



The effect of nitrogen on the cycling performance in thin-film $\text{Si}_{1-x}\text{N}_x$ anode

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ABSTRACT

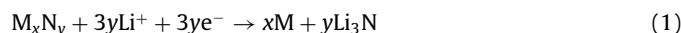
The effects of nitrogen on the electrochemical properties of silicon–nitrogen ($\text{Si}_{1-x}\text{N}_x$) thin films were examined in terms of their initial capacities and cycling properties. In particular, $\text{Si}_{0.76}\text{N}_{0.24}$ thin films showed negligible initial capacity but an abrupt capacity increase to ~ 2300 mA h/g after ~ 650 cycles. The capacity of pure Si thin films was deteriorated to $\sim 20\%$ of the initial level after 200 cycles between 0.02 and 1.2 V at 0.5 C ($1\text{ C} = 4200$ mA/g), whereas the $\text{Si}_{0.76}\text{N}_{0.24}$ thin films exhibited excellent cycle-life performance after ~ 650 cycles. In addition, the $\text{Si}_{0.76}\text{N}_{0.24}$ thin films at 50°C showed an abrupt capacity increase at an earlier stage of only ~ 30 cycles. The abnormal electrochemical behaviors in the $\text{Si}_{0.76}\text{N}_{0.24}$ thin films were demonstrated to be correlated with the formation of Li_3N and Si_3N_4 .

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1. Introduction

In recent years, research on lithium-ion batteries with higher energy density and better cycle-life performance has become critical with the development of portable electronics and hybrid electric vehicles. The theoretical capacity of the commercially used graphite anode (372 mA h/g for LiC_6) is insufficient to satisfy the energy demands. The use of silicon and several metals as a high-capacity anode have been investigated to alloy lithium with a high molar ratio [1–5]. However, these materials show poor capacity retention due to the serious volume change with lithium alloying/dealloying. Recently, various metal composites, metal oxides, and metal sulfides have also been studied extensively based on their transformations to lithium-metal alloys [6–10].

As alternatives, nitrides (Cu_3N , Ni_3N , Co_3N , Fe_3N , $\text{SiSn}_{0.87}\text{O}_{1.20}\text{N}_{1.72}$, etc.), have been investigated to improve the cycle-life performance and elucidate their electrochemical mechanisms [11–14]. These nitrides may undergo conversion reactions that lead to the formation of Li_3N and metal (M):



Among the few reports on silicon nitrides, investigated due to the large specific capacity of silicon (4200 mA h/g for $\text{Li}_{4.4}\text{Si}$), the ground Si_3N_4 powders exhibited a relatively poor capacity of ~ 40 mA h/g despite the expectation that Si_3N_4 would convert Si and Li_3N in reaction with lithium [15].

In this study, we examined the electrochemical properties of $\text{Si}_{1-x}\text{N}_x$ thin films as a negative electrode. The motivation of this work was to fabricate well-dispersed nanocomposites of silicon, silicon nitride, and lithium nitride from the initial silicon–nitrogen alloy, while maintaining the large capacity of silicon, the mechanical stability of Si_3N_4 , and the high Li-ion conductivity of Li_3N .

2. Experimental

Amorphous $\text{Si}_{1-x}\text{N}_x$ thin films were deposited using a Si target (2-in. diameter) by rf magnetron sputtering at 200°C , with a typical deposition rate of 10 nm/min. The substrate was a copper foil as a current collector for the electrochemical analysis. Prior to the $\text{Si}_{1-x}\text{N}_x$ deposition, the copper foils were etched with acetic acid (99.7%) to remove copper oxide or any surface impurities, and then pre-annealed at $\sim 200^\circ\text{C}$ in the sputtering chamber under vacuum [21,22]. The film thickness was confirmed by scanning electron microscopy (SEM: JSM-6330F, JEOL), and the elemental analysis was performed using a carbon, hydrogen, nitrogen, and sulfur (CHNS) instrument (Flash EA 1112, CEI).

The electrochemical properties of 200 nm-thick amorphous $\text{Si}_{1-x}\text{N}_x$ thin films were examined. Beaker-type half-cells were used to evaluate the electrochemical properties of the $\text{Si}_{1-x}\text{N}_x$ thin films. The electrochemical cells were comprised of Li Metal sheets as the counter and reference electrode, $\text{Si}_{1-x}\text{N}_x$ thin films (1-cm diameter) as the working electrode, and 1 M LiPF_6 in ethylene carbonate/diethyl carbonate (EC/DEC: 1/1 vol.%) (Cheil Industries, Inc.) as the electrolyte. The cells were discharged from the initial open-circuit voltage to 0.02 V, and cycled over the voltage range of 0.02 and 1.2 V at a current rate of 0.5 C ($1\text{ C} = 4200$ mA/g).

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The chemical-bond states of the $\text{Si}_{1-x}\text{N}_x$ thin films with charged/discharged state were analyzed by X-ray photoelectron spectroscopy (XPS: AXIS, Kratos) with $\text{MgK}\alpha$ radiation.

3. Results and discussion

Fig. 1 shows the nitrogen effect on the cycle-life performance of $\text{Si}_{1-x}\text{N}_x$ ($x = 0, 0.24, 0.41$) thin films between 0.02 and 1.2 V at 0.5 C rate. In the pure Si thin films, most of the initial capacity of ~ 3000 mA h/g is rapidly lost during cycling, and is reduced to ~ 700 mA h/g (with a retention of $\sim 20\%$) at the 200th cycle. However, the $\text{Si}_{0.76}\text{N}_{0.24}$ thin films show a negligible initial capacity with a meager increasing rate over 645 cycles, but then an abrupt increase to the maximum charge capacity of ~ 2300 mA h/g at the 750th cycle. In particular, the $\text{Si}_{0.76}\text{N}_{0.24}$ samples show the excellent cycle-life performance after the 750th cycle, while the $\text{Si}_{0.59}\text{N}_{0.41}$ thin films (Fig. 1c) exhibited negligible capacity during the whole 850 cycles.

The voltage profiles of the $\text{Si}_{0.76}\text{N}_{0.24}$ thin films are shown in Fig. 2. The charge and discharge capacities of the thin films are less than 80 mA h/g up to 645 cycles, as shown in the inset of Fig. 2. After a plateau at ~ 0.03 V at the 646th discharge, the following cycles exhibit a smoothly sloped shape on the following cycles. Moreover, the polarization in charge and discharge get reduced after the 647th cycle.

The Si 2p and N 1s XPS spectra for the as-deposited and discharged/charged (0.02 V/1.2 V) states, after the abrupt capacity increase at the 646th cycle, are shown in Fig. 3. The peak positions marked are the binding energies for Si 2p of Si_3N_4 (101.8 eV) and Si (99.3 eV), and those for N 1s of Si_3N_4 (397.4 eV) and Li_3N (403.1 eV) [23]. In the as-deposited $\text{Si}_{0.76}\text{N}_{0.24}$ thin films, the binding energies of Si 2p and N 1s are ~ 101 and ~ 397 eV, respectively, which is attributed to the solid solution of silicon and nitrogen.

After the abrupt capacity increase, the $\text{Si}_{0.76}\text{N}_{0.24}$ samples at the 0.02 V discharged state show a broadened Si 2p peak composed of Si_3N_4 and Si, and the N 1s peaks attributed to Si_3N_4 and Li_3N . The electrochemical reaction of Si–N alloy with lithium yields the evolution of Li–Si alloy, Li_3N , and Si_3N_4 . Since Li_3N is

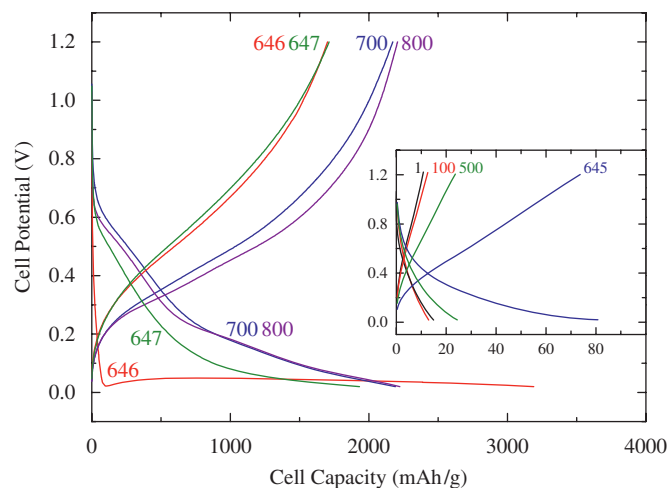


Fig. 2. (Color on the web) Voltage profiles of $\text{Si}_{0.76}\text{N}_{0.24}$ thin film between 0.02 and 1.2 V at 0.5 C rate. The inset shows the profiles up to the 645th cycle.

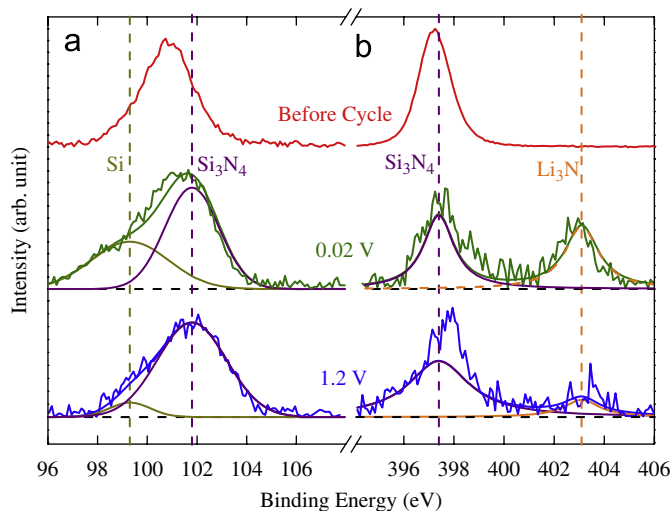


Fig. 3. (Color on the web) XPS spectra corresponding to (a) Si 2p and (b) N 1s of $\text{Si}_{0.76}\text{N}_{0.24}$ thin films before cycling, and for the 0.02 V discharged and 1.2 V charged states, after the abrupt capacity increase (646th cycle).

one of the best lithium-ion conducting compounds ($\sigma_{\text{Li}^+} \cong 10^{-4}$ S/cm at RT and $D_{\text{Li}} \cong 10^{-3}$ cm²/s at 500 °C) [16–20], it seems that the Li_3N generated during cycling in the $\text{Si}_{0.76}\text{N}_{0.24}$ thin films enhances the kinetics of the Li–Si alloying/dealloying.

At the 1.2 V charged state, the decrease in the N 1s peak for Li_3N and the increase for Si_3N_4 may be attributed to the partial decomposition of Li_3N at the charged state. While the exact phase evolutions cannot be determined from XPS, the integrated-intensity ratios of Si: Si_3N_4 : Li_3N are approximately 30:40:30 and 20:65:15, respectively, at 0.02 and 1.2 V. The partial decomposition of Li_3N at 1.2 V may increase the Si_3N_4 XPS fraction, even with the non-stoichiometric compounds, such as SiN_x and LiN_y , and the difficulty in separation of Si and Li–Si alloy from XPS. The decomposition and formation of Li_3N have been reported in the electrochemical reaction of lithium with metal nitrides [12,24].

After the abrupt capacity increase, the SEM images of the $\text{Si}_{0.76}\text{N}_{0.24}$ thin films for discharged/charged (0.02 V/1.2 V) states indicate typical island structures and crack morphologies on the Cu-foil substrates, as shown in Fig. 4. It has been reported that the island structures on the Cu foils reduced the stress that arises

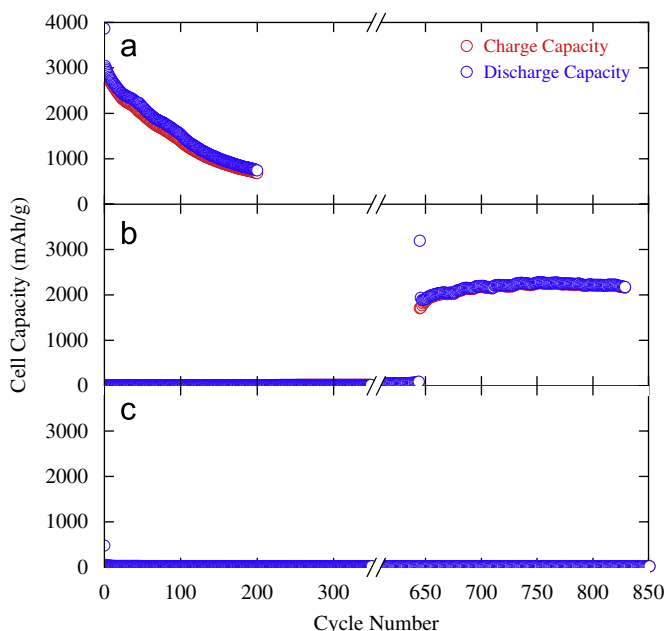


Fig. 1. (Color on the web) Cycle-life performance of amorphous, 200 nm-thick (a) Si, (b) $\text{Si}_{0.76}\text{N}_{0.24}$, and (c) $\text{Si}_{0.59}\text{N}_{0.41}$ thin films at 0.5 C rate (1 C = 4200 mA/g) at 25 °C.

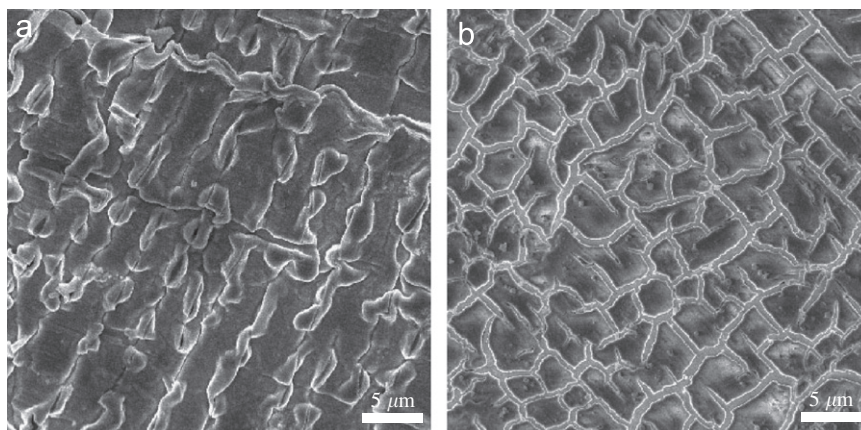


Fig. 4. SEM images of $\text{Si}_{0.76}\text{N}_{0.24}$ thin films for (a) 0.02 V discharged and (b) 1.2 V charged states, after the abrupt capacity increase.

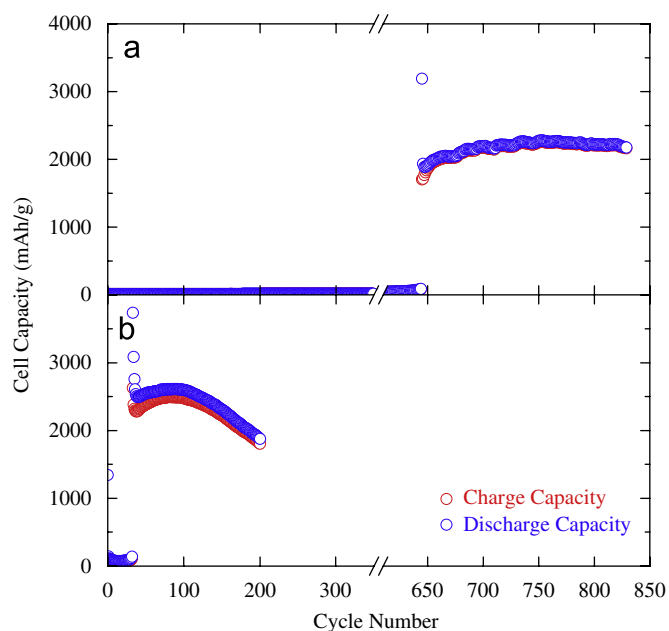


Fig. 5. (Color on the web) Cycle-life performance of $\text{Si}_{0.76}\text{N}_{0.24}$ thin films cycled at (a) 25 °C and (b) 50 °C between 0.02 and 1.2 V at 0.5 C rate.

from volume expansion/contraction during cycling (312% volume increase from Si to $\text{Li}_{4.4}\text{Si}$) [25,26]. In the $\text{Si}_{0.76}\text{N}_{0.24}$ thin films, the formation of Si_3N_4 and Li_3N which act as matrices that surround active Si grains may improve the cycle-life performance because Li_3N and mechanically stable Si_3N_4 maintain the integrity of Si grains against the large volume change with lithium alloying/dealloying.

The electrochemical reactions in the $\text{Si}_{0.76}\text{N}_{0.24}$ thin films should depend on the kinetics of Li_3N formation. The cycle-life performance of the $\text{Si}_{0.76}\text{N}_{0.24}$ thin films are tested at 25 °C and 50 °C, as shown in Fig. 5. Although cycling test at 25 °C shows an abrupt capacity increase after 645 cycles, cycling at 50 °C exhibits comparable capacity increase after only 34 cycles. Also, several different $\text{Si}_{0.76}\text{N}_{0.24}$ samples reproducibly exhibited the abrupt increases of capacities in the range of 400–650 and 30–55 cycles, respectively, at 25 °C and 50 °C, which are attributed to the enhanced formation of the ionic conductor (Li_3N) at the elevated temperature.

4. Conclusions

The effects of nitrogen on the electrochemical properties of $\text{Si}_{1-x}\text{N}_x$ thin films were studied. The Si–N alloyed thin films exhibited an enhanced cycle-life performance compared with that of pure Si thin films. In particular, the $\text{Si}_{0.76}\text{N}_{0.24}$ thin films at 25 °C showed the negligible capacity during ~650 cycles followed by an abrupt capacity increase to ~2300 mAh/g, while the electrochemical performance at 50 °C increased abruptly after only ~30 cycles. Furthermore, the $\text{Si}_{0.59}\text{N}_{0.41}$ thin films exhibited negligible capacity over the complete 850-cycle range. The abnormal electrochemical behaviors were correlated with the formation of Li_3N (for lithium-ion conductor) and Si_3N_4 (for mechanical stability) during cycling. Further studies will be needed to identify the phases and nanostructures of Li_3N and Si_3N_4 in the Si–N alloyed thin films.

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