharge tests were performed using a computer-controlled galvanostatic system (LAND CT2001A) at 25 ± 1 °C.

3. Results and discussion

3.1. Morphology and microstructure of the as-prepared film

Fig. 1 shows the high-resolution TEM (HRTEM) image with the inset selection area electron diffraction (SAED) pattern of the sputtered Si film before cycling. It can be found that no ordered lines indicating crystalline Si phase appear in the HRTEM image. The inset SAED image taken from the sputtered Si film shows absence of clear rings or dots of crystalline Si phase. Only a diffused halo is observed, illustrating the amorphous structure of the sputtered Si film.

Fig. 2 shows the SEM image of the sputtered Si film anode before cycling. It reveals the average thickness of the Si layer is about 2 μm. It can be seen that this film with a rough and regular surface is covered on the Cu substrate.

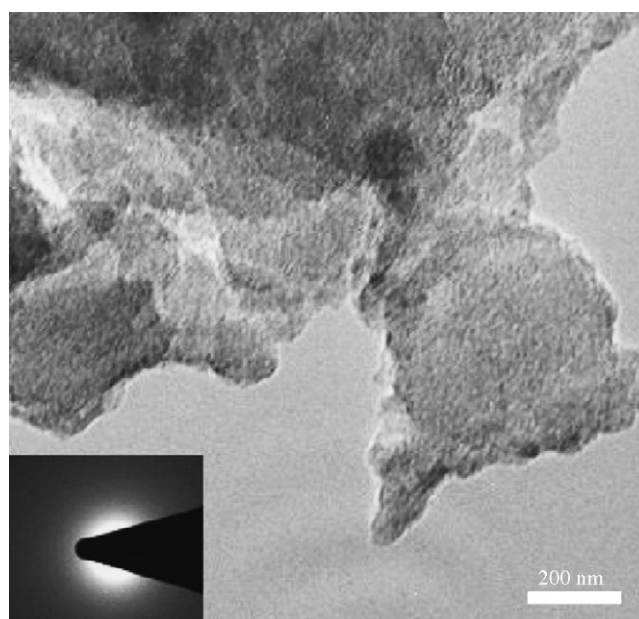


Fig. 1. HRTEM image with SAED image inset of the sputtered Si film before cycling.

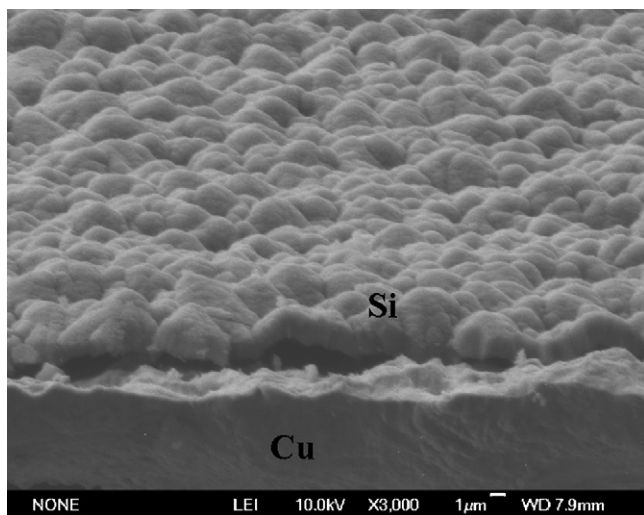


Fig. 2. SEM image of the sputtered Si film anode before cycling.

3.2. Cycleability of the LiCoO₂/Si cell

3.2.1. Cyclic performance

Fig. 3 presents the cyclic performance and columbic efficiency of LiCoO₂/Si cell at 0.2C between 2.5 and 3.9 V. It can be found that the lithiation/delithiation capacity increases obviously during the preliminary 80 cycles, and then maintains stable during the following cycles. The increase of the capacity is probably due to the formation process of the electrodes. During the first 80 cycles the delithiation capacity reaches its highest value of 0.55 mAh cm⁻² (about 1180 mAh g⁻¹, estimated using a density of 2.33 g cm⁻³ for the Si film [4]), which is about 28% higher than the initial delithiation capacity. Here, because the practically obtained specific capacity of the cell is 0.55 mAh cm⁻², the 0.2C is equal to 0.11 mA cm⁻². After 80 cycles, only a comparatively slow capacity fade is observed. The capacity can still retain 0.54 mAh cm⁻² (1159 mAh g⁻¹) after 300 cycles with an average capacity fade ratio of 0.01% per cycle. The relatively large irreversible capacity loss of the initial cycle should

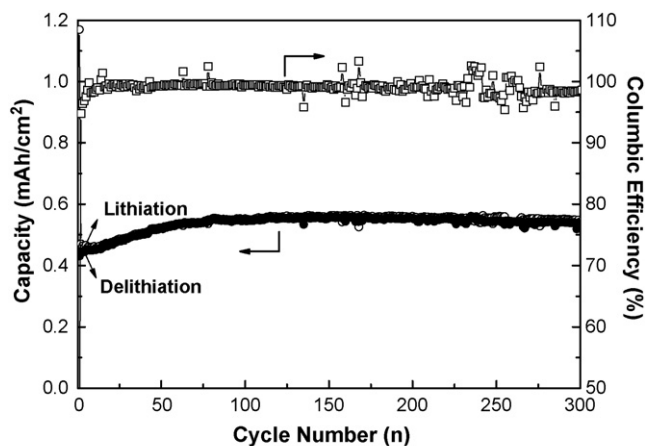


Fig. 3. Lithiation/delithiation capacity and columbic efficiency as a function of cycle number for the cell with the sputtered Si film as the anode and LiCoO₂ as the cathode.

be attributed to the electrolyte decomposition reactions during the formation of the Solid Electrolyte Interface (SEI) layer on the Si film surface and the residual lithiated phases within the Si layer. During the following cycles, the columbic efficiency increases to 85% at the 2nd cycle and retains over than 95% within 10 cycles. After 10 cycles the columbic efficiency is close to 100%, which suggests the reversibility is improved during the following cycles.

3.2.2. Morphology and microstructure of the Si film after cycling

Fig. 4 shows the SEM image of the sputtered Si film after 300 cycles. It can be found that this film becomes incompact and has a rough and irregular surface, which is completely different from the before-cycled one. The average thickness of this film is about 6 µm. The volume expansion ratio is about 300%, which is in a good agreement with the literatures, where the Si anodes had short cycle lives when the thickness of the prepared films were in the scale of micrometers [2,10]. By contrast, in this work, nearly no capacity fade is observed. Within 300 cycles, the capacity fade ratio was less than 0.01% per cycle. Therefore, it seems that the volume expansion might not be responsible for its capacity fade.

In order to further make the mechanism of the improvement of the cycle performance clear, the microstructure of the delithiated Si film anode after 300 cycles was determined by TEM and its HRTEM image is shown in Fig. 5. It can be observed that the Si film after cycling still keeps an amorphous structure, which suggests that the sputtered Si film could recover to an amorphous structure after each delithiation process during cycling. This result is consistent with Dahn's [1] and Obrovac's results [9], where they considered the Si film anode was very easy to convert to the crystalline structure from the amorphous one, while during delithiation the amorphous Si phase reformed. Amorphous Si structure has been reported to be beneficial for the prolonged cycles due to the homogeneous volume expansion by eliminating the existence of any two-phase regions during cycling [1,9,15]. Therefore, the amorphous structure observed

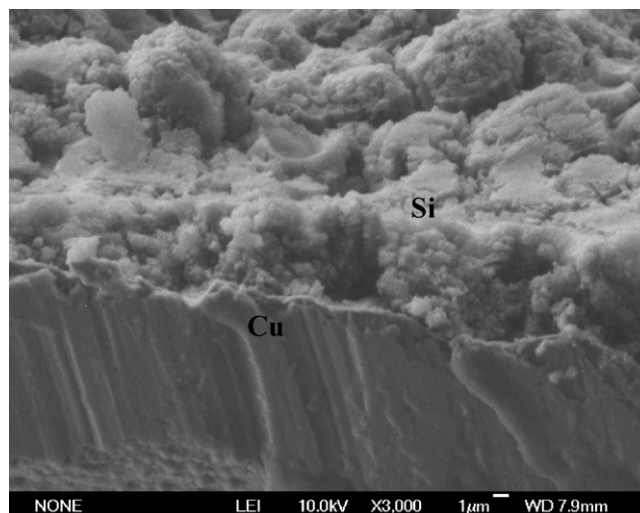


Fig. 4. SEM image of the sputtered Si film anode after cycling.

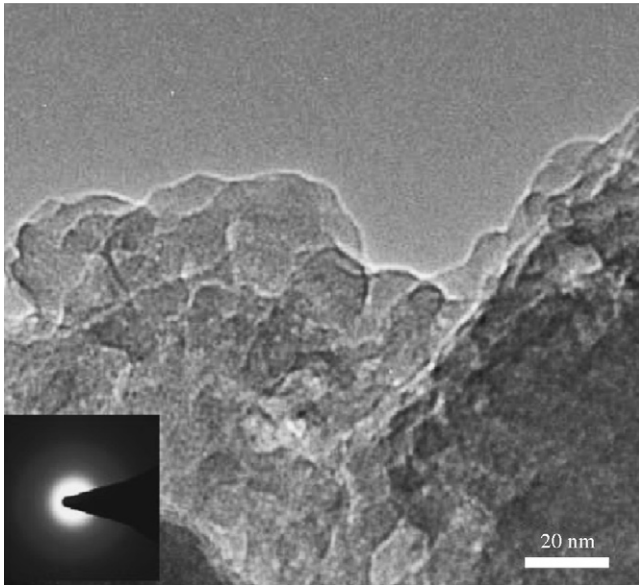


Fig. 5. HRTEM image with SAED image inset of the Si film after cycling.

after each delithiation in this work is believed to be an essential factor responsible for the improved cycle life of the sputtered Si film anodes.

3.3. Rate capability of the LiCoO₂/Si cell

In order to further investigate the possibility for the application of the 2 μm thick Si film anodes in Li-ion batteries, the rate capability of the cells were conducted. Fig. 6 shows the cyclic performances at different rates of the LiCoO₂/Si cell after 80 cycles at 0.2C. It can be seen that the reversible capacity decreases with increasing of the lithiation/delithiation rates. At 0.2C, the cell can deliver a capacity of 0.55 mAh cm⁻². At 1C, 5C, 10C, 20C, and 30C it decreases to 0.52 mAh cm⁻², 0.34 mAh cm⁻², 0.44 mAh cm⁻², 0.26 mAh cm⁻², and 0.14 mAh cm⁻², which is 94%, 89%, 73%,

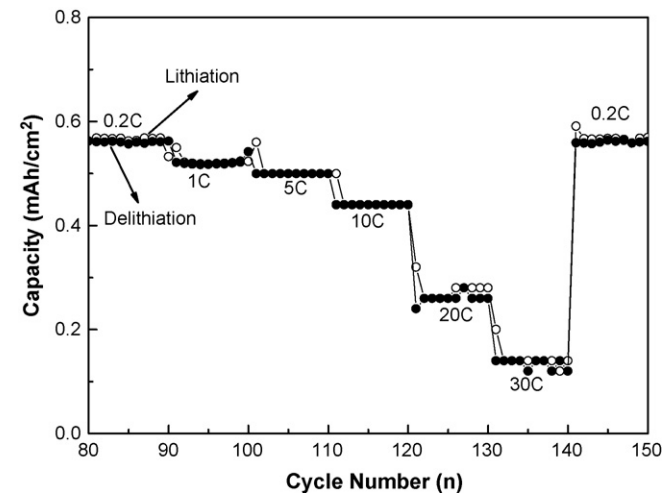


Fig. 6. Lithiation/delithiation capacities at different rates as a function of cycle number of the cell with the sputtered Si film as the anode and LiCoO₂ as the cathode.

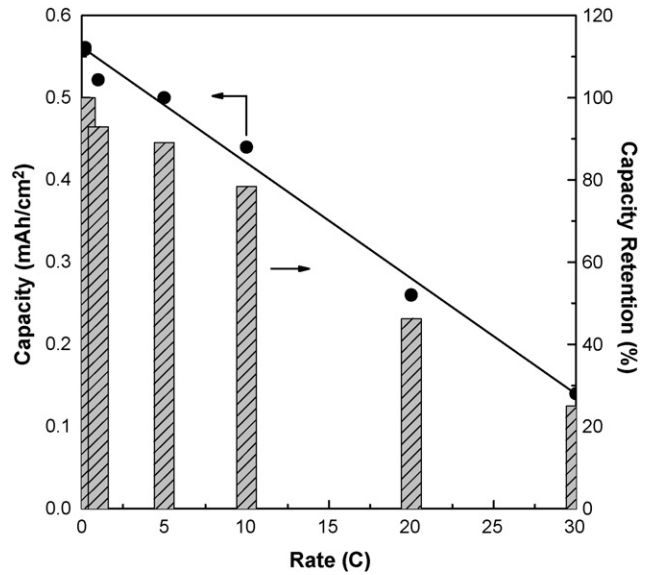


Fig. 7. Capacity as a function of discharge rates of the cell with the sputtered Si film as the anode and LiCoO₂ as the cathode.

46% and 25% of the capacity at 0.2C, respectively (Fig. 7). Here, this cell can yield a high capacity at 1C. Even at 30C, it still reaches 25% of that at 0.2C. When the C rate is set back to 0.2C, the capacity recovers to 0.55 mAh cm⁻² and keeps a stable trend in the subsequent cycles. Neither at the lower rate nor at the higher rate is the capacity fade observed, which indicates the cell is able to endure relatively high current densities during the cycling. From the plot of capacity versus C rate (Fig. 7) it can be found that the capacity declines linearly with increasing the C rate, which implies good diffusion of lithium in the both electrodes.

Fig. 8 presents the lithiation/delithiation voltage profiles at different C rates. At 0.2C and 1C, the flat lithiation and delithiation voltage plateaus are at about 3.7 and 3.5 V, respectively. At 5C, they are at 3.7 V and 3.4 V, respectively. When increased to 10C, the sloping voltage plateaus appear at around 3.8 and

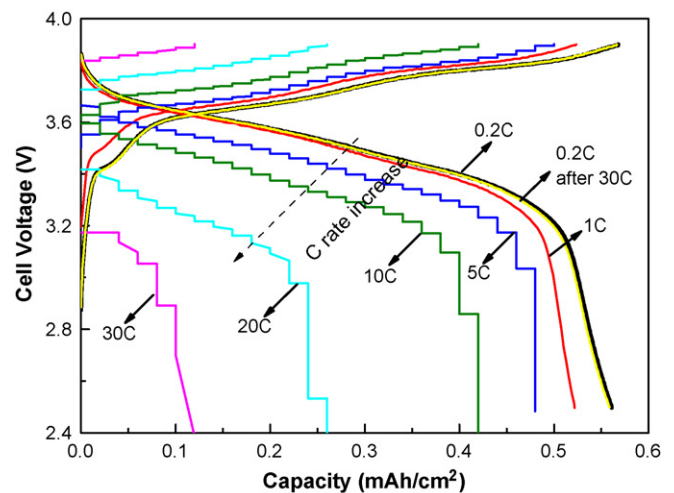


Fig. 8. Voltage profiles during lithiation/delithiation at different rates of the cell with the sputtered Si film as the anode and LiCoO₂ as the cathode.

3.3 V, respectively. While increased to 20C, the voltage plateaus shift to 3.8 and 3.2 V, respectively. At 30C, they are 3.9 and 3.0 V, respectively. These results imply that the cells with the sputtered Si film as the anode and commercial LiCoO₂ cathode exhibit promising rate capability.

4. Conclusions

A silicon film was successfully deposited on a rough copper foil by dc magnetron sputtering and combined with commercial LiCoO₂ cathode to form cells.

The HRTEM and SAED images showed that this sputtered film had an amorphous structure, and its average thickness was about 2 μm observed from the SEM image. In the voltage range 2.5–3.9 V at 0.2C (0.11 mA cm⁻²), this cell reached its largest capacity over 0.55 mAh cm⁻² (1180 mAh g⁻¹) after 80 cycles and retained 0.54 mAh cm⁻² (1159 mAh g⁻¹) after 300 cycles. Nearly no capacity fade was observed within 300 cycles. The HRTEM and SAED images indicated that the film could recover to amorphous structure during cycling although the volume expansion ratio was still up to 300% after 300 cycles observed from the SEM image. This recovered amorphous structure was believed to be beneficial for the improvement of the cycle life of the cells. Though the lithiation and delithiation capacities had a declined liner relationship with the C rates, no obvious capacity fade was observed at each rate. At 30C, its lithiation/delithiation capacity remained 25% of that at 0.2C, which implied that these cells employed the amorphous Si film anodes also had a promising high rate capability. It suggests this sputtered Si film could serve as a promising anode in the next generation of Li-ion battery.

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