



## Short communication

Surface-modified Si thin film electrode for Li ion batteries (LiFePO<sub>4</sub>/Si) by cluster-structured Ni under layer

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## ABSTRACT

An amorphous Si film with thickness of 350 nm was fabricated on both Cu substrate and Ni film (under layer)/Cu substrate by direct current (DC) and radio frequency (RF) magnetron sputtering. The surface morphology, crystallographic structure and electrochemical properties were investigated. Flat surface was formed in Si/Cu film, whereas in Si/Ni/Cu film a rough surface was formed consisting of Si clusters. In a Si/Li half-cell test with current densities of 210 (0.05 C-rate), 810 (0.2 C-rate) and 4200 mA g<sup>-1</sup> (1 C-rate), the surface-modified Si film electrode exhibited a significantly improved cycle performance compared to the Si film deposited on only Cu substrate. LiFePO<sub>4</sub>/Si full cell tested at current density 85 mA g<sup>-1</sup> of (0.5 C-rate) displayed the first charge capacity of 154.0 mAh g<sup>-1</sup>, corresponding to 90.5% of theoretical capacity of LiFePO<sub>4</sub> and the capacity retention of 79.4% at 20th cycle.

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## 1. Introduction

Silicon (Si) is a very promising anode material that can replace the graphitic carbon because of its high theoretical capacity of 4200 mAh g<sup>-1</sup> on the basis of Li<sub>4.4</sub>Si formation [1]. The value is 11 times higher than the capacity of graphite used in commercial anode material. Such a characteristic allows the Si electrode to be applied in the form of a thin film. However, when Si is reacted with lithium (Li), alloying phases are formed and a large volume expansion of electrode is accompanied at the same time [2]. The volume change of the Si film electrode during alloying–dealloying process induces cracks in the film electrode and leads to an abrupt capacity fade.

To overcome the problem, much of the experimental effort has been focused on enhancing the structural stability of Si film electrodes [3–8]. Their results pointed out that enhancing the adhesive force between an active material and a current collector was a key to prolong the cycle life even as maintaining high capacity. Particularly, Si film electrodes deposited on a nickel (Ni) foil substrate exhibited a good cycle performance because of good adhesion between film and substrate [4,6], because Ni is an inactive material for Li and the mixing enthalpy of Ni–Si system is lower than that of Si–Cu system.

In the present study, a cluster-structured Ni film is deposited between a Si film and copper (Cu) substrate (Si/Ni/Cu film) to mod-

ify the surface morphology of Si film and support the Si film during charge–discharge (alloying–dealloying) process. Moreover, the surface morphology of Ni film can be artificially controlled by thickness of film. The change in morphology of Ni film with different thicknesses has been studied in a previous study by the authors [9].

Although there were some reports on electrochemical properties of Si thin film electrode coupled with LiCoO<sub>2</sub> composite electrode [10,11], research on LiFePO<sub>4</sub>/Si cell has not been reported yet. Lithium iron phosphate (LiFePO<sub>4</sub>) with theoretical capacity of 170 mAh g<sup>-1</sup> has attracted considerable attention as a substitute for commercial cathode materials such as LiMO<sub>2</sub> (M = Co, Ni, Mn) because of its low cost, high-energy density and nontoxicity.

This article reports the effects of Ni under layer on the surface morphology and the electrochemical properties of Si film electrode. The improved electrochemical properties of Si/Ni/Cu electrode are presented by comparing with those of Si/Cu electrode. Finally, the authors demonstrate that the surface-modified Si thin film can be applied for the anode of Li ion battery through LiFePO<sub>4</sub>/Si full cell test.

## 2. Experimental procedure

Ni and Si films were deposited on a Cu foil substrate using two kinds of sputtering systems. Radio frequency (RF) magnetron sputtering and direct current (DC) magnetron sputtering were applied for Ni and Si films deposition, respectively. Especially, a vertical deposition technique was applied for Si deposition. Cu substrate was ultrasonically cleaned and annealed in vacuum-sealed

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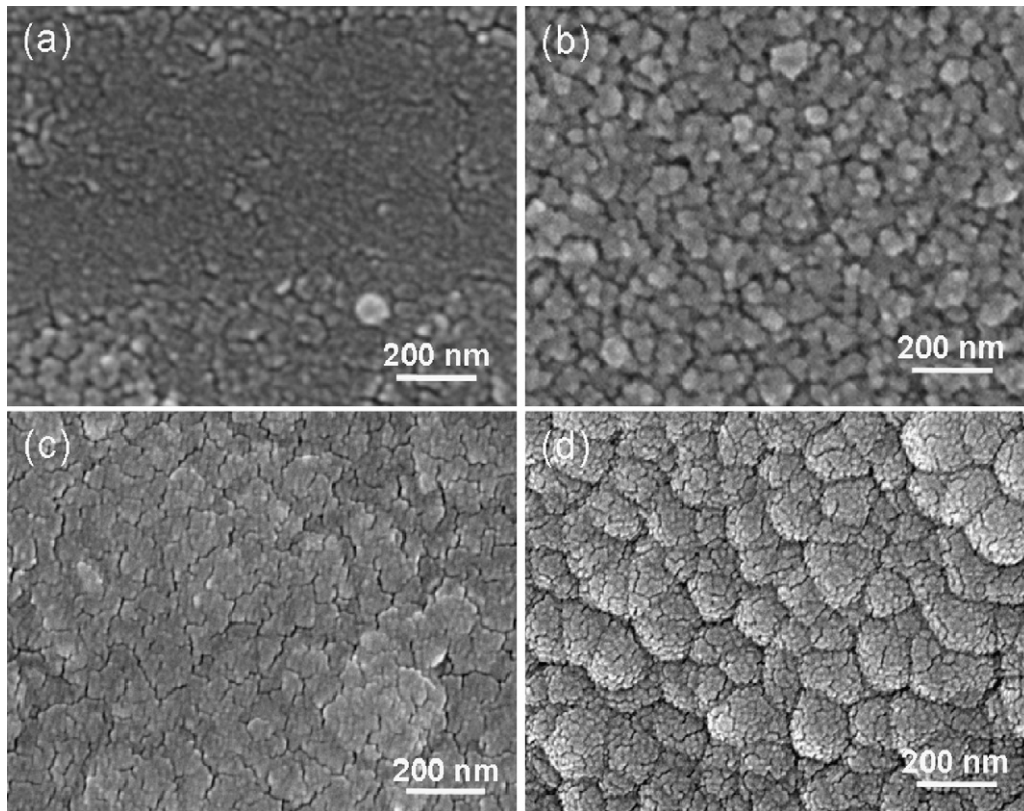


Fig. 1. FE-SEM photographs of (a) Cu substrate, (b) Ni/Cu film, (c) Si/Cu film and (d) Si/Ni/Cu film.

ampoules at 573 K for 30 min to remove the residual impurity gases at surface. The films were grown in a vacuum chamber under a pressure of  $5 \times 10^{-3}$  torr in argon (Ar) atmosphere. The growth rate of Ni film was 10 nm/min and that of the Si film was  $3 \text{ nm min}^{-1}$ , respectively. A cross-sectional analysis was performed to measure thickness of film with an alpha step profiler. Thicknesses of films fabricated in this study were 350 nm for Si and 800 nm for Ni, respectively. Finally, Si/Cu film and Si/Ni/Cu film were fabricated to investigate their structural and electrochemical properties.

Crystallinity of Si films deposited on both Cu substrate and Ni/Cu film was investigated by means of transmission electron microscopy (TEM). Surfaces of Ni/Cu, Si/Cu and Si/Ni/Cu films were observed with field emission scanning electron microscopy (FE-SEM).

Electrochemical measurements were performed in CR2032 coin cells with Si/Cu and Si/Ni/Cu film electrodes. For a half-cell test, a metal Li foil was used as a counter electrode. Electrolyte was 1 M  $\text{LiPF}_6$  in a 1:1 (v/v) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). The separator was a porous polypropylene (Celgard 2400). The cells were assembled in an Ar-filled glove box. Galvanostatic charge–discharge half-cell tests were performed at various current densities of 210 (0.05 C-rate), 810 (0.2 C-rate) and  $4200 \text{ mA g}^{-1}$  (1 C-rate) at ambient temperature. The test was conducted between the initial open circuit voltage (OCV) and 0.01 V versus  $\text{Li/Li}^+$ , followed by a test between 0.01 V and 1.2 V after the first cycle. Gravimetric capacity was calculated from the density of a crystalline Si ( $2.33 \text{ g cm}^{-3}$ ).

For a full cell test,  $25 \mu\text{m}$ -thick  $\text{LiFePO}_4$  composite electrode was used as a cathode.  $\text{LiFePO}_4$  was synthesized by a modified mechano-chemical method [12]. Full cell tests were performed at current density of  $85 \text{ mA g}^{-1}$  (0.5 C-rate) at ambient temperature. Electrolyte and separator were the same as those used in a half-

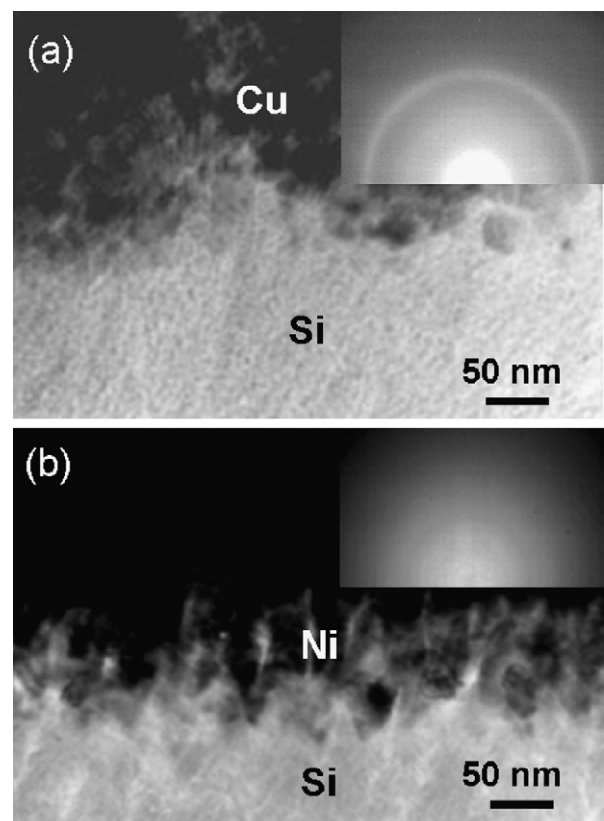
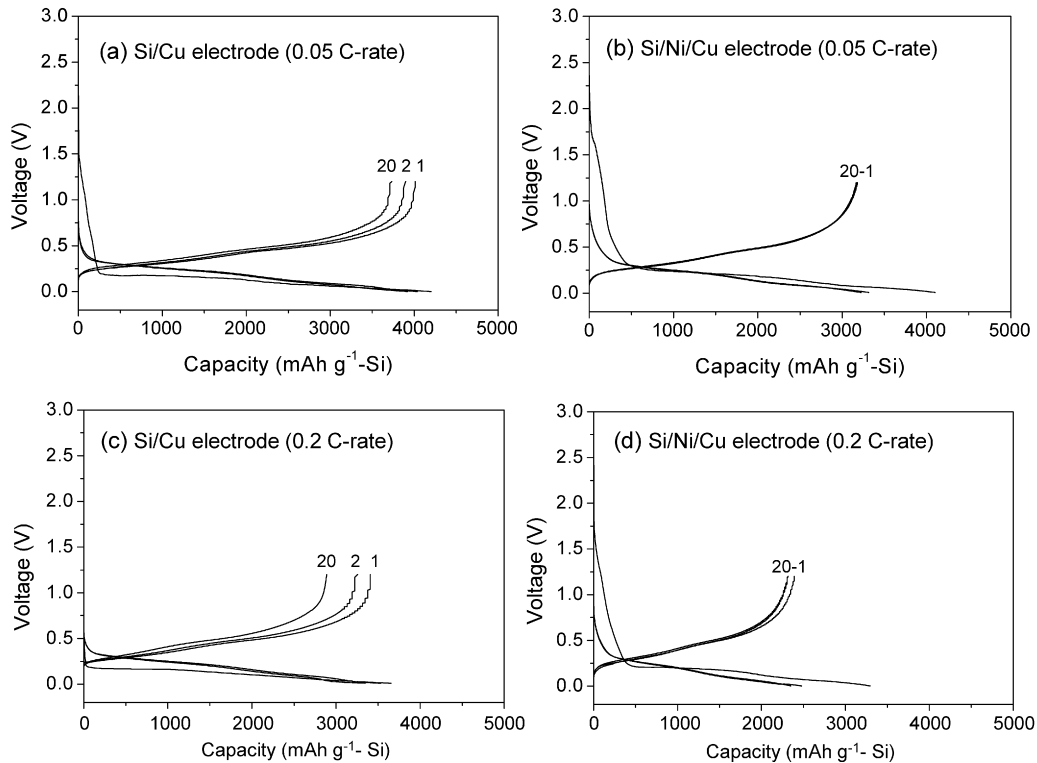


Fig. 2. TEM images and electron diffraction patterns of (a) Si/Cu film and (b) Si/Ni/Cu film. Electron diffraction pattern obtained Si film is shown in the inset of each figure.



**Fig. 3.** Voltage profiles of Si/Li cells with different current densities of  $210 \text{ mA g}^{-1}$  (0.05 C-rate) and  $840 \text{ mA g}^{-1}$  (0.2 C-rate). Cycle number is designated at the top of curve. (a) Si/Cu electrode (0.05 C-rate), (b) Si/Ni/Cu electrode (0.05 C-rate), (c) Si/Cu electrode (0.2 C-rate), and (d) Si/Ni/Cu electrode (0.2 C-rate).

cell. The test was conducted between OCV and 4.5 V versus Li/Li<sup>+</sup>, followed by a test between 4.5 V and 2.0 V after the first cycle.

### 3. Results and discussion

#### 3.1. Structural properties of Si/Cu film and Si/Ni/Cu film

Fig. 1 shows FE-SEM photographs of Cu substrate, Ni film on Cu substrate (Ni/Cu film), Si/Cu film, and Si/Ni/Cu film. Surface of Cu substrate seems to be smooth and flat, whereas surface of Ni/Cu film is rough because of the formation of small Ni clusters. A study related to morphology of Ni film was reported in a previous article [9]. When Si film is directly deposited on Cu substrate (Fig. 1(c)), the surface of the film is generally flat and crevice-like cracks are formed in the Si film because of relatively low diffusivity of Si during film growth [13]. On the other hand, Si film deposited on Ni/Cu film consists of clusters that can be distinguished by the grain boundary as shown in Fig. 1(d). The modified surface morphology of Si film is a result of the presence of small Ni clusters that act as a nucleation site for the formation of Si cluster. Average size of Si clusters is about 110 nm and crevices also exist in the Si cluster. Thus, it is known that the surface morphology of Si film depends on surface feature of the Cu substrate and the predeposited Ni film.

Crystallinity of Si/Cu film and Si/Ni/Cu film is investigated by TEM observation. Their cross-sectional TEM image and electron diffraction pattern are shown in Fig. 2. Specimen was prepared by the Ar ion milling in the direction of substrate side. Gray areas in two TEM images correspond to Si film. Scattered hallow rings are obtained from the areas indicating that an amorphous Si film is formed on both Cu substrate and Ni/Cu film. Furthermore, no peaks related to Si were found in the XRD profiles of two films (not shown here). Amorphous Si is known to be an effective structure to obtain the high capacity and the improved cycle performance compared

to crystalline Si [14,15]. Dark areas in Fig. 2(a) and (b) correspond to Cu substrate and Ni film, respectively. When comparing the interface of two films, round Cu grains are observed in the Si/Cu film, whereas Ni clusters with sharp edges are observed in the Si/Ni/Cu film. Therefore, a rough interface is formed in the Si/Ni/Cu film compared to Si/Cu film as shown in Fig. 1(c) and (d), and the Ni clusters projected into Si film is expected to enhance the structural stability of Si film.

#### 3.2. Electrochemical properties of Si/Li cell

Fig. 3 shows charge–discharge curves of Si/Li cells with Si/Cu and Si/Ni/Cu electrodes obtained at current density of  $210 \text{ mA g}^{-1}$  (0.05 C-rate) and  $840 \text{ mA g}^{-1}$  (0.2 C-rate). Fig. 3(a) and (b) show the curves of the cells tested at current density of  $210 \text{ mA g}^{-1}$ . Notice that voltage decreases in charging. Typical charge–discharge behavior of amorphous Si can be observed in the two cells [16–18]. Two voltage plateaus in the charge curve are associated with the formation of  $\text{Li}_2\text{Si}$  (0.25 V) and  $\text{Li}_{4.4}\text{Si}$  (0.1 V) phases. Two cells exhibit the first charge capacity over  $4100 \text{ mAh g}^{-1}$ , approaching to the theoretical capacity ( $4200 \text{ mAh g}^{-1}$ ). However, Si/Ni/Cu electrode exhibits the low reversible capacity ( $3200 \text{ mAh g}^{-1}$ ) compared to Si/Cu electrode ( $4010 \text{ mAh g}^{-1}$ ). The irreversible capacity of the cell with Si/Ni/Cu electrode is probably because of the formation of solid electrolyte interphase (SEI) during the first charge process, where a smooth voltage curve at  $\sim 1.5 \text{ V}$  is seen as shown in Fig. 3(b). Moreover, Si clusters on the surface have the wide surface area and provide numerous nucleation sites of SEI film [7,19]. In comparing the discharge curves up to the 20th cycle, the capacity gradually decreases with increasing cycle number in the cell with Si/Cu electrode, whereas the cell with Si/Ni/Cu electrode exhibits similar voltage curves and excellent cycle performance. Such a cycle performance is maintained at the current density of  $840 \text{ mA g}^{-1}$ , as shown in Fig. 3(c) and (d).

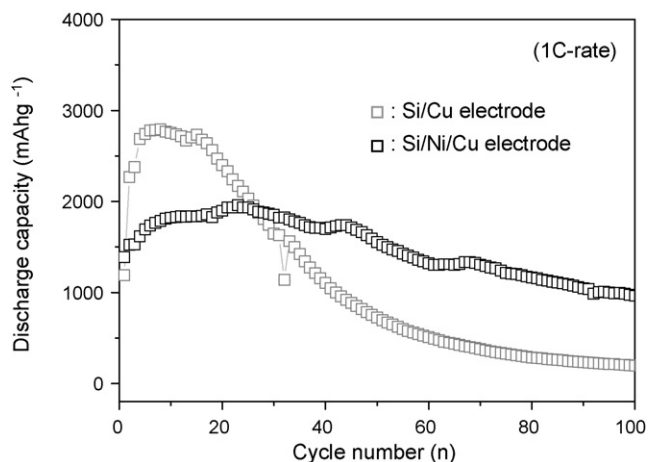


Fig. 4. Discharge capacity vs. cycle number plots of Si/Li cells with Si/Cu electrode and Si/Ni/Cu electrode, obtained at current density of  $4200 \text{ mA g}^{-1}$  (1 C-rate).

Difference in cycle performance of two cells can be clearly observed at the high current density. Fig. 4 shows discharge capacity of Si/Li cells with different film electrodes as a function of cycle number. The test was performed at high current density of  $4200 \text{ mA g}^{-1}$  corresponding to 1 C-rate. For the two cells, capacity increases at initial cycles and then decreases with an increase of cycle number. The low capacity at initial cycles is because of the high current density that induces the local reaction between Li and Si. Although the high capacity could be obtained from the cell with Si/Cu electrode, the capacity abruptly decreases after 20 cycles and the cycleability of the cell almost deteriorated after 100 cycles. On the other hand, a dull decrease of capacity is observed in the cell with Si/Ni/Cu electrode and the capacity over  $900 \text{ mA h g}^{-1}$  is maintained up to 100 cycles. The rates of capacity retention with respect to the maximum capacity are 12.5% for Si/Cu electrode and 55.0% for Si/Ni/Cu electrode, respectively. The low capacity of Si/Ni/Cu electrode at initial cycles may be because of the increased internal resistance induced by both the addition of Ni film and the formation of SEI film during the first charge process. Therefore, it is known that the cycle performance of surface-modified Si electrode is significantly improved by using a Ni film as an under layer. This suggests that the Si film with cluster structure can withstand the lateral volume change during charge–discharge process. Additionally, Ni clusters under Si film geometrically help to enhance the structural stability on cycling. The structural stability was confirmed by the surface observation of cycled electrode.

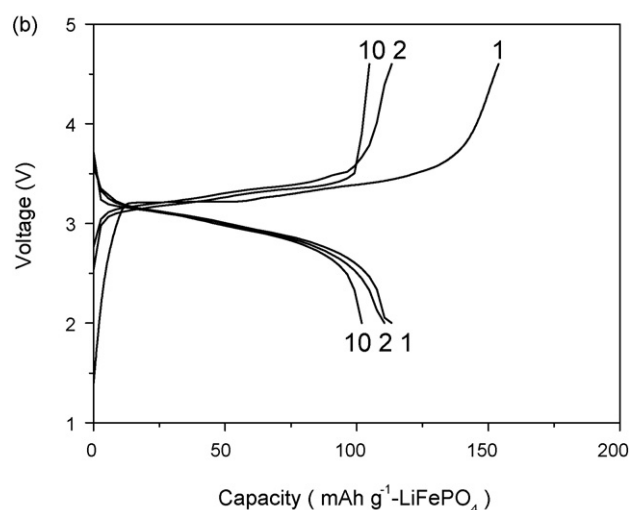
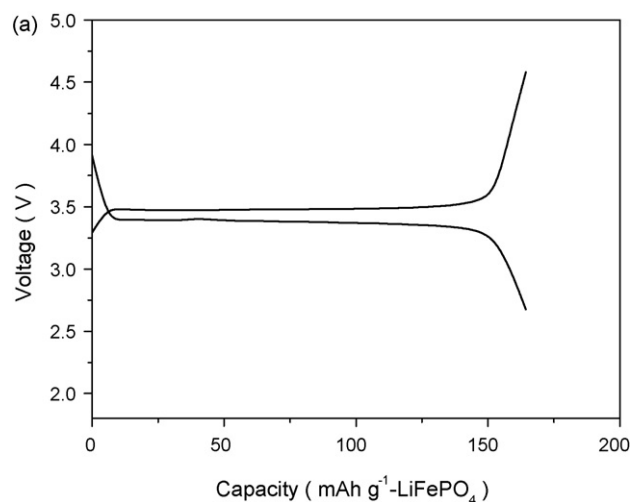


Fig. 6. Voltage profiles of LiFePO<sub>4</sub>/Li half cell and LiFePO<sub>4</sub>/Si full cell with current density of  $85 \text{ mA g}^{-1}$  (0.5 C-rate).

Fig. 5 shows FE-SEM photographs of Si/Cu and Si/Ni/Cu electrodes obtained after 10 cycles. Severe damage of Si film is observed on the surface of Si/Cu electrode and the Si film is mostly exfoliated from the Cu substrate. On the other hand, well-stuck Si film is observed in Si/Ni/Cu electrode, although some cracks are partially generated in the Si film. This means that a more stable structure

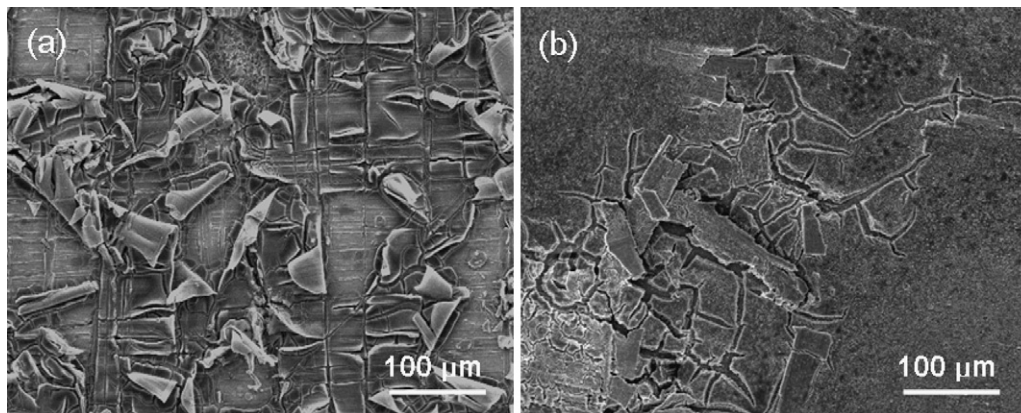


Fig. 5. FE-SEM photographs of (a) Si/Cu electrode and (b) Si/Ni/Cu electrode after 10 cycles.

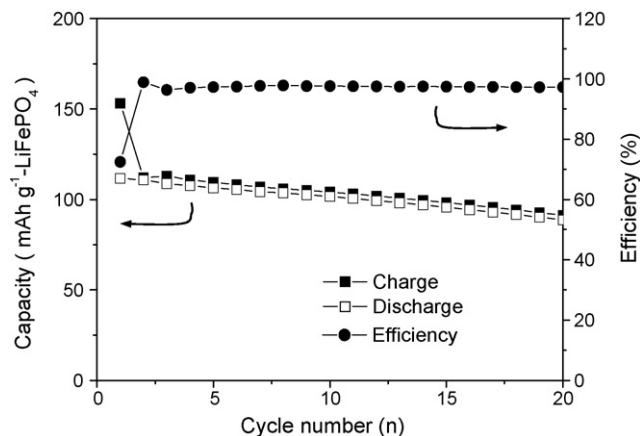


Fig. 7. Charge–discharge capacity and Coulombic efficiency as a function of cycle number for LiFePO<sub>4</sub>/Si full cell.

was formed in Si/Ni/Cu film. These electrochemical properties of the Si film electrode present the possibility of its application to Li ion batteries and/or thin film batteries. Thus, a full cell was assembled with Si/Ni/Cu film as an anode and LiFePO<sub>4</sub> as a cathode and its electrochemical properties were investigated.

### 3.3. Electrochemical properties of LiFePO<sub>4</sub>/Si cell

Charge–discharge curves of LiFePO<sub>4</sub>/Li and LiFePO<sub>4</sub>/Si cells are shown in Fig. 6. The LiFePO<sub>4</sub>/Si cell consists of LiFePO<sub>4</sub> composite electrode and Si/Ni/Cu film electrode. The curves were obtained at the same current density of 85 mA g<sup>-1</sup> corresponding to 0.5 C-rate of LiFePO<sub>4</sub>. Notice that from here, voltage increases in charging. In LiFePO<sub>4</sub>/Li cell, flat voltage plateaus are observed at ~3.5 V during charging and at ~3.4 V during discharging. On the other hand, slope voltage curves with two plateaus appear in LiFePO<sub>4</sub>/Si cell and their average voltages are ~3.3 V during charging and ~3.0 V during discharging. It is found that voltage drops of 0.2 V for charge and 0.4 V for discharge occur by replacing Li with Si.

LiFePO<sub>4</sub>/Li cell exhibits the charge capacity of 165.2 mAh g<sup>-1</sup> and the discharge capacity of 164.0 mAh g<sup>-1</sup>. In LiFePO<sub>4</sub>/Si cell, the charge capacity is 154.0 mAh g<sup>-1</sup>, corresponding to 90.5% of theoretical capacity of LiFePO<sub>4</sub> and the discharge capacity is 111.7 mAh g<sup>-1</sup>. It is noticeable that 350 nm thick Si electrode can accommodate a large amount of Li ion coming from 25 μm-thick LiFePO<sub>4</sub> electrode. However, relatively low coulombic efficiency of 73.0% is yielded in LiFePO<sub>4</sub>/Si cell compared to LiFePO<sub>4</sub>/Li cell (99.3%). The low efficiency is the result of the initial capacity loss

for Si/Ni/Cu film electrode as shown Fig. 3(b) and (d). The cycle performance of LiFePO<sub>4</sub>/Si cell is shown in Fig. 7. After the first cycle, the charge–discharge capacity decreases gradually, and the discharge capacity of 88.7 mAh g<sup>-1</sup> is obtained at the 20th cycle, corresponding to the capacity retention of 79.4%. Coulombic efficiency is maintained over 97% after the first cycle.

## 4. Conclusions

Surface morphology of amorphous Si film was modified by inserting a cluster-structured Ni film between Si film and Cu substrate. Si film with flat surface was formed on a Cu substrate, whereas a cluster-structured Si film was obtained on the Ni/Cu film. A Si/Li cell with Si/NiCu film electrode exhibited the significantly improved cycle performance compared to Si/Cu film electrode. A LiFePO<sub>4</sub>/Si cell with Si/NiCu film electrode exhibited the first charge capacity of 154.0 mAh g<sup>-1</sup>, corresponding to 90.5% of theoretical capacity of LiFePO<sub>4</sub> and the capacity retention of 79.4% at 20th cycle.

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