Short communication

Amorphous silicon anode for lithium-ion rechargeable batteries

Hunjoon Jung[*], Min Park, Yeo-Geon Yoon, Gi-Bum Kim, Seung-Ki Joo

School of Materials Science and Engineering, Seoul National University, Seoul 151-744, South Korea

Abstract

Amorphous silicon is investigated as a negative electrode (anode) material for lithium-ion batteries. A thin (500 Å) film of amorphous silicon is cycled versus a lithium electrode. A maximum discharge capacity of 4 Ah g^{-1} is observed by cycling over a voltage window of 0–3 V, but capacity fading is rapid after 20 cycles. This capacity fading can be overcome, to more than 400 cycles, by changing the lower voltage limit to 0.2 V. In this situation, the discharge capacity is about 400 mAh g^{-1}.
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1. Introduction

Elemental lithium is the most favorable material for negative electrodes in Li-ion batteries in terms of electrode potential and specific energy. Unfortunately, however, potential safety problems and loss of capacity upon cycling has been an impediment to using lithium as a practical negative electrode (anode) in rechargeable lithium batteries [1,2]. Present commercial rechargeable lithium cells use carbon materials for negative electrodes because lithium can be reversibly inserted into them [3]. Since the carbons suffer irreversible capacity loss (ICL) on the first cycle [4], various alternative materials such as lithium alloys [5–9] and metal oxides [10–13] have been extensively studied. Some have larger charge capacities than graphite but cycle-life is still unsatisfactory. In this study, the electrochemical performance of an amorphous silicon electrode is examined. To enhance durability, the voltage window is controlled and a LiMn$_2$O$_4$ positive electrode (cathode) is coupled with the amorphous silicon anode to demonstrate charge–discharge characteristics.

2. Experimental

Silicon thin films were prepared by chemical vapor deposition. Fifty sccm flows of Si$_2$H$_6$ were introduced into the reaction chamber and the process pressure was maintained at 300 mTorr during deposition. The thin films (thickness ~500 Å) were deposited at 450 °C over a molybdenum (3000 Å)/glass substrate. The molybdenum layer, which was deposited by sputtering, served as a current-collector. The thickness of the silicon layer was measured by an ellipsometer, and X-ray diffraction was used to characterize the material. Part of the silicon layer was masked and dry etched with SF$_6$ gas to allow connection of the current-collector to the outside circuit. The amount of silicon deposited was calculated by assuming a density of 2.33 for the silicon film.
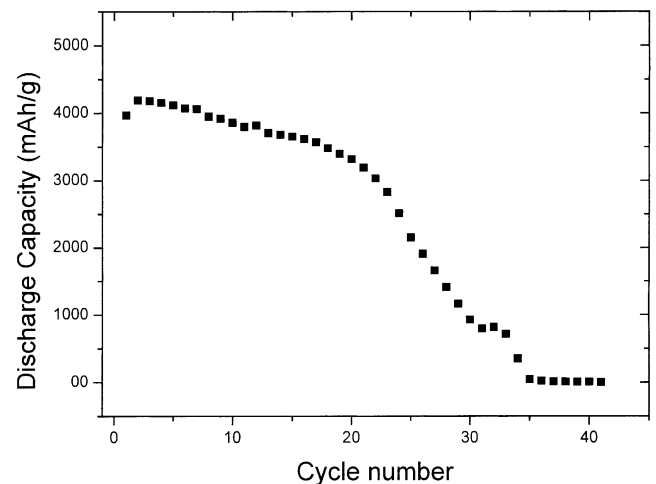

Fig. 1. Cycle performance of amorphous silicon electrode (voltage window 0–3 V).

[*] Corresponding author. Tel.: +82-2-880-7442; fax: +82-2-887-8791.
E-mail address: hunjoon1@snu.ac.kr (H. Jung).

Cells were operated in an argon-filled glove-box. LiClO$_4$ (1 M) in propylene carbonate (PC) was used as the electrolyte, and lithium foil as the counter and the reference electrodes. A silicon|1 M LiClO$_4$, PC|LiMn$_2$O$_4$ cell was also tested for evaluation of the silicon electrode as an anode. Thin films of LiMn$_2$O$_4$ (2000 Å) were deposited by sputtering. The moisture and the oxygen in the glove-box were each maintained below 1 ppm. An WonA Tech (WBCS3000) testing system was used for galvanostatic cycling. All cells were cycled at 100 μA cm^{-2} at room temperature unless otherwise stated.

3. Results and discussion

No reflections except those of the molybdenum substrate was detected by XRD analysis of the sample. Thus, the deposited silicon is considered amorphous (a-Si).

Cycling tests were performed for the Li|electrolyte|a-Si cell. The data shows that the discharge capacity of a-Si is as high as 4 Ah g^{-1} (Fig. 1). To the authors knowledge, this is the highest capacity reported to date. The value indicates that each silicon atom can uptake as many as 4.2 Li atoms (Li$_{4.2}$Si) at room temperature reversibly, which approaches
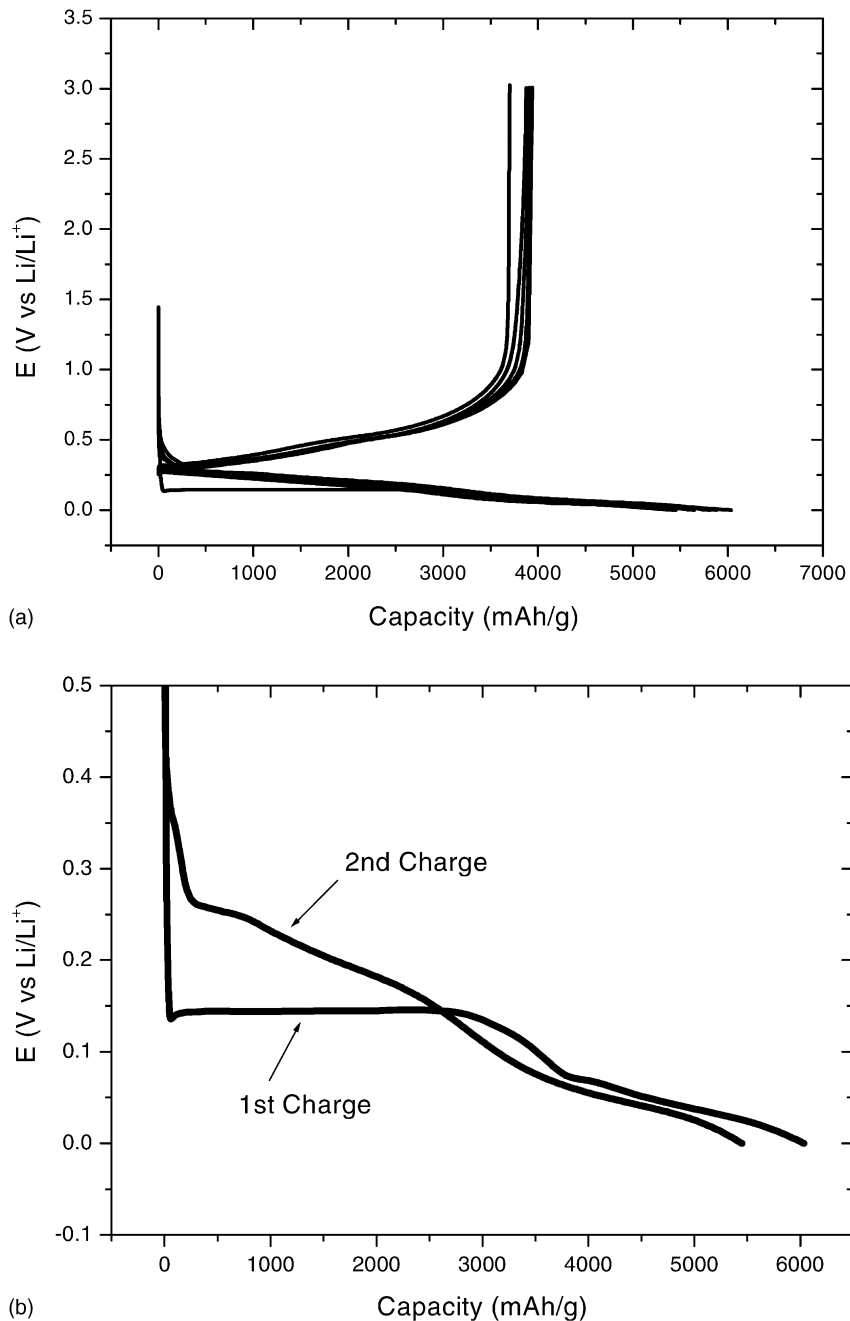

Fig. 2. Potential profile of amorphous Si electrode at constant current of 100 μA cm^{-2} (voltage window 0–3 V): (a) charge–discharge voltage profile; (b) enlarged charge voltage profile.

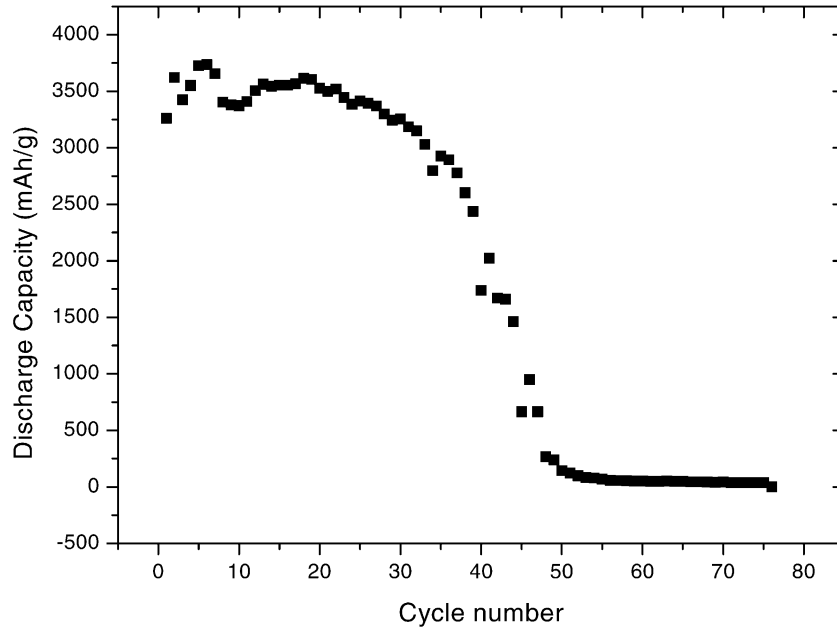Fig. 3. Cycle performance of amorphous silicon electrode (voltage window 0.1–3 V).

the theoretical capacity limit of $Li_{22}Si_5$. After 20 cycles, however, the capacity feeds rapidly. The profile shown in Fig. 2a shows that the a-Si potential window is 0.3–0 V during charging and 0.3–0.7 V during discharging. The enlarged potential profile, when charged, is shown in Fig. 2b. A potential plateau at 140 mV is found only in the first charge. This means that two phases (a-Si and $Li_{13}Si_4$ are assumed by charge quantity calculation) are present during the first charging stage. On the second charge, however, an equilibrium plateau is not observed. According to Huggins [2], a plateau does not develop when the nucleation process is kinetically hindered so that the next equilibrium phase is impeded, further compositional changes occur only within the structure of the initial phase.

If the lower voltage limit of cycling is increased from 0 to 100 mV, the cycleability is enhanced, as shown in Fig. 3, with sacrifice of discharge capacity. Because of the plateau in the first charge stage, however, it is difficult to set up experimentally a voltage window around the plateau potential. In the operation of a lithium-ion cell, a fixed quantity of
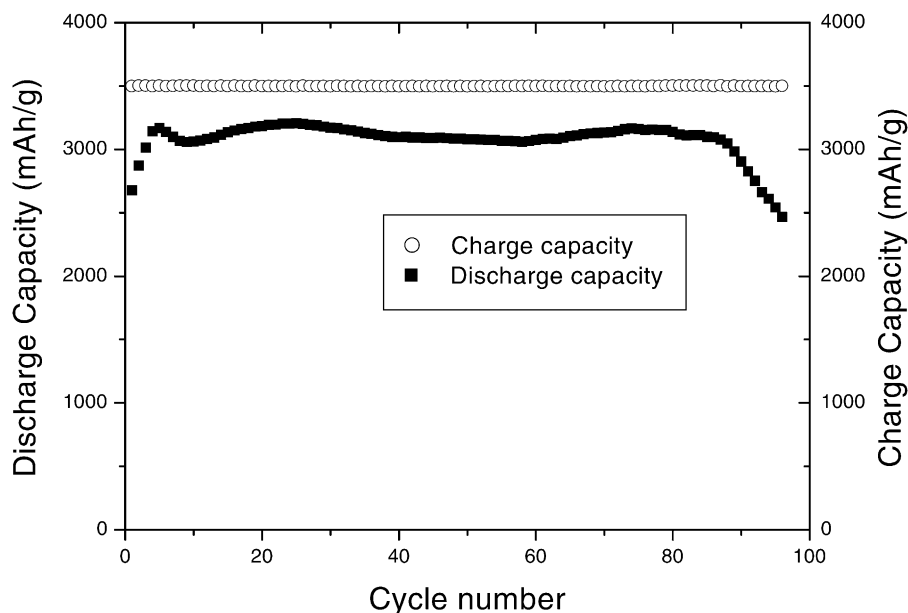

Fig. 4. Cycle performance of amorphous silicon electrode (charged at 250 μA cm^{-2} for 10 min and discharged at 250 μA cm^{-2} up to 3 V).
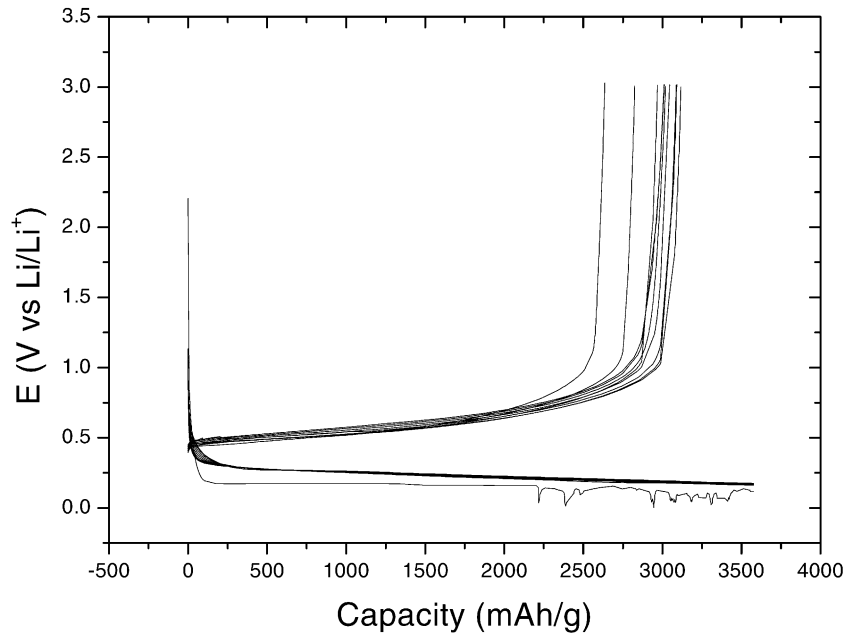
Fig. 5. Potential profile of amorphous Si electrode (charged at 250 μA cm^{-2} for 10 min and discharged at 250 μA cm^{-2} up to 3 V).

charge goes back and forth repeatedly. Thus, a fixed amount of charge (250 μA cm^{-2} for 10 min, 3.5 Ah g^{-1}) is inserted in each cycle and then removed until the cell voltage reaches 3 V. The cycle-life is up to 90 cycles, as shown in Fig. 4. The lower voltage limit is about 0.2 V as shown in Fig. 5.

Two cells with configuration structures of a-Si|1 M LiClO$_4$, PC|LiMn$_2$O$_4$ cell and Li|1M LiClO$_4$, PC|LiMn$_2$O$_4$ were cycled. The resulting data are plotted in Fig. 6. for

comparison. The voltage profiles are almost the same, except that the overall voltage is lower by 0.2–0.5 V in the case of the cell with the a-Si anode, The potential profile of the a-Si electrode measured in situ with a lithium reference electrode, is shown in Fig. 7 and coincides with the cell voltage profile. Furthermore, the amorphous anode cell can be cycled without notable capacity fading for up to 400 cycles (Fig. 8). This is attributed to the charging depth of the
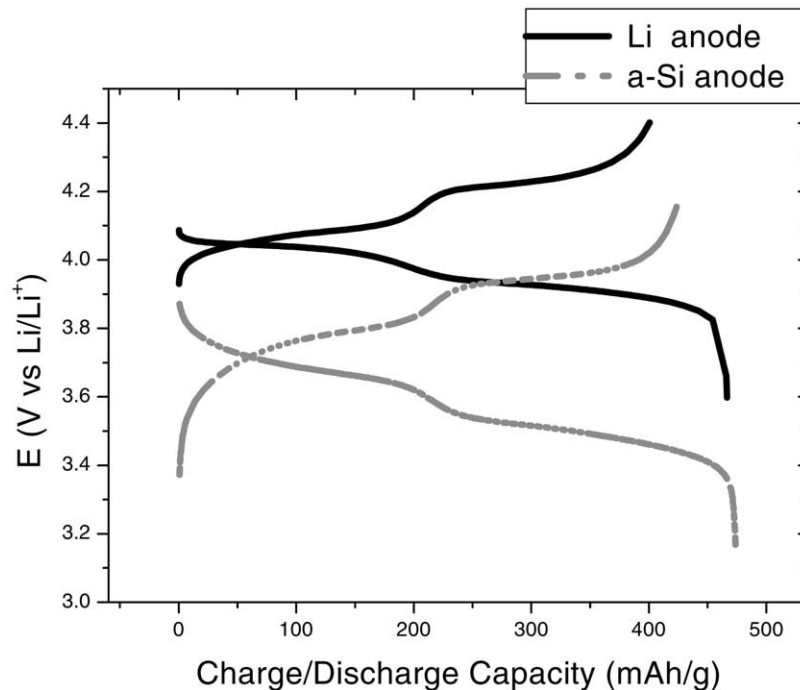

Fig. 6. Comparison of potential profile of Li anode and a-Si anode cell (anode|1 M LiClO$_4$, PC|LiMn$_2$O$_4$ cell, charged and discharged at 100 mA cm^{-2}).
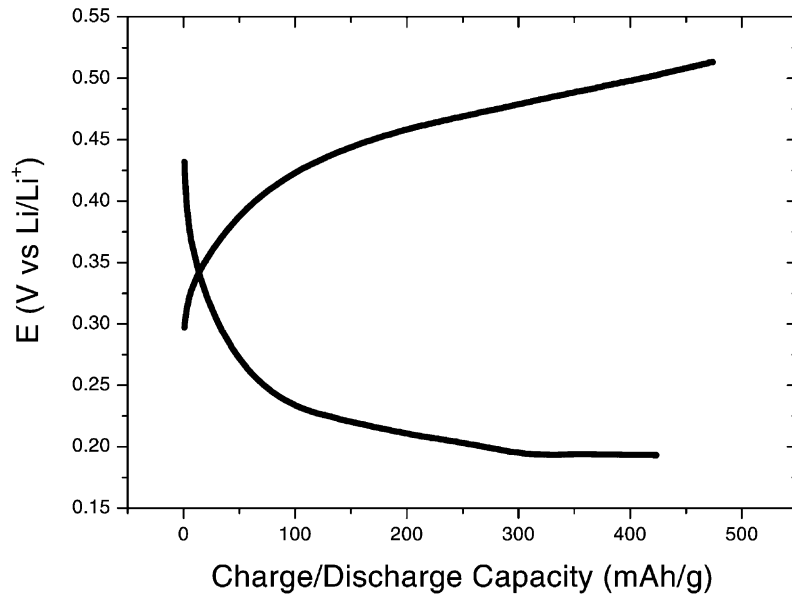
Fig. 7. Potential profile of amorphous Si electrode vs. Li (during cycling of a a-Si|1 M LiClO$_4$, PC|LiMn$_2$O$_4$ cell at 100 μA cm^{-2}).
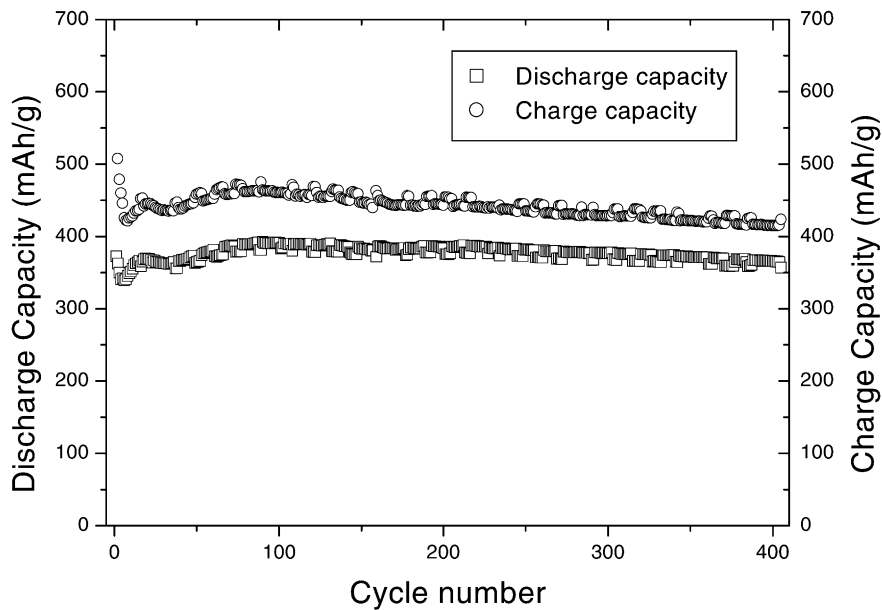

Fig. 8. Cycle performance of a-Si|1 M LiClO$_4$, PC|LiMn$_2$O$_4$ cell.

amorphous silicon anode. If all of the charge capacity of the a-Si electrode material (~4 Ah g^{-1}) is not used, then the cycle-life can be extended.

4. Conclusions

An thin film of amorphous silicon can be cycled with a maximum discharge capacity of 4 Ah g^{-1}, but this value fades rapidly after 20 cycles. This decline in performance can be overcome and the durability extended to more than 400 cycles changing the lower limit of the voltage window from 0 to 0.2 V. With this condition the discharge capacity is about 400 mAh g^{-1}.

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