



Silicon nitride as anode material for Li-ion batteries: Understanding the SiN_x conversion reaction



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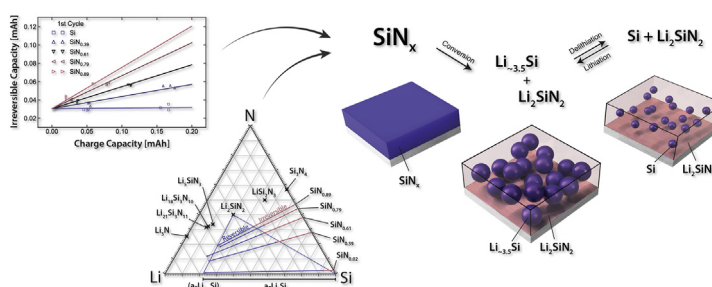
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HIGHLIGHTS

- A model reaction is developed to describe the SiN_x conversion reaction.
- This model is fitted to cycling data from amorphous SiN_x thin film electrodes.
- The conversion is determined to result in cyclable silicon in a Li_2SiN_2 matrix.
- The bulk capacity and reversibility of SiN_x of any given composition is predicted.
- The matrix is found to slowly delithiate at potentials exceeding ~ 0.5 V vs. Li^+/Li .

GRAPHICAL ABSTRACT



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ABSTRACT

An extensive research effort is being made to develop the next generation of anode materials for lithium ion batteries. A large part of this effort has been related to silicon, primarily due to its considerable theoretical capacity; however, very limited cycling stability has prevented widespread commercial adoption. A potential solution for this is to use convertible sub-stoichiometric silicon nitride ($a\text{-SiN}_x$), which goes through an irreversible conversion reaction during the initial lithiation cycle, producing active silicon domains in an inactive, lithium conducting matrix. Relative to pure silicon, the resulting composite material has gained cycle life at the cost of reduced specific capacity. The specifics of the conversion reaction, however, have not yet been determined; hence, the impact of varying nitrogen content remains uncertain. In this work we develop a model reaction which relates the reversible and irreversible capacities of an electrode to the composition of the conversion products. By fitting this model to experimental data from a large number of $a\text{-SiN}_x$ thin film electrodes with different thickness and composition, we determine with a high probability that the matrix composition is Li_2SiN_2 . From this, the reversible and irreversible capacities of the material can be predicted for a nitride of a given composition.

1. Introduction

The invention of the lithium ion battery has been one of the key factors in enabling the revolution of portable electronic devices seen

over the last decades. Increasing power-demands of these devices, as well as the incorporation of Li-ion batteries in electric vehicles place ever higher demands on the batteries. This has led to a significant research effort into the development of new electrode materials with

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improved volumetric and specific capacity, cycle life and rate capability, which do not compromise on safety. For Li-ion batteries, silicon has attracted a lot of attention as anode material due to its very high specific capacity (3579 mAh/g) compared to that of the commonly used carbonaceous anodes (372 mAh/g) [1]. Silicon does, however, have several issues related to the large volume change the material undergoes during cycling. Attempts to resolve these issues are generally based on what is termed dimensional stabilization – using nanostructured materials to reduce internal stress formation [2–17]. The very large specific surface areas of these nanostructures present a number of new problems, which have called for further research on surface modification and coatings [12,18–24].

A class of materials which are not necessarily nanostructured but inherently utilize dimensional stabilization is commonly known as in-situ convertible oxides [25–27]. These materials rely on an irreversible conversion reaction during the first lithiation cycle which causes a phase separation of a finely dispersed active alloy component and an inactive matrix component [28]. This reaction was first described for the tin based composite oxide electrode in a report by Fuji Photo Film Co. in 1997 [26], and have later been extended to silicon sub-oxides (SiO_x) [29–31]. There have also been reports on different nitrides undergoing reversible electrochemical reactions with lithium, with a wide variety of different reaction mechanisms. Several ternary nitrides, e.g. Li_3FeN_2 [32] and Li_7MnN_4 [33], are assumed to function by reversible reconstitution reactions. Some binary nitrides M_3N ($\text{M} = \text{Co}, \text{Fe}, \text{Ni}$) have been shown to function by partially reversible displacement reactions on the form $\text{M}_3\text{N} + \text{Li} = \text{M} + \text{Li}_3\text{N}$ [34,35]. Others again, like Sn_3N_4 [36] and Ge_3N_4 [37], function along the same lines as the convertible oxides, with the reversible capacity stemming from the lithiation and delithiation of the metal formed during conversion. Titanium nitride (TiN), on the other hand, is regarded as inactive, and has instead been used as a structural stabilizer and conductive component [38,39].

Silicon nitride was initially regarded as an inactive material in the context of lithium ion batteries, and has been used as an inactive scaffolding material for silicon based anodes [40]. However, in the last decade, several groups have reported reversible charge-discharge behavior of silicon nitrides of different compositions and crystallinity [23,41–46], albeit with varying performance. As the properties of the silicon nitride in these works differ in many aspects, a direct comparison of the reported results can hardly be made. While most are of the opinion that a conversion type reaction is taking place, there is disagreement as to what the products of said reaction are; whether it is lithiated silicon and lithium nitride (Li_3N) [42,46], lithiated silicon, silicon nitride (Si_3N_4) and Li_3N [41], or lithiated silicon and a ternary lithium silicon nitride (Li_2SiN_2) [44].

Understanding the conversion reaction allows targeted tailoring of the material properties, and is crucial for the continued development of this electrode system. The purpose of this work has therefore been to investigate the first cycle conversion reaction by comparing the performance of different substoichiometric amorphous nitrides (a-SiN_x) cycled under comparable conditions. Here we introduce a model which, when fit to experimental results, allows the separation of surface and bulk losses; and moreover, an estimation of the matrix phase composition. Using this model in conjunction with experimental measurements from a large number of different SiN_x thin film electrodes of varying composition and thickness, the composition of the matrix has been estimated to be approximately Li:Si:N 2:1:2. Furthermore, by analysis of the matrix delithiation at higher voltages, we have shown that the matrix in all probability consists of a single phase, Li_2SiN_2 , rather than a combination of Li_3N and Si_3N_4 . This information enables us to predict the reversible and irreversible capacities of an amorphous silicon nitride of any given composition.

2. Materials and methods

The model derived in this work is fitted to experimental data

obtained from a number of amorphous silicon nitride thin film electrodes. The long term cycling performance and degradation mechanisms of these films have been the subject of previous publications [47,48], in which a thorough characterization of the films can be found; hence this paper will only contain a brief summary of the characterization results, necessary for a proper evaluation of the model. The thin film electrodes were prepared by plasma enhanced chemical vapor deposition (PECVD, Oxford Instruments Plasmalab System133), with silane (SiH_4) and ammonia (NH_3) as precursors. The films were deposited on rolled copper substrates, and different compositions were obtained by varying the flow rate of the precursor gasses in the plasma. The silane flow rate was held at 25 sccm, while the ammonia flow rate was varied from 0 to 40 sccm in 10 sccm intervals, resulting in films of five different compositions. Different thicknesses were made by depositing for different durations. Of the most nitrogen rich composition five different thicknesses were made, nominally 40 nm, 80 nm, 120 nm, 160 nm, and 200 nm, while the other four compositions were made in two thicknesses, nominally 40 nm and 120 nm.

The surface morphology and coverage of the pristine films were characterized using optical microscopy and scanning electron microscopy (SEM, Hitachi TM3000 & JEOL JIB-4500). The thicknesses of the films were measured using spectroscopic ellipsometry (V-VASE[®] J.A. Woollam Co.), which was conducted on films simultaneously deposited on polished silicon wafers, as it requires a smooth surface. Selected films were also characterized using transmission electron microscopy (TEM) using a monochromated and probe corrected FEI Titan G2 60–300 operated at 300 kV in both projection and scanning TEM mode (STEM). For this analysis cross section TEM samples were prepared from the films using a Jeol JIB-4500 focused ion beam (FIB) system. The compositions of the films were determined using X-ray photoelectron spectroscopy (XPS) analysis, which was conducted on a Kratos Axis Ultra DLD spectroscope using monochromated Al $\text{K}\alpha$ X-rays (1486.6 eV). Any surface contamination was removed by argon sputtering at 2 kV and 100 μA for 2 min before characterization. The densities of the films were estimated using the characteristic bulk plasmon energy as measured in the TEM using electron energy loss spectroscopy (EELS). Detailed descriptions of these analyses can be found in Ulvestad et al. [47] and Ulvestad et al. [48].

Electrochemical testing was performed using $\text{\O}15$ mm electrodes mounted in 2032 coin cells against a lithium metal counter electrode, separated by a Celgard 3401 separator. The electrolyte used consisted of 1 M LiPF_6 in ethylene carbonate (EC)/propylene carbonate (PC)/dimethyl carbonate (DMC) (1:1:3 by mass), with 1 wt.% vinylene carbonate (VC) and 5 wt.% fluoroethylene carbonate (FEC) additives. The cells were assembled in an argon filled glove box with $\text{O}_2 < 0.1$ ppm and $\text{H}_2\text{O} < 0.1$ ppm, and cycled using an Arbin BT-2000 galvanostat/potentiostat at ambient temperature. Cycling was conducted galvanostatically between 0.05 V vs. Li^+/Li and 1 V vs. Li^+/Li unless otherwise indicated.

3. Results and discussion

3.1. Characterization of the pristine SiN_x films

Table 1 gives an overview of the measured thicknesses, compositions and densities of the different thin films. Films deposited using the same process parameters are assumed to have the same composition and density. Compositions were determined using XPS to range from pure a-Si to a- $\text{SiN}_{0.89}$. This analysis was conducted on the 40 nm and 120 nm films, and the average value was used for each composition. Density determination from TEM-EELS measurements were conducted on the 120 nm films of each composition. As a confirmation of this method's applicability, the same measurements and analysis were conducted on samples of pure crystalline silicon and stoichiometric c- Si_3N_4 (Sigma Aldrich). The densities of these samples were determined to be 2.38 g/cm^3 and 3.24 g/cm^3 , respectively, which, compared to the

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