Silicon Nitride Coated Silicon Thin Films as Anodes for Li-Ion Batteries

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When using silicon in anodes for Li-ion batteries, there is a tradeoff between using small silicon structures to avoid cracking and having small surface area to reduce electrolyte degradation due to an unstable Solid Electrolyte Interface (SEI). To facilitate the growth of a stable and thin SEI, we propose to coat silicon with a thin layer of silicon nitride. Silicon nitride by itself has been determined to function as a conversion electrode material, forming lithium nitride and elemental silicon during the initial lithiation. Using a thin film model system, we demonstrate the effect of using nitride coatings with different stoichiometry on the cyclability and high rate capacity of the electrodes. The results show that a nitride coating has a positive effect on both the cycling stability and high rate performance.

Introduction

The development of the lithium ion battery has been one of the key factors in facilitating the revolution of portable electronic devices seen in the last decades. The vast majority of currently available commercial cells use anodes based on carbonaceous materials. The limited theoretical capacity of these anodes (372 mAh/g (1)) has led to an extensive effort to develop alternative anode materials to fulfill the ever increasing demands of modern devices. One group of anodes which have shown promise is the alloying anodes. These have attracted much attention due to their high theoretical capacity stemming from the formation of lithium rich intermetallic compounds during lithiation. Silicon excels in this regard with theoretical capacities of 4200 mAh/g at high temperature and 3579 mAh/g at low temperature, corresponding to the intermetallic phases $Li_{22}Si_5$ and $Li_{15}Si_4$ (2), respectively. This, in addition to its low cost and abundance, has resulted in silicon being extensively studied (3).

During lithiation, however, silicon expands to more than four times its original size. The expansion creates stresses both in the interface between the current collector and the electrode material, as well as in the material itself, causing delamination and fracturing (3). This loss of mechanical integrity also compromises the electronic conductivity of the electrode, rendering parts of it inactive, hence reducing the electrode capacity. Since the deactivated material usually contains at least some lithium, the Coulombic efficiency is similarly affected. For a bulk silicon electrode, this effect could easily render it useless within only a few cycles. The most common solution for this problem has been so-called dimensional stabilization; to use nanostructured materials, like nanoparticles or thin films, since the stresses formed are dependent on the characteristic size of the material (3).

Dimensionally stabilized electrodes of pure silicon (4-8) and composite anodes of silicon together with carbonaceous materials (9-15) have both proven to be promising.

However, as the specific surface area of the silicon becomes larger, surface effects play an increasingly significant role in the deterioration of the electrodes. Of these, the formation of the Solid Electrolyte Interface (SEI) is among the most important. While the SEI does the important job of limiting electrolyte decomposition on the electrode surface, it also binds some lithium, thereby reducing the specific capacity and Coulombic efficiency of the cell. A thin and stable SEI should therefore ideally form on the electrode surface. Unfortunately, this does not happen natively on silicon in most common electrolytes, so in order to change this, we have modified the surface of silicon thin film electrodes by coating them in silicon nitride. Silicon nitride by itself has been determined to function as a conversion electrode material, forming lithium nitride and elemental silicon during lithiation (16). After the first cycle, these electrodes are therefore expected to be silicon coated in a composite layer of Si/LiN_x. It is hypothesized that this coating will alter the electrochemical environment on the electrode surface to facilitate the growth of a thinner and more stable SEI.

Materials and Methods

40 nm silicon thin films were deposited on copper foil by plasma-enhanced chemical vapor deposition (PECVD) using silane (SiH_4) as precursor. A 5 nm coating of silicon nitride was formed by addition of ammonia (NH_3) to the gas flow in the late stages of the deposition, and different stoichiometries were obtained by changing the ratio of the gases. Five films with different coatings were made, ranging in composition from pure silicon to stoichiometric Si_3N_4, denoted A-E, respectively.

The films were characterized using TEM to determine the actual thickness of the layers and interface quality. For this work an FEI Titan 60-300 monochromated and probe corrected (S)TEM was used, which was equipped with EELS and EDS detectors. For electrochemical testing electrodes were punched from the films and mounted in 2032 coin cells with a lithium metal counter electrode, BASF LP30 electrolyte and Celgard 3401 separator. All cells underwent an initial slow cycle at a current rate of C/20 in order for the conversion reaction to run to completion. After this initial cycle, two complete series (A-E) of cells were then cycled at C/3 for 200 cycles to measure their cycling stability. To investigate the effect of the coating on current handling ability, two additional cells, one of type A and one of type E, were cycled at a current rate which doubled every 6th cycles, starting at C/4. C-rate was calculated based on a total capacity of 3579 mAh/g silicon.

Results and Discussion

From the TEM/EELS analysis it was determined that the thickness and coverage of the different layers were as expected. In the electrochemical testing all the cells experienced a general capacity degradation during cycling. This may be attributed to a poor interface quality between the copper substrate and silicon film revealed by
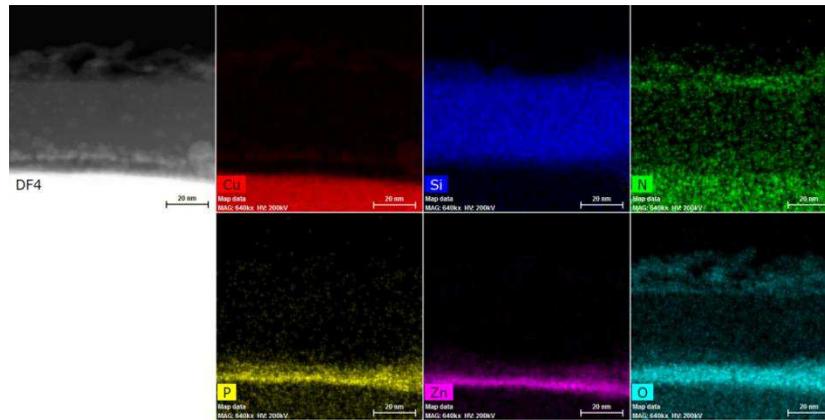
Figure 1: Dark field STEM image and EDS maps of sample E, showing high concentrations of P, Zn and O in the interface between the cupper substrate and silicon film.
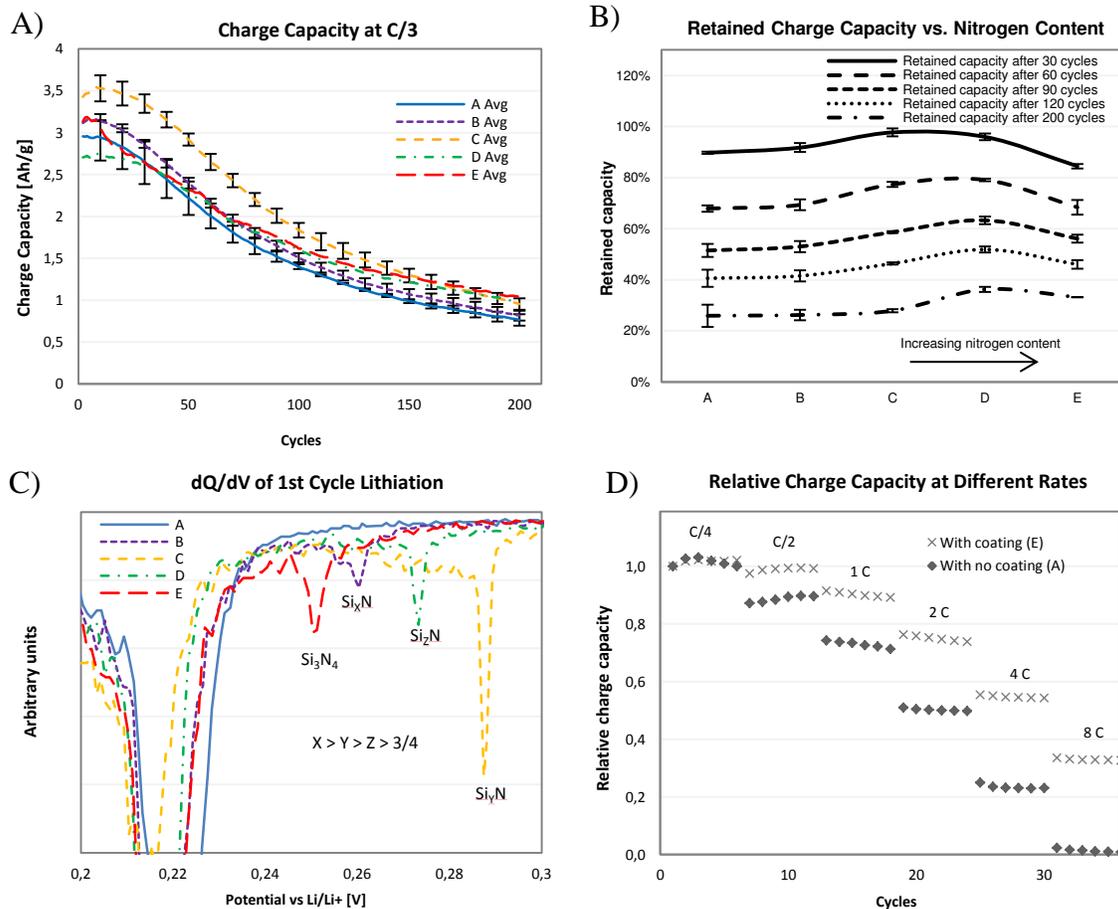

Figure 2: A) Charge capacity of the cells that were cycled at C/3 for 200 cycles. B) Retained charge capacity of cells A-E normalized to the charge capacity of the first cycle of each cell. C) A section of a dQ/dV plot for the first cycle of cells A-E, showing the changing position of the peak corresponding to the silicon nitride conversion reaction. D) The charge capacity of a coated electrode and an uncoated electrode cycled at increasing current rate. The capacity is normalized to the capacity of the first cycle of each cell.

TEM/EDS analysis, as seen in figure 1, where a Zn, P and O rich region is observed between the silicon and the Cu-foil. However, as the effect of this layer is expected to be similar for all the electrodes, the variations between the cells are believed to be caused by the nitride coating.

The charge capacities and capacity retention of the different electrodes after different numbers of cycles is plotted in figure 2A and 2B. We observe a general increase in capacity retention with increasing nitrogen content of the coating. The exception is electrode E, indicating that the stoichiometric nitride has an increased conversion resilience. This is supported by dQ/dV analysis (figure 2C), which shows that the peak corresponding to the nitride conversion reaction occurs at a lower potential for electrode E than its nonstoichiometric counterparts. This also implies that there exists an ideal nitride composition with respect to the conversion reaction. High rate cycling shows that the nitride coated electrode performs better than the pure silicon electrode (figure 2D). The diffusion kinetics in the SEI region thus seems to be improved by the addition of a nitride layer.

Conclusion

In this work it has been shown that adding a silicon nitride coating to silicon thin film electrodes improves their cycling stability and that the magnitude of this effect is dependent on the composition of the nitride. The effect increases with nitrogen content up until it reaches an ideal point close to the stoichiometric composition, where the effect drops off. The nitride coating also improves the electrodes performance at high current rates, indicating that the hypothesized SEI improving effect does indeed occur.

Acknowledgments

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