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

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The effects of nitrogen on the electrochemical properties of silicon–nitrogen (Si$_{1-x}$N$_x$) thin films were examined in terms of their initial capacities and cycling properties. In particular, Si$_{0.3}$(N$_{0.4}$)$_{24}$ 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 ~20% of the initial level after 200 cycles between 0.02 and 1.2 V at 0.5 C (1 C = 4200 mA/g), whereas the Si$_{0.3}$(N$_{0.4}$)$_{24}$ thin films exhibited excellent cycle-life performance after ~650 cycles. In addition, the Si$_{0.3}$(N$_{0.4}$)$_{24}$ thin films at 50 °C showed an abrupt capacity increase at an earlier stage of only ~30 cycles. The abnormal electrochemical behaviors in the Si$_{0.3}$(N$_{0.4}$)$_{24}$ thin films were demonstrated to be correlated with the formation of Li$_3$N and Si$_3$N$_4$.

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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$_3$N, Ni$_3$N, Co$_3$N, Fe$_3$N, SiSn$_{0.87}$O$_{1.22}$, 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$_3$N and metal (M):

$$M_N + 3yLi^+ + 3ye^- \rightarrow xM + yLi_3N \quad (1)$$

$$M + zLi^+ + ze^- \rightarrow Li_2M \quad (2)$$

Among the few reports on silicon nitrides, investigated due to the large specific capacity of silicon (4200 mA h/g for Li$_4$Si), the ground Si$_3$N$_4$ powders exhibited a relatively poor capacity of ~40 mA h/g despite the expectation that Si$_3$N$_4$ would convert Si and Li$_3$N in reaction with lithium [15].

In this study, we examined the electrochemical properties of Si$_{1-x}$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$_3$N$_4$, and the high Li-ion conductivity of Li$_3$N.

2. Experimental

Amorphous Si$_{1-x}$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 Si$_{1-x}$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 ~200 °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 Si$_{1-x}$N$_x$ thin films were examined. Beaker-type half-cells were used to evaluate the electrochemical properties of the Si$_{1-x}$N$_x$ thin films. The electrochemical cells were comprised of Li metal sheets as the counter and reference electrode, Si$_{1-x}$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 C = 4200 mA/g).
The chemical-bond states of the Si$_{1-x}$N$_x$ thin films with charged/discharged state were analyzed by X-ray photoelectron spectroscopy (XPS: AXIS, Kratos) with MgK$_\alpha$ radiation.

3. Results and discussion

Fig. 1 shows the nitrogen effect on the cycle-life performance of Si$_{1-x}$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 $\sim$3000 mAh/g is rapidly lost during cycling, and is reduced to $\sim$700 mAh/g (with a retention of $\sim$20%) at the 200th cycle. However, the Si$_{0.76}$N$_{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 $\sim$2300 mAh/g at the 750th cycle. In particular, the Si$_{0.76}$N$_{0.24}$ samples show the excellent cycle-life performance after the 750th cycle, while the Si$_{0.59}$N$_{0.41}$ thin films (Fig. 1c) exhibited negligible capacity during the whole 850 cycles.

The voltage profiles of the Si$_{0.76}$N$_{0.24}$ thin films are shown in Fig. 2. After a plateau at $\sim$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$_3$N$_4$ (101.8 eV) and Si (99.3 eV), and those for N 1s of Si$_3$N$_4$ (397.4 eV) and Li$_3$N (403.1 eV) [23]. In the as-deposited Si$_{0.76}$N$_{0.24}$ thin films, the binding energies of Si 2p and N 1s are $\sim$101 and $\sim$397 eV, respectively, which is attributed to the solid solution of silicon and nitrogen.

After the abrupt capacity increase, the Si$_{0.76}$N$_{0.24}$ samples at the 0.02 V discharged state show a broadened Si 2p peak composed of Si$_3$N$_4$ and Si, and the N 1s peaks attributed to Si$_3$N$_4$ and Li$_3$N. The electrochemical reaction of Si–N alloy with lithium yields the evolution of Li–Si alloy, Li$_3$N, and Si$_3$N$_4$. Since Li$_3$N is one of the best lithium-ion conducting compounds ($D_L$ $\approx$ 10$^{-4}$S/cm at RT and $D_L$ $\approx$ 10$^{-3}$ cm$^2$/s at 500 °C) [16–20], it seems that the Li$_3$N generated during cycling in the Si$_{0.76}$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$_3$N and the increase for Si$_3$N$_4$ may be attributed to the partial decomposition of Li$_3$N at the charged state. While the exact phase evolutions cannot be determined from XPS, the integrated-intensity ratios of Si$_3$N$_4$/Li$_3$N are approximately 30:40:30 and 20:65:15, respectively, at 0.02 and 1.2 V. The partial decomposition of Li$_3$N at 1.2 V may increase the Si$_3$N$_4$ 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$_3$N have been reported in the electrochemical reaction of lithium with metal nitrides [12,24].

After the abrupt capacity increase, theSEM images of the Si$_{0.76}$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...
from volume expansion/contraction during cycling (312% volume increase from Si to Li\textsubscript{4.4}Si) [25,26]. In the Si\textsubscript{0.76}N\textsubscript{0.24} thin films, the formation of Si\textsubscript{3}N\textsubscript{4} and Li\textsubscript{3}N which act as matrices that surround active Si grains may improve the cycle-life performance because Li\textsubscript{3}N and mechanically stable Si\textsubscript{3}N\textsubscript{4} maintain the integrity of Si grains against the large volume change with lithium alloying/dealloying.

The electrochemical reactions in the Si\textsubscript{0.76}N\textsubscript{0.24} thin films should depend on the kinetics of Li\textsubscript{3}N formation. The cycle-life performance of the Si\textsubscript{0.76}N\textsubscript{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 Si\textsubscript{0.76}N\textsubscript{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\textsubscript{3}N) at the elevated temperature.

4. Conclusions

The effects of nitrogen on the electrochemical properties of Si\textsubscript{1-x}N\textsubscript{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 Si\textsubscript{0.76}N\textsubscript{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 Si\textsubscript{0.59}N\textsubscript{0.41} thin films exhibited negligible capacity over the complete 850-cycle range. The abnormal electrochemical behaviors were correlated with the formation of Li\textsubscript{3}N (for lithium-ion conductor) and Si\textsubscript{3}N\textsubscript{4} (for mechanical stability) during cycling. Further studies will be needed to identify the phases and nanostructures of Li\textsubscript{3}N and Si\textsubscript{3}N\textsubscript{4} in the Si–N alloyed thin films.

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Electromagnetic transport properties and magnetoresistance of La$_{0.7}$Ca$_{0.2}$Sr$_{0.1}$MnO$_3$–Ag composites prepared by electroless process
C.S. Xiong, Y.F. Cui, Y.H. Xiong, H.L. Pi, X.C. Bao, Q.P. Huang, Y. Zeng, F.F. Wei, C.F. Zheng and J. Zhu
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Magnetic field dependence of the MR for the composites at 298 K. The inset is the different silver-plating time dependence of the variation of MR at 2 T.

Hydrothermal synthesis of antimony oxychloride and oxide nanocrystals: Sb$_4$O$_5$Cl$_2$, Sb$_8$O$_{11}$Cl$_2$, and Sb$_2$O$_3$
Xiang Ying Chen, Hyun Sue Huh and Soon W. Lee
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We described herein a facile solution-phase route to three nanocrystals of antimony oxychlorides and oxides (Sb$_4$O$_5$Cl$_2$, Sb$_8$O$_{11}$Cl$_2$, and Sb$_2$O$_3$). In particular, the solvent composition controlled the selective preparation of cubic Sb$_2$O$_3$ (senarmontite) and orthorhombic Sb$_2$O$_3$ (valentinite).

Wet chemical synthesis and photocatalytic activity of potassium niobate K$_6$Nb$_{10.8}$O$_{30}$ powders
Gaoke Zhang, Yanjun Hu, Xinmiao Ding, Jin Zhou and Junwei Xie
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The K$_6$Nb$_{10.8}$O$_{30}$ powders with TB-type structure were synthesized by a wet chemical method at lower temperature. The particle size of the as-prepared powders is much smaller than that of the sample by obtained solid-state method and its photocatalytic activity is much higher than that of the latter and slightly higher than that of P25-TiO$_2$.

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The Si$_{0.76}$N$_{0.24}$ thin films showed negligible initial capacity, but an abrupt capacity increase to ~2300 mA h/g after ~650 cycles, followed by excellent cycle-life performance. This abnormal electrochemical behavior was demonstrated to be correlated with the formation of Li$_3$N and Si$_3$N$_4$. 