

Thick vacuum deposited silicon films suitable for the anode of Li-ion battery

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Abstract

Vacuum deposited silicon film on a Ni foil substrate showed very stable Li charge/discharge performance in PC containing 1 M LiClO₄. The performance, however, became poorer rapidly with the increase in the film thickness.

In an attempt to attain long cycleability with large capacity for the vacuum deposited thicker silicon film, surface morphology of the depositing substrate metal was examined. Filing with a sand paper was quite effective for providing longer cycleability as compared to the pristine Ni foil. Etching with aqueous solution of FeCl₃ resulted in giving the surface roughened to a great extent. A 1.1 μm thick silicon film deposited on the well-etched substrate maintained the specific capacity over 1500 mAh g⁻¹ even after 400 cycles with 1 C rate constant current charge/discharge.

The most roughened surface could be obtained by depositing electrolytically on a copper foil. The surface revealed a jammed group of tiny pyramid like steeple-crowned caps. A 3.6 μm thick silicon film deposited on the copper substrate thus obtained maintained constantly around 2000 mAh g⁻¹ during 50 cycles.

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Keywords: Li-ion batteries; New anode material; Silicon film; Vacuum deposition; Surface roughening

1. Introduction

The third generation (3G) of the portable electronic IT equipments is expected to be mounted with far expanded new software, which requires the powering batteries to have doubled energy and power densities. The most promising batteries that can respond to this requirement are Li-ion batteries. The materials practically used in the batteries now, however, should be replaced by novel high performance materials. In case of the anode, the active materials now presently used are graphite materials having a specific capacity of about 360 mAh g⁻¹ which is 97% of the theoretical capacity, and hence, this should be replaced by some new materials having over doubled energy density.

One of the most attractive anode materials for this purpose are those based on silicon. The cycle performance of silicon,

however, is quite poor due to the large expansion and shrinkage during insertion/extraction of large amount of Li [1,2]. Attempts to solve this issue have been performed, remarkable improvement being provided [3,4], but the cycle life appears to be required to be improved further. We have examined a vacuum deposited silicon film and verified that it can keep huge capacity and long cycle life even under high rate charge and discharge [5]. The performance, however, was obtained for a film whose thickness was rather thin. Yazami and co-workers have shown similar results [6]. For applying to the practical batteries, it is required to examine with a sufficiently thicker film. We have succeeded partially to attain good performance for thicker film but not sufficiently thick [7,8].

In the present study, we investigated with thicker films whose thickness was over 3000 nm. We would like to show how we could realize satisfactory performance with films as thick as over 3000 nm, especially in view of modifying the substrate surface.

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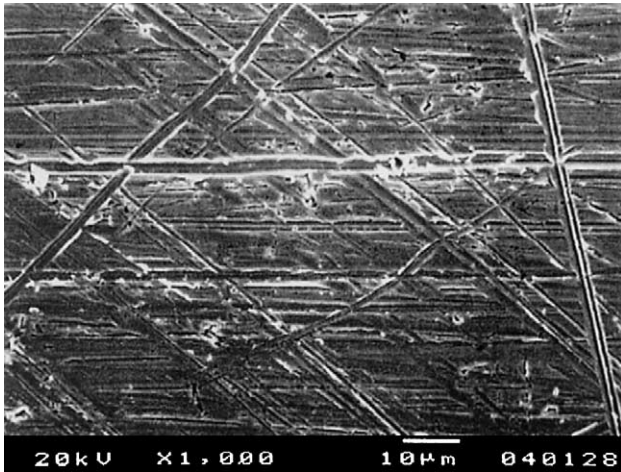


Fig. 1. SEM image of the surface of a 30 μm thick Ni foil filed with a No. 1000 sand paper.

2. Experimental

A metallic silicon film was vacuum deposited up to a 4 μm thick film on a 30 μm thick Ni foil or surface modified Cu foil. The thickness of the vacuum deposited silicon film was controlled by a quartz vibrating micro-balance mounted near the substrate in the vacuum chamber. Negative carrier doped Si (5×10^{-22} mol m^{-3} of phosphor doped) was used as the evaporation source.

Modifying the surface morphology of the substrate was done by filing with a sand paper, etching the substrate with aqueous solution of FeCl_3 , or with electrolytical deposition of copper on a copper foil in an aqueous CuSO_4 bath under controlled condition. The SEM image of the surface of the sand paper filed Ni is shown in Fig. 1. The SEM images of the surface of Ni foil etched with three different treatments with

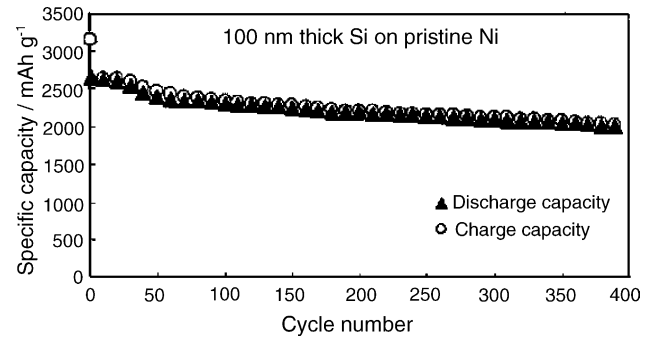


Fig. 3. 1C rate Li charge/discharge cycle performance of a 100 nm thick silicon film deposited on an untreated pristine Ni foil (in PC containing 1 M LiClO_4).

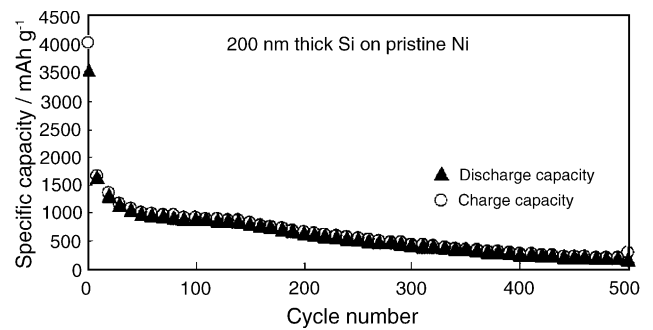


Fig. 4. 1C rate Li charge/discharge cycle performance of a 200 nm thick silicon film deposited on an untreated pristine Ni foil (in PC containing 1 M LiClO_4).

FeCl_3 solutions are shown in Fig. 2. The obtained Ni substrate with a Si film was cut into 1 cm \times 1 cm and was offered to the constant current cycle evaluation in PC containing 1 M LiClO_4 in a glove box filled with dried Ar.

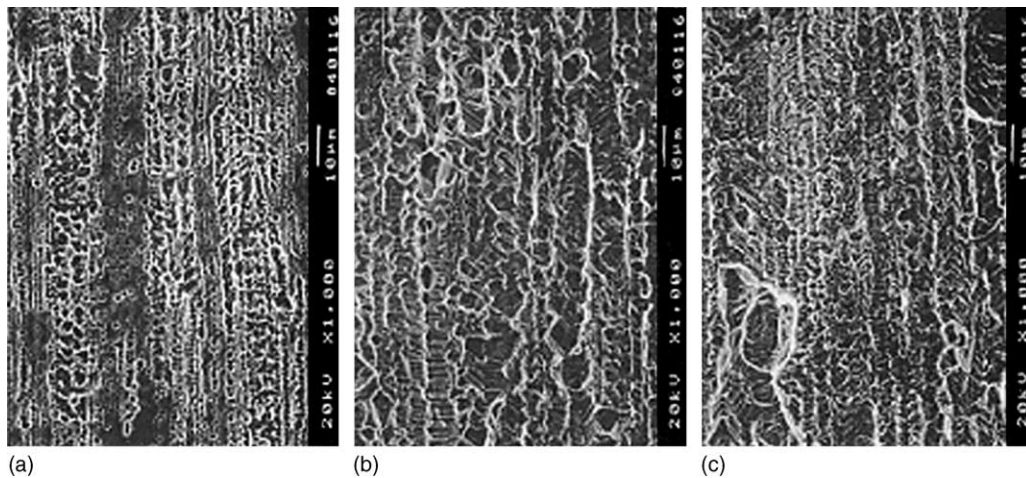


Fig. 2. SEM images of a Ni foil whose surface was etched by aqueous solutions of FeCl_3 with three different etching conditions: (a) with 0.3 M FeCl_3 for 3 min; (b) with 1 M FeCl_3 for 3 min; (c) at first with 1 M FeCl_3 for 3 min, then with 0.3 M FeCl_3 for 3 min.

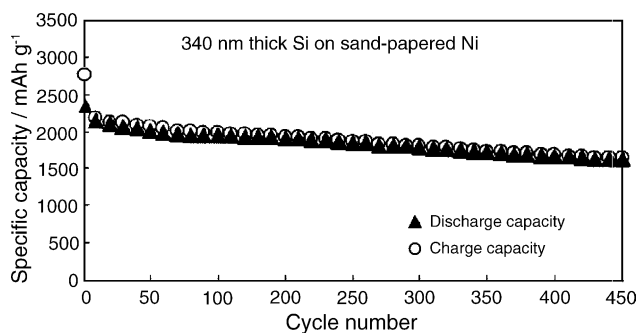


Fig. 5. 1 C rate Li charge/discharge cycle performance of a 340 nm thick silicon film deposited on a Ni foil whose surface was roughened with a No. 1000 sand paper (in PC containing 1 M LiClO₄).

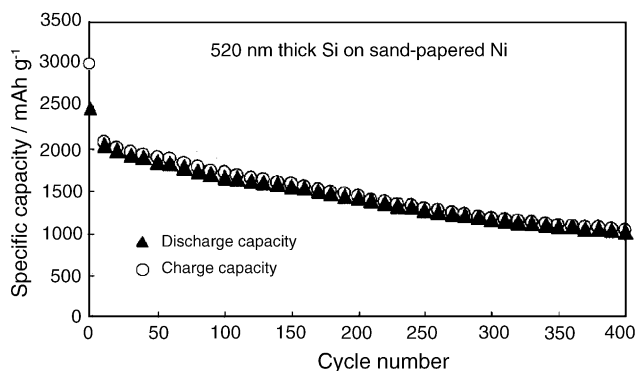


Fig. 6. 1 C rate Li charge/discharge cycle performance of a 520 nm thick silicon film deposited on a Ni foil whose surface was roughened with a No. 1000 sand paper (in PC containing 1 M LiClO₄).

3. Results and discussion

The cycle performance of a thin film was satisfactory even with a Ni substrate whose surface was untreated as seen in Fig. 3. The performance, however, became poor for thicker film (Fig. 4). During the course of experiment, we noticed that the roughened surface of the substrate gave better results. Only with a simple filing with a sand paper, we could improve the cycleability for thicker film as seen in Fig. 5. The surface

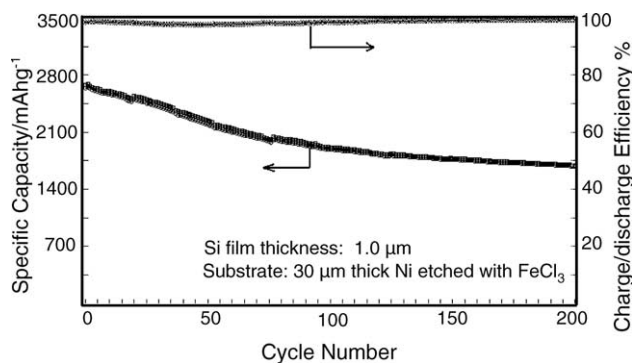


Fig. 8. Cycle performance of a 1.0 μm thick silicon film deposited on the surface roughened 30 μm thick Ni etched under the most favorable etching condition using aqueous solutions of FeCl₃.

roughening with a sand paper became less effective with the increase of the film thickness as shown in Fig. 6. We examined the surface roughening by etching with aqueous solutions of FeCl₃ by varying the concentration and treating period. As shown in the experimental part, the state of the roughened surface differed depending on the choice of the etching solution and etching period (Fig. 2).

To examine how depends the performance of the deposited film on the substrate etching condition, we compared the SEM image after cycling for the film having the same thickness on different surfaces. The results obtained after 20 cycles for 440 nm thick films are shown in Fig. 7, where we see the most stable film was on the surface treated with combined etching. By the use of the etched Ni foil with the most preferable etching condition, we deposited a 1 μm thick silicon film and examined the cycle performance. The results are shown in Fig. 8. We could obtain far better results as compared with the case of simple filing even with a thicker film.

More improved surface roughening was successful with a copper foil on which a number of pyramid-like cap structures were covered by the controlled electrolysis deposition in a CuSO₄ bath. A 3.6 μm thick silicon film was deposited on it, the surface structure being shown in Fig. 9, which was obtained with a oblique viewing of SEM. The cycle

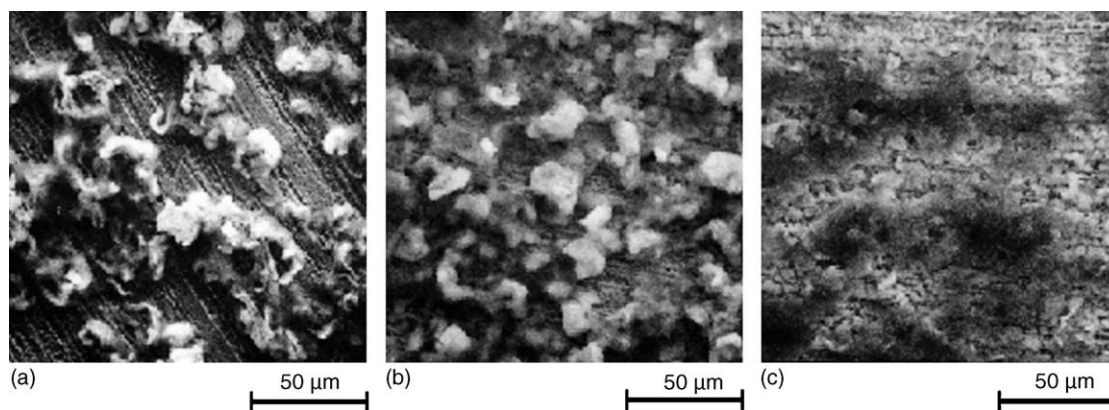


Fig. 7. SEM images of 440 nm thick silicon film after 1 C rate 20 cycles on Ni foils whose surface was etched by aqueous solutions of FeCl₃ with three different etching conditions: (a) with 0.3 M FeCl₃ for 3 min; (b) with 1 M FeCl₃ for 3 min; (c) first with 1 M FeCl₃ for 3 min, then with 0.3 M FeCl₃ for 3 min.

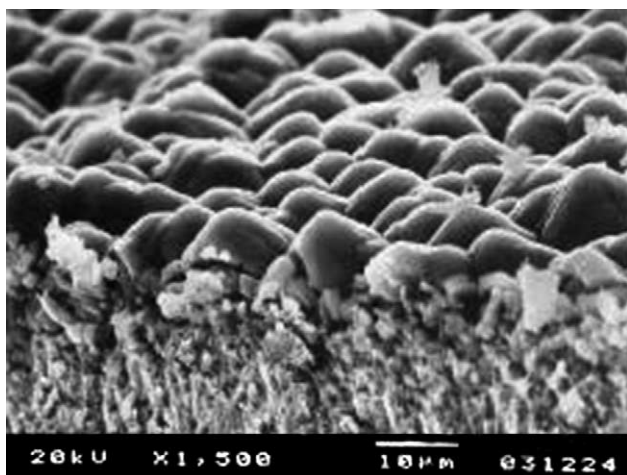


Fig. 9. SEM image with oblique view of the electrolytically modified copper surface covered with a 4 μm thick silicon film.

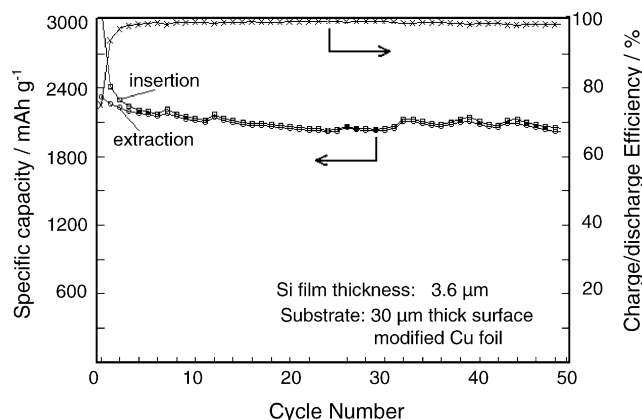


Fig. 10. A 0.5C rate cycle performance of a 3.6 μm thick silicon film deposited on a 30 μm thick surface electrolytically modified copper foil.

performance of the film is shown in Fig. 10. The extraction capacity over 2000 mAh g^{-1} could be kept stable during 50 cycles with about 100% charge/discharge efficiency, where the cycle test is still continuing.

4. Conclusions

Although only poor cycle performance could be obtained for thicker silicon film on the untreated Ni substrate, the surface treatment to roughen was found quite effective for improving the cycleability for thicker deposited silicon films. Especially, combined etching with aqueous solutions of FeCl_3 with different concentrations revealed remarkable improvement. Electrolytically deposited pyramid like tiny caps covering over the substrate copper foil gave the best results. The effect may be attributed to the so-called anchor effect to fix the deposited silicon film tightly on the substrate, being durable against large volume change during Li insertion/extraction cycles.

References

- [1] R.A. Huggins, *Solid State Ionics* 113–115 (1998) 57.
- [2] H. Li, X. Huang, L. Chen, Z. Wu, Y. Liang, *Electrochem. Solid State Lett.* 2 (1999) 547.
- [3] T. Umeno, K. Fukuda, H. Wang, N. Dimov, M. Yoshio, *Chem. Lett.* (2001) 1186.
- [4] I. Yonezu, H. Tarui, S. Yoshimura, S. Fujitani, T. Nohma, 12th International Meeting of Li batteries, 27 June–2 July, 2004, Nara, Abstract No. 58.
- [5] S. Ohara, J. Suzuki, K. Sekine, T. Takamura, *J. Power Sources* 119–121 (2003) 591.
- [6] C. Graez, C. Ahn, R. Yazami, B. Fultz, *Electrochem. Solid State Lett.* 6 (2003) 194.
- [7] S. Ohara, J. Suzuki, K. Sekine, T. Takamura, *Electrochemistry* 71 (2003) 1126.
- [8] T. Takamura, S. Ohara, M. Uehara, J. Suzuki, K. Sekine, *J. Power Sources* 129 (2004) 96.