Effects of Amorphous Silicon Film on Elevated-Temperature Cycle Performance of Li$_4$Ti$_5$O$_{12}$ for Lithium Ion Battery

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Amorphous silicon (α-Si) film was deposited on the surface of Li$_4$Ti$_5$O$_{12}$ electrode by vacuum thermal evaporation technique and the effect of α-Si film on electrochemical performance at elevated temperature in different voltage range was investigated. Galvanostatic charge-discharge testing indicates that α-Si film/Li$_4$Ti$_5$O$_{12}$ has better cycling performance than that of Li$_4$Ti$_5$O$_{12}$ in the voltage range of 1.0–3.0V, especially at high C-rate. The enhancement might result from the injecting electron due to the chemical dissolution of oxide film at the silicon/electrolyte interface in HF. In the voltage range of 0–3.0V, α-Si film/Li$_4$Ti$_5$O$_{12}$ has a higher discharge capacity at low C-rate as the Li-Si phase formation in lithiation/delithiation while degrade more distinctly with increasing the C-rate, which might be attributed to the electrolyte decomposition, affinity effect of dangling bonds in α-Si or silicon delamination at low voltage range.

Keywords: Lithium-ion battery; Spinel Li$_4$Ti$_5$O$_{12}$; Amorphous silicon; Elevated temperature.

1. INTRODUCTION

Recently, the spinel Li$_4$Ti$_5$O$_{12}$ anode material has become the interested subjects both in the areas of high-power Li-ion batteries and asymmetric hybrid batteries due to its unique characters, such as excellent structure stability, good lithium ion mobility and no risk of Li-plating during charge/discharge process [1, 2]. However, the low conductivity of Li$_4$Ti$_5$O$_{12}$ induced by empty Ti 3d-states does negatively impact its high-rate capability and initial capacity [3]. To improve the conductivity of spinel Li$_4$Ti$_5$O$_{12}$, extensive work has been concentrated on the microstructure modification, including the substitution of Li$^+$ or Ti$^{4+}$ by different valence metal ions [4,5] or surface-modification of particle with metallic grains or carbon [6,7] and so on. In contrast, amorphous silicon (α-Si) seem to be more promising surface-modification materials besides its much higher capacity and dangling bonds, which represent defects in the continuous random network and may cause anomalous
electric behaviors [8,9]. However, to the best of our knowledge, there are scarce investigations on the deposition of silicon on anode electrode surface for lithium-ion batteries and its effects on the electrochemical performance of Li$_4$Ti$_5$O$_{12}$. In present work, we report the effect of α-Si film deposition on the electrochemical performance at elevated temperature of Li$_4$Ti$_5$O$_{12}$/Li cell in different voltage range to investigate the potential application of α-Si as surface modification in high-power Li-ion batteries. The results unequivocally demonstrated α-Si film does enhance the electrochemical performance at elevated temperature.

2. EXPERIMENTAL

The Li$_4$Ti$_5$O$_{12}$ powder was synthesized via a sol-gel route using tetrabutyl titanate [Ti(OC$_4$H$_9$)$_4$] and lithium nitrate [LiNO$_3$·H$_2$O] as the precursors. In a typical procedure, the desired amount of Ti(OC$_4$H$_9$)$_4$ was dissolved in 50 mL anhydrous ethanol to obtain solution A. Stoichiometric amounts of LiNO$_3$·H$_2$O, deionized H$_2$O, C$_2$H$_4$O$_2$ and nitric acid were dissolved in 50 mL anhydrous ethanol to obtain solution B. With stirring, solution B was gradually dropped to solution A to get a clear solution. The mixed solution was kept stirring till the polymerized gel was formed as Ti(OCH$_3$)$_4$ hydrolyzing. After aging for 3 days, the obtained gelatin was dried at 85°C to extract out excess solvents and yield organic precursor. The gel precursor was subsequently calcined at 900°C over 12 h in air. The crystal structures of as-prepared powder was characterized by X-ray powder diffraction with a Cu Kα radiation source.

The anode electrode was prepared by mixing Li$_4$Ti$_5$O$_{12}$ powder, super-P and polyvinylidene fluoride with a weight ratio of 7:2:1 in N-methylpyrroline. The slurry was pasted onto a copper foil and subsequently dried at 120°C in vacuum. The Li$_4$Ti$_5$O$_{12}$ coated with α-Si film was prepared by depositing α-Si film about 400 nm thick on the surface of Li$_4$Ti$_5$O$_{12}$ electrode through vacuum thermal evaporation deposition. Coin type (CR 2025) test cells were assembled in an argon-filled glove box (Mikrouna, Super 1220/750) using a metal lithium foil as reference electrode, Celgard 2300 microporous polyethylene membrane as the separator and 1M LiPF$_6$ in a mixture of ethyl carbonate (EC) and dimethyl carbonate (DMC) (1:1 in vol. ratio) as the electrolyte. The cells were galvanostatically cycled at elevated temperature in a voltage range of 1.0-3.0V or 0-3.0V. Cyclic voltammetry measurement was performed using an Arbin BT2000 battery testing system.

3. RESULTS AND DISCUSSION

Fig. 1 shows XRD pattern of Li$_4$Ti$_5$O$_{12}$ calcined at 900°C for 12 h. All the observed diffraction peaks can be absolutely indexed on the basis of a cubic spinel lithium titanate phase (ICSD file no. 15787) and the presence of second phase such as TiO$_2$ or Li$_2$TiO$_3$, is not detected within the sensitivity of measurement.

Fig. 2 shows the rate discharge-capacity versus cycle number for both Li$_4$Ti$_5$O$_{12}$ and α-Si film/Li$_4$Ti$_5$O$_{12}$ at different current densities in the voltage range of 1.0 ~ 3.0 V. The charge-discharge
processes of the samples are taken for 10 cycles at 0.5 C, 1.0 C, 2.0 C and 3.0 C, respectively. It is
found that the electrochemical performances are enhanced at low C-rate with α-Si film deposition, especially at 60 C°.

Figure 1. XRD patterns of standard spinel Li$_4$Ti$_5$O$_{12}$ (JCPDS Card No. 49-0207, denoted as S) and the samples calcined at 900°C for 12 h.
Figure 2. The discharge-capacity at (a) 25°C and (b) 60°C versus cycle number in a potential range from 1.0 to 3.0V for pristine and α-Si film/Li₄Ti₅O₁₂ at different current densities.
Figure 3. Cyclic voltammograms at (a) 25°C and (b) 60°C of cells using the Li$_4$Ti$_5$O$_{12}$ and α-Si film/Li$_4$Ti$_5$O$_{12}$ sample as electrode materials.

As seen in Fig. 2(b), α-Si film/Li$_4$Ti$_5$O$_{12}$ exhibits much higher specific capacity (0.5C: 160 mAhg$^{-1}$; 1C: 152 mAhg$^{-1}$; 2C: 125 mAhg$^{-1}$; 3C: 100 mAhg$^{-1}$, respectively) than that of pristine one at the same current densities. The formation of an oxide film at the silicon/electrolyte interface is considered in accounting for the enhancement of electrochemical performance with α-Si film deposition. It has been assumed that an oxide film of several monolayers at the silicon/electrolyte interface will form due to the preparation or possible reaction with Si-F species in non-aqueous electrolyte [11-13]. The partially oxidized silicon atoms have relatively high energy levels and are capable of injecting electrons into the conduction band and generating a current during the chemical dissolution in HF [14-16] which is generated as a product of the LiPF$_6$ decomposing reaction at elevated temperature. As a result, the electrochemical performance at elevated temperature is correspondingly enhanced.

Fig. 3 shows the cyclic voltammetry curves at 25 and 60°C of the Li$_4$Ti$_5$O$_{12}$ and α-Si film/Li$_4$Ti$_5$O$_{12}$, respectively. A couple of anodic and cathodic peaks appear at around 1.55 V, corresponding to the typical characteristic of electrochemical lithium insertion/extraction of Li$_4$Ti$_5$O$_{12}$ [17, 18] At 25°C, shown in Fig. 3(a), the potential differences between anodic and cathodic peaks for pristine and α-Si film/Li$_4$Ti$_5$O$_{12}$ are 264 and 204 mV, respectively, indicating the lower electrode polarization and high lithium ion diffusivity in solid-state body of sample Li$_4$Ti$_5$O$_{12}$/α-Si composite. [19] These phenomena confirm that the injecting electrons induced by α-Si film is beneficial to the reversible intercalation and de-intercalation of Li$^+$. Fig. 3(b) presents the 5th cyclic voltammetry
curves in 60 C\(^0\) of the Li\(_4\)Ti\(_5\)O\(_{12}\) and α -Si film/Li\(_4\)Ti\(_5\)O\(_{12}\) at a scanning rate of 0.05mV/s. Compared with α -Si film/Li\(_4\)Ti\(_5\)O\(_{12}\), the symmetrical redox peaks of Li\(_4\)Ti\(_5\)O\(_{12}\) look quite broad, suggesting that there is a notable polarization even if they have the same potential difference. With α -Si film deposition, the α -Si film/Li\(_4\)Ti\(_5\)O\(_{12}\) composite is endowed with quite narrow and sharp redox peaks, along with the increased peak current. The obtained results indicates that the deposition of film on anode electrode indeed be beneficial to the enhancement of electrochemical activity for the α -Si film/Li\(_4\)Ti\(_5\)O\(_{12}\) composite.

![Figure 4](image-url)  
**Figure 4.** The discharge-capacity at 60C\(^0\) versus cycle number in a potential range from 0 to 3.0V for pristine and α -Si film/Li\(_4\)Ti\(_5\)O\(_{12}\) at different current densities.

It is important to investigate the electrochemical behaviors of anode materials at lower voltage due to the higher cell voltage for lithium-ion batteries. Fig. 4 shows the rate discharge-capacity at 60C\(^0\) versus cycle number for both pristine and α -Si film/Li\(_4\)Ti\(_5\)O\(_{12}\) at different current densities in the voltage range of 0 - 3.0 V. It is found that α -Si film/Li\(_4\)Ti\(_5\)O\(_{12}\) has higher specific capacity at low C rate (0.2C: 350 mAhg\(^{-1}\); 0.5C: 252 mAhg\(^{-1}\); 1C: 160 mAhg\(^{-1}\), respectively) than that of pristine one, which is attributed to the formation of Li-Si phase in lithiation/delithiation\(^{20}\). However, with increasing the charge-discharge current rate, the discharge capacity of α -Si film/Li\(_4\)Ti\(_5\)O\(_{12}\) decreases more rapidly than that of Li\(_4\)Ti\(_5\)O\(_{12}\). The negative effect of α -Si film in the low voltage range could be attributed to two reasons: 1) propylene carbonate in electrolytes decomposes irreversibly on the anode electrode below 1.0 V \(^{21, 22}\) and consequently leads to irreversible process of Li\(_4\)Ti\(_5\)O\(_{12}\) and α -Si
film/Li$_4$Ti$_5$O$_{12}$. 2) an irreversible consumption of Li occurs because of dangling bonds in $\alpha$-Si, which have a strong affinity to capture Li ions [23, 24]. Hence, Li ions could not extract all from lithiated $\alpha$-Si film into Li$_4$Ti$_5$O$_{12}$ particles or electrolyte during charge and discharge. 3) Li atoms prefer to stay at the surface of Si film due to the high barrier energy and promote the formation of Li$_x$Si phase. The interfacial Si atoms are peeled off with the increasing of C-rate, leading to low rate capability [25]. Hence, the discharge capacity of $\alpha$-Si film/Li$_4$Ti$_5$O$_{12}$ decreases more dramatically than that of Li$_4$Ti$_5$O$_{12}$ in a potential range from 0 to 3.0V.

![Figure 5](image_url) **Figure 5.** The charge-discharge processes at 60C$^0$ of Li$_4$Ti$_5$O$_{12}$ and $\alpha$-Si film/Li$_4$Ti$_5$O$_{12}$ at 0.2 C, 0.5 C 1.0 C, 2.0C and 4.0 C, respectively.
Fig. 5 shows the charge-discharge curve at 60 °C for the electrodes of Li$_4$Ti$_5$O$_{12}$ and α-Si film/Li$_4$Ti$_5$O$_{12}$ recorded over the potential range between 0 and 3.0V at different current rates. As can be seen in Fig. 5(a) and (b), α-Si film/Li$_4$Ti$_5$O$_{12}$ exhibits excellent electrochemical performance at low current rate while shows a rapid loss of the 1.55V plateau with increasing the current rate. More rapid loss of the plateau in α-Si film/Li$_4$Ti$_5$O$_{12}$ at high C-rate further confirms Si peeling off at the interface is responsible for the degradation in electrochemical performance at low discharge voltage (discharged to 0 V).

4. CONCLUSIONS

α-Si film/ Li$_4$Ti$_5$O$_{12}$ was prepared via depositing α-Si film on the surface of Li$_4$Ti$_5$O$_{12}$ electrode using vacuum thermal evaporation technique and the effect of α-Si film on electrochemical performance at elevated temperature in different voltage range was investigated. The excellent rate capability and cycling performance in the voltage range of 1.0–3.0V of α-Si film/ Li$_4$Ti$_5$O$_{12}$ is mainly attributed to the injecting electron due to the chemical dissolution of oxide film at the silicon/electrolyte interface in HF. However, α-Si film/Li$_4$Ti$_5$O$_{12}$ shows a more rapid loss of capacity with increasing the current rate, which may be due to the electrolyte decomposition, affinity effect of dangling bonds in α-Si or silicon delamination at low voltage range.

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