Tin nitride thin films as negative electrode material for lithium-ion solid-state batteries

Citation for published version (APA):

DOI:
10.1149/1.3290778

Document status and date:
Published: 01/01/2010

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher’s website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the “Taverne” license above, please follow below link for the End User Agreement:
www.tue.nl/taverne

Take down policy
If you believe that this document breaches copyright please contact us at:
openaccess@tue.nl
providing details and we will investigate your claim.

Download date: 29. May. 2019
Tin nitride thin films have been reported as promising negative electrode materials for lithium-ion solid-state microbatteries. However, the reaction mechanism of this material has not been thoroughly investigated in the literature. To that purpose, a detailed electrochemical investigation of radio-frequency-sputtered tin nitride electrodes of two compositions (1:1 and 3:4) is presented for several layer thicknesses. The as-prepared thin films have been characterized by Rutherford backscattering spectrometry, inductively coupled plasma optical emission spectrometry, scanning electron microscopy, X-ray diffraction, and transmission electron microscopy. The electrochemical data show that more than 6 Li per Sn atom can be reversibly exchanged by this material, whereas only about 4 are expected. Moreover, the electrochemical performance of the material is discussed, such as electrode cycle life, and a method for improving the cycle life is presented. Finally, thicker films have been characterized by Mössbauer spectroscopy. This technique opens a new route toward integrating similar thin-film batteries into electronic chips.

For the purpose of integration, silicon is a good negative electrode material candidate. Silicon presents interesting properties with respect to Li-ion reversible alloying, i.e., very high volumetric density and very fast charge-transfer kinetics and diffusion, resulting in a very high rate capability. However, alloying with Li causes tremendous volume expansion, which can be detrimental to the material lifetime that is often reduced to a few cycles for thick electrodes. This poor lifetime is attributed to the high compressive stress resulting from the insertion, which leads to the pulverization or delamination of the material. To suppress this problem, one can adequately adjust the electrode thickness, but this has a negative impact on the total storage capacity. Other methods consist of improving the adhesion of the electrode film onto the substrate or adopting different types of insertion material.

With respect to improved cycling performance, the so-called “chemical conversion materials” such as oxide- and nitride-based materials are very attractive negative electrodes. The well-accepted scenario to explain their favorable conversion mechanisms is that Mn and Li nitride (Li2O or Li3N) matrix is irreversibly formed during the first Li-ion insertion. These matrices are expected to accommodate part of the stress associated with the large volume expansion/contraction resulting from the insertion/ extraction of Li ions into/from the active elemental clusters. In turn, this accommodation by the matrix materials could noticeably improve the adhesion of the electrode film onto the substrate and in a nitride-based electrode.

Based on this mechanism, one would expect that a higher O and N content would lead to an increased electrode lifetime at the expense of the reversible capacity as more inert Li2O or Li3N “buffer” materials would be formed.

Rechargeable thin-film solid-state lithium-ion batteries often utilize a pure Li metal negative electrode. These storage devices, however, exhibit several drawbacks. Pure lithium melts at about 181°C, a temperature usually lower than that applied during the reflow soldering process widely used in the electronic industry. Therefore, an alternative negative electrode material is required to integrate similar thin-film batteries into electronic chips.

For tin nitride, the conversion mechanism as well as the electrochemical properties of the material have not been thoroughly investigated thus far. Tin nitride thin films grown by sputtering and having a stoichiometry close to Sn3N4 were studied. They suggested that the initial reaction of Ge,N with Li occurred via a limited conversion process. Surprisingly, about 60% of the starting material was inactive. The large particle size of the GeN2 starting material might explain the poor performance observed and suggests, as the authors proposed, that the core of the particles remained intact. As the diffusion length and electrical resistance are minimized for a thin layer, one can very well imagine that thin films of similar materials are able to fully convert and are thus very interesting to be studied.

For tin nitride, the conversion mechanism as well as the electrochemical properties of the material have been reported as potential negative electrode materials. For germanium nitride, a detailed characterization was performed on the bulk material. This study concluded that the reaction of Ge,N with Li occurred via a limited conversion process. Surprisingly, about 60% of the starting material was inactive. The large particle size of the GeN2 starting material might explain the poor performance observed and suggests, as the authors proposed, that the core of the particles remained intact. As the diffusion length and electrical resistance are minimized for a thin layer, one can very well imagine that thin films of similar materials are able to fully convert and are thus very interesting to be studied.

Neudecker and Zühr discussed the reaction mechanism of sputtered indium and tin nitrides. They suggested that the initial reaction of these nitrides occurs via the concurrent formation of a nanocrystalline Li,N matrix and the alloying of metal nanocrystals with Li according to Reactions 3 and 4. These conclusions were based on in situ XRD results. However, these data were not published. In addition, electrochemical half-cell measurements were not presented for tin nitride. The results of the capacity and the lifetime of batteries comprising these nitride electrode materials of various compositions have been reported. However, the capacities presented in this work are related to the thickness of the positive electrode material.
and the thickness of the negative electrodes is not mentioned, making the analysis of irreversible and reversible capacities rather ambiguous. The paper presents results of the electrochemical reaction of tin nitride thin-film electrodes in a half-cell configuration. The electrode conversion mechanism of tin nitride thin films with a layer thickness ranging from 50 to 500 nm and compositions of 1:1 and 3:4 is discussed, as well as the electrode lifetime. To characterize the material, Rutherford backscattering spectrometry (RBS), inductively coupled plasma optical emission spectrometry (ICP-OES), scanning electron microscopy (SEM), XRD, and transmission electron microscopy (TEM) were employed on the as-prepared materials. RBS was used to determine the amount and composition of the tin nitride starting material, which allowed the calculation of the quantity of Li reacting (ir)reversibly with the electrode material. In situ XRD was performed to characterize the structure of the converted material for different Li contents. To reveal the chemical environment of Sn atoms, thicker films were prepared and analyzed by Mössbauer spectroscopy.

Experimental

**Thin-film deposition.**—Titanium nitride was deposited at room temperature on top of 6 in. n$^{+}$-doped silicon substrates or polyetheretherketone (PEEK) substrates by dc magnetron sputtering using Veeco Nexus 800 equipment and conditions reported elsewhere. The choice of titanium nitride as a current collector lies in the fact that it is almost inert toward Li-ion (de)insertion. Using an Emerald sputter tool by Leybold, tin nitride films were radio-frequency (rf)-sputtered (13.56 MHz) on top of TiN through a shadow mask using an 8 in. tin target in a reactive argon/nitrogen atmosphere. The deposition parameters are listed in Table I. The substrate holder was water-cooled to keep the substrate holder temperature between 40 and 50°C. The temperature of the substrate, however, was not measured. By adjusting the argon and nitrogen flows inside the vacuum chamber and by performing RBS on the thus deposited materials, layers with a preselected composition could be obtained. Thicker or thinner layers were grown by adapting the process time. Sputtering layers with a preselected composition could be obtained. Thicker or thinner layers were grown by adapting the process time.

**Electrochemical investigation.**—Three-electrode cylindrical electrochemical cells were assembled in an argon-filled glove box. The tin nitride electrodes were mounted as the working electrodes, whereas pure lithium foils were used as counter and reference electrodes, as schematically represented in Ref. 25. The liquid electrolyte used for most of the experiments, denoted as electrolyte 1, comprised 1 M LiClO$_4$ dissolved in propylene carbonate (PC). 1 M LiPF$_6$ salt (1 M) dissolved in ethylene carbonate (EC)/dimethyl carbonate (DMC)/diethyl carbonate (DEC) (2/2/1 wt %), denoted as electrolyte 2, was also used to evaluate the impact of the solid electrolyte interface (SEI) formation on the electrode material. Both electrolytes were provided by Puriel Techno Semichem Co., Ltd, Korea. The cells were placed in a stainless steel holder that was thermostatically controlled to 25°C. Contaminants in the glove box (water and oxygen) were monitored and controlled below 1 ppm.

Galvanostatic cycling was performed with an M4300 galvanostat (Maccor, Tulsa). The galvanostatic loading of the in situ XRD cell was performed using an Autolab PGSTAT30 (Ecochemie, Utrecht, The Netherlands).

**Material characterization.**—The samples were analyzed by SEM using a Philips SEM XL40 FEG microscope. The layers were prepared for TEM analysis using FIB200 focused ion beam (FIB) equipment. TEM was conducted using TECNAI F30ST equipment operating at 300 kV. The bright-field (BF) high resolution TEM and high angle annular dark field (HAADF) images were employed. The HAADF detector uses the electrons scattered over large angles for imaging and is therefore mass sensitive, implying that a higher brightness in the image corresponds to the presence of (a larger concentration of) heavier atoms.

Ex situ XRD was performed using a Panalytical X’Pert Pro MPD diffractometer equipped with a Cu source to generate Kα radiation (1.54 Å). An ω-offset of 3° was applied during measurements to suppress the strong diffraction signals resulting from the single-crystalline Si substrate. In situ XRD was employed using the same setup described in Ref. 26 and layers deposited onto the PEEK substrate.

To determine the amount and composition of tin nitride electrodes, RBS was conducted in the center of the samples with a spot size of 2 × 2 mm using conditions described elsewhere. To obtain a more accurate determination of the Sn:N ratio, the N signal was not used during fitting. Instead, by assuming a dilution of Sn by N, the height of the Sn signal was fitted with various Sn:N ratios. This way of fitting reduced the error of the N content within an accuracy of ± 0.1.

To check the homogeneity of deposition, ICP-OES was conducted on a 250 nm thick Sn$_x$N$_y$ layer. The layer was dissolved in a mixture of hydrochloric and nitric acids under a high temperature and a high pressure in a microwave oven (Multiwave 3000 system from Anton Paar). After cooling down, the solution was diluted to a known volume, and the amount of Sn was determined using a 4300 DV ICP-OES system from Perkin Elmer. 119Sn transmission Mössbauer spectra were recorded on thicker layers in the constant acceleration mode using components manufactured by ORTEC and WissEl. The source used for these experiments was 119mSn embedded in a CaSnO$_3$ matrix, and all spectra were collected at room temperature. The velocity scale was calibrated with the magnetic sextet of a high purity iron foil as the reference absorber, and 57Co (Rh) was used as the source. The spectra were fitted to Lorentzian profiles by the least-squares method using the WinIS0 program. The quality of the refinement was controlled by the classical χ$^2$ test. All isomer shifts are given with respect to the room-temperature spectrum of BaSnO$_3$. The maximum experimental error on hyperfine parameters is estimated to be ±0.05 mm/s.

**Results and Discussion**

**Material characterization of the as-prepared tin nitride thin films.**—Tin nitride layers were subjected to RBS for mass and composition determination. The resulting material properties derived from RBS are listed in Table II. Within the RBS fitting accuracy, 1:1 and 3:4 ratios were confirmed for various thicknesses. ICP-OES...
measurements on a 250 nm thick film of composition 3:4 and surface area of 2.01 cm² revealed a total amount of 314 µg of Sn, which agrees very well with the RBS results.

To visualize the morphology and thickness of the various layers, cross sections of the samples were imaged with SEM. Typical photographs are shown for Fig. 1 for nominally 100 and 250 nm thick layers of both compositions. SEM revealed that for both compositions, the morphology of the different layers is independent of the thickness. The texture occasionally visible in the pictures is an artifact resulting from the fracture.

The thickest layers were analyzed with XRD, and the corresponding results are presented in Fig. 2. The broad peak around 69° originates from the Si substrate, and several peaks from the cubic TiN structure are detected. However, the broad peaks at about 32 and 55° originate from an amorphous material that matches the positions of some diffraction peaks for the spinel Sn₃N₄ and of Sn. This indicates the presence of an amorphous or nanocrystalline material. Using XRD, clearly the structure of the materials cannot be determined unambiguously.

Therefore, the materials were also analyzed with TEM, as presented in Fig. 3. For both compositions, the BF mode revealed crystalline domains within the TiN layer, but no sign of lattice fringes was observed for the tin nitride film. However, areas with a darker intensity were randomly visible all over the layers. Using the HAADF detector, it was possible to distinctly visualize the same areas, which are now represented as white spots. This difference in contrast usually corresponds to a difference in density or to the presence of nanocrystalline domains having dimensions smaller than the thickness of the sample.

Electrochemical characterization of tin nitride thin films.— The potential profiles of the first two discharge cycles of a 50 nm thick SnNₓ layer are shown in Fig. 4a. The initial insertion is accompanied with a plateau around 700 mV followed by a slope and a quasi-plateau. During Li-ion extraction, a quasi-plateau and a slope are measured. During the subsequent cycle, a reversible response is measured. The absence of a plateau around 700 mV during insertion indicates that the plateau found during the initial insertion is representative of an irreversible reaction. Typical initial potential profiles of SnNₓ 1:1 electrodes are presented for various thicknesses in Fig. 4b. In this experiment, a 1C-rate was employed for all thicknesses, which corresponds to 80 and 40 µA cm⁻² in 100 and 50 nm thick electrodes, respectively, and to 200 µA cm⁻² for the 250 nm thick electrodes.
Several identical 100 nm thick electrodes were cycled at various currents from 0.4 to 1C-rate in electrolyte 1 (1 M LiClO4 in PC) and at 0.4C-rate in electrolyte 2 (1 M LiPF6 in EC/DMC/DEC). The results corresponding to the initial cycles are presented in Fig. 5. Decreasing the current intensity can promote the formation of the SEI and result in a different amount of charge transferred during the plateaus. Moreover, the insertion of Li ions into an electrode material from different electrolytes leads to the formation of an SEI layer with a different chemical composition and morphology, resulting in reactions occurring at other electrode potentials and consuming a different amount of charge.28 However, it is clear from the potential profiles of Fig. 5 that the three electrodes cycled in electrolyte 1 at various rates present almost the same total capacity. In addition, the width of the plateau at about 700 mV is very similar. This indicates that the irreversibility associated with this plateau does not depend on the employed rate (i.e., current density). Moreover, cycling the same electrode material in another electrolyte does not modify the position and the width of the plateau (cf. electrode cycled in electrolyte 2). The start of the plateau is shifted toward higher Li/Sn compositions when the electrode is cycled in electrolyte 2 (cf. inset of Fig. 5). Small plateaus are visible at 1.15 V when the electrode is cycled in electrolyte 1, whereas cycling in electrolyte 2 leads to a small plateau at 2.1 V. Most likely, these small plateaus represent the formation of their respective SEI layers, which clearly happens at potentials higher than that of the main plateau at about 700 mV. To conclude, the plateaus observed at about 700 mV cannot be ascribed to the SEI formation.

Another reaction that may explain the plateaus around 700 mV is the conversion reaction. This hypothesis agrees well with the fact that the Li/Sn ratios associated with the plateaus are almost independent of the film thickness and can therefore be considered as a bulk effect. According to Reaction 3, the reaction of the tin nitride starting material with Li would result in the irreversible formation of Li3N. However, the amount of Li3N consumed in the reaction does not match the value deduced from Reaction 3 as only about 1 Li/Sn is irreversibly reacted, whereas 3 Li/Sn would be expected. This discrepancy could mean that the reaction proposed for other conversion materials does not hold for the present electrode materials and that Li3N is not irreversibly formed. The literature lacks detailed information concerning ternary Li–Sn–N compounds. Assuming the possible existence of such a ternary compound, the reaction mechanism could be described as

\[ \text{Li}_x \text{Sn}_y \text{N}_z + x \text{Li}^+ + x^- \rightarrow \text{Li}_3 \text{Sn}_y \text{N}_z \]  

[5]

\[ \text{Li}_x \text{Sn}_y \text{N}_z + x \text{Li}^+ + x^- \rightarrow z \text{Li}_4 \text{N} + y \text{Li}_4 \text{Sn} \]  

[6]

when assuming conversion into \( \text{Li}_4 \text{Sn} \). The irreversible conversion of tin nitride via a ternary compound might be reasonable analogously to what was reported for zinc nitride.25 Results contradicting
reaction mechanisms 1 and 2 were also found for tin oxide materials, as thoroughly discussed in the existing literature.\textsuperscript{23-36} Using various advanced characterization techniques (nuclear magnetic resonance, Mössbauer spectroscopy, and extended X-ray absorption fine structure), it was shown that oxygen partly reversibly participates during the insertion reaction. Therefore, one can very well imagine that the reaction mechanism of tin nitride may differ from the usually accepted reaction scheme. Similar conclusions were drawn for germanium nitride, for which the formation of an intermediate ternary compound was also suggested.\textsuperscript{20}

To determine the nature of the converted material, in situ XRD was performed during the second insertion of the material on a 200 nm thick film. The electrochemical potential profile and the corresponding XRD patterns are presented in Fig. 6. Apart from broad reflections originating from the amorphous PEEK substrate and characteristic diffractions resulting from cubic TiN, no diffraction is observed in the lithiated tin nitride during the insertion reaction. This absence of reflections indicates that the material is either nanocrystalline or amorphous.

The reaction of stoichiometric 3:4 thin films was also investigated. Typical initial potential profiles of SnN\textsubscript{3:4} electrodes for different layer thicknesses plotted as a function of the Li/Sn ratio calculated from RBS results. The current is approximately 1C-rate for cutoff potentials of 0 and 2 V vs Li/Li\textsuperscript{+}. 1C-rate represents 40 $\mu$A cm\textsuperscript{-2} in a 50 nm thick film.

Based on the arguments given above, other sources for the irreversible capacity reported by Park et al. must be considered. The SEI formation could explain part of this large irreversibility. However, using the same and another electrolyte, no substantial capacity loss related to the SEI formation was observed in our work (cf. Fig. 5). Maybe the adhesion of tin nitride onto Pt was too poor to prevent the loss of the active material by pulverization or electrical isolation upon expansion of the layer, which could also explain the low capacity value observed in their study for films deposited at room temperature (less than 300 $\mu$Ah cm\textsuperscript{-2} $\mu$m\textsuperscript{-1}).

The similar electrochemical results measured for our films of compositions 1:1 and 3:4 (cf. Fig. 4 and 7) might result from the fact that part of nitrogen in the SnN\textsubscript{3:4} films would not be bonded to Sn atoms but was present in the form of N\textsubscript{2} molecules. Several groups investigated the material properties of sputtered tin nitride films.\textsuperscript{37-44} None, however, successfully prepared the single-phase stoichiometric Sn\textsubscript{3}N\textsubscript{4} material using reactive sputtering, and only N-deficient compositions were characterized. A minor presence of thickest layers than what is found for the 1:1 composition. The irreversible, reversible, and total capacities are plotted in Fig. 8 as a function of the layer thickness. Evidently, the irreversible capacity is much smaller than the expected 3 or 4 Li/Sn based on Reaction 3 for the 1:1 and 3:4 compositions, respectively, and the reversible capacities are also much higher than the values expected from Reaction 4. This discrepancy again suggests that the reaction mechanism expressed by Reactions 3 and 4 does not apply for the present tin nitride materials.

Park et al. investigated 100 nm thick stoichiometric 3:4 thin films deposited at room temperature up to 300°C onto Pt-covered Si substrates.\textsuperscript{23} Using 300 $\mu$A cm\textsuperscript{-2} (about 3C-rate) between 0.1 and 1.1 V vs Li/Li\textsuperscript{+}, they reported that the initial insertion of the room-temperature-deposited films was accompanied by a plateau at about 1100 mV. The capacity used on this plateau corresponds to about 25% of the total insertion capacity of the material. Assuming that the reaction mechanisms 3 and 4 hold for Sn\textsubscript{3}N\textsubscript{4}, 4 Li/Sn should be irreversibly consumed and 4.4 Li/Sn should be reversibly (de)inserted. This would mean that 47.5% of the initial capacity should be irreversible and 52.5% should be reversible. The reversible capacity of their films was only about 40%, whereas about 60% of the total capacity was lost. The limitation at 1.1 V during delithiation limited the extraction of all Li ions, whereas the restriction at 0.1 V during insertion limited the material to fully store Li ions. It is quite reasonable to consider that both limitations compensate each other so that the relative amounts of irreversible and reversible charges stay realistic. The plateau observed during the first insertion around 1100 mV does not explain the total irreversibility (60%) as it represents only 25% of the total charge.

Based on the arguments given above, other sources for the irreversible capacity reported by Park et al. must be considered. The SEI formation could explain part of this large irreversibility. However, using the same and another electrolyte, no substantial capacity loss related to the SEI formation was observed in our work (cf. Fig. 5). Maybe the adhesion of tin nitride onto Pt was too poor to prevent the loss of the active material by pulverization or electrical isolation upon expansion of the layer, which could also explain the low capacity value observed in their study for films deposited at room temperature (less than 300 $\mu$Ah cm\textsuperscript{-2} $\mu$m\textsuperscript{-1}).

The similar electrochemical results measured for our films of compositions 1:1 and 3:4 (cf. Fig. 4 and 7) might result from the fact that part of nitrogen in the SnN\textsubscript{x} 3:4 films would not be bonded to Sn atoms but was present in the form of N\textsubscript{2} molecules. Several groups investigated the material properties of sputtered tin nitride films.\textsuperscript{37-44} None, however, successfully prepared the single-phase stoichiometric Sn\textsubscript{3}N\textsubscript{4} material using reactive sputtering, and only N-deficient compositions were characterized. A minor presence of
pure Sn and absorbed N2 molecules was sometimes observed, as well as partial oxidation of the material. The Sn/N ratio determination was conducted by Auger electron spectroscopy or XPS. However, contamination and partial oxidation of the surface material resulted in an underestimation of the N content. To remove the surface contaminants, Lima et al. and Kamei et al. used Ar+ sputtering. However, large N deficiencies were observed and attributed to preferential sputtering of nitrogen. In addition, Lima et al. performed RBS for measuring the N content. Again, only N-deficient films were found in the whole range of investigated Ar/N2 mixtures. The highest N/Sn composition reported was found by Maruyama and Morishita. By investigating the impact of various deposition condition parameters (power, pressure, and Ar/N2 ratios), they found N/Sn ratios up to 1.1 using XPS surface measurements.

In our case, no O was detected with RBS, which means that the O content is below the detection limit (5 atom %). The RBS spectra can be very well fitted using compositions 1:1 and 3:4; however, it is impossible to differentiate the signal coming from N2 molecules bonded to Sn atoms and that from N2 molecules trapped inside the material. During the initial insertion of the SnN2 thin films of composition 3:4, it might very well be that N2 is released from the host structure when the material starts to expand due to the electrochemical insertion reaction.

To gain more insights about the structure of these tin nitride films, Mössbauer spectroscopy was utilized, aimed at determining the chemical environment of the Sn atoms. Mössbauer spectroscopy has already demonstrated its potential for determining the reaction mechanism of some tin-based electrode materials. However, very thick layers are necessary to obtain enough absorption and to subsequently generate a measurable signal. Therefore, layers as thick as 5 μm were prepared using the same deposition conditions employed for thin layers.

The Mössbauer spectra corresponding to both compositions are shown in Fig. 9. The spectrum for SnN2 3:4 presented in Fig. 9a shows the sum of the characteristic absorptions of Sn4+ located in the octahedral and tetrahedral sites of the SnN2 spinel structure. Deconvolution of the spectrum into the response from the octahedral (isomer shift δ = 0.58 mm s−1, red curve) and tetrahedral (δ = 1.07 mm s−1, green curve) sites results in a quantitative determination of the amount of Sn occupying each type of site, which is equal to 60 and 40%, respectively. This agrees very well with the crystallographic data where 2/3 of Sn4+ occupies the octahedral positions and 1/3 occupies the tetrahedral positions. The Mössbauer spectrum for SnN2 1:1 presented in Fig. 9b displays a complex response that can be deconvoluted into four sub-spectra. The isomer shifts at 0.54 mm s−1 (red curve) and 1.20 mm s−1 (green curve) are attributed to Sn4+ located at the octahedral and tetrahedral positions of the spinel SnN4 structure, respectively. The isomer shift at 2.41 mm s−1 (blue curve) corresponds to pure β-Sn, and the isomer shift at 2.43 mm s−1 with a quadrupole splitting of 1.48 mm s−1 (black curve) is attributed to Sn2+ species. The contributions of octahedral Sn4+, tetrahedral Sn4+, β-Sn, and Sn2+ are 16, 25, 10, and 49%, respectively. If SnN2 1:1 would be the result of 0.25 SnN4 + 0.25 Sn, the starting material would have respective contributions for octahedral Sn4+, tetrahedral Sn4+, and β-Sn of 50, 25, and 25%. The present sputtered SnN2 1:1 material shows the same amount of tetrahedral Sn4+ (25%) but low amounts of octahedral Sn4+ (16%) and β-Sn (10%) and a large presence of Sn2+ species (49%).

Clearly, from the Mössbauer spectroscopy results, the structure of tin nitride thick films significantly differs when the material is sputtered with a gas mixture of Ar/N2 of 33/7 or 25/15 (cf. previous discussion and Table 1). For the thin films, however, there is only little difference in the electrochemical response (compare Fig. 4 and 7), and XRD (Fig. 2) or TEM (Fig. 3) cannot describe the structure of the starting material. RBS is capable of measuring the Sn:N ratio with good accuracy, and it is clear from this data that the films, referring to compositions 1:1 and 3:4, have a different stoichiometry. To explain the similarity of the electrochemical responses, the possible trapping of N2 molecules inside the SnN2 3:4 material during sputter growth is an alternative explanation. However, it is clear from the Mössbauer spectroscopy results that the structure of the 3:4 thick films is close to that of the desired spinel structure. Moreover, it is also evident that SnN2 1:1 has a structure very different from the 3:4 material. Therefore, the similarity in electrochemical response is most certainly related to a similarity in the reaction mechanism, which would be independent of the tin nitride composition.

The formation of a ternary compound has been proposed (cf. Reactions 5 and 6). Perhaps both materials decompose into the same ternary material, which would be accompanied by the irreversible consumption of the same amount of Li/Sn (about 1 Li/Sn in both cases; cf. Fig. 8). As a result, the excess of N from SnN2 3:4 would be released in the form of N2 molecules or transformed into Li3N. The conversion of the excess of N into Li3N would correspond to the reaction of Li/Sn, which was not experimentally observed. Thus, in the current scenario, it is most likely that the N surplus is liberated through the formation of N2.

It has been made clear that Mössbauer spectroscopy is a powerful technique for describing the difference between tin nitride films sputtered with various Ar/N2 mixtures. SnN2 films of 3:4 composition reveals a response that can unambiguously be analyzed, whereas the analyses of films with a 1:1 composition are less obvious. Therefore, the elucidation of the reaction mechanism of tin nitride films will be performed on the SnN2 3:4 material in the future. For various Li contents, Mössbauer spectroscopy will be employed to determine the different chemical environments of Sn during the complete conversion reaction. This will ultimately reveal the reaction mechanism of tin nitride. This work in progress will be part of a forthcoming publication.
Thick-film electrodes of various layer thicknesses. The current is approximately 1C-rate with cutoff potential set at 2 V vs Li/Li$^+$. Based on Reactions 3 and 4, more N in the starting material can result in the reversible formation of more Li$_3$N. As a consequence, the material with the higher N content might expand to a higher extent, resulting in poorer capacity retention. To improve the material lifetime, the Li-ion extraction cutoff potential was restricted. It is expected that a restriction to 0.8 V would prevent full delithiation, thus full shrinkage, of the layer and would therefore ensure better capacity retention. This improvement is clearly shown in Fig. 11 for the thickest layer of composition 1:1.

The 500 nm thick film is now capable of reversibly extracting about 80% of its full capacity for 120 cycles without noticeable decay. Restricting the potential during Li-ion extraction reduces the volume shrinkage of the material. In turn, a significant improvement of the lifetime is achieved, whereas the capacity is not drastically reduced. Beattie et al. observed an improvement of the capacity retention for pure tin negative electrodes when restricting the Li-ion extraction cutoff potential.$^{13}$ However, the capacity retention improvement was attributed to a difference between the kinetics of the electrolyte decomposition onto pure tin (fully delithiated) and that of partially lithiated tin (with restriction of cutoff potential). In the present case, however, the fast capacity decay observed within the first cycles when charging up to 2 V is not caused by a difference in electrolyte decomposition chemistry but by the mechanical delamination of the layer, which was observed experimentally once the electrochemical cell was opened.

**Conclusions**

Tin nitride is a very promising negative electrode material for thin-film battery applications, showing very high volumetric capacity (700 µAh cm$^{-2}$ µm$^{-1}$) and good cycle life when cycled in a liquid electrolyte. Moreover, films of composition 1:1 present better capacity retention than those of composition 3:4. Furthermore, by restricting the extraction of Li ions from the material, much better capacity retention is obtained. The conversion reaction of tin nitride was discussed based on RBS results and the electrochemical data. The results point out that the accepted mechanism (Reactions 3 and 4) is probably incomplete for the present materials. The present findings indicate that nitrogen partially participates reversibly in the conversion reaction. In turn, tin nitride is capable of reversibly inserting more than 6 Li per Sn atom. This large amount is probably related to the formation of a Li–Sn–N ternary compound as a first intermediate, which would reversibly decompose upon further Li-ion insertion into lithiated Sn and Li$_3$N. The structure of Sn$_x$N$_y$ films of composition 1:1 and 3:4 has been discussed using Mössbauer spectroscopy. The expected response of Sn$^{4+}$ located in octahedral and tetrahedral sites of the spinel structure was measured, whereas the 1:1 composition showed a more complex response. As the next step for understanding the reaction mechanism of these sputtered tin nitride films, a Mössbauer spectroscopy investigation is now underway for films of composition 3:4 (de)inserted at different Li contents. These corresponding results will be part of a future publication.

**Acknowledgments**

We gratefully thank Martien Maas, Jeroen van Zijl, Tiny den Dekker, and Loc Quang Huynh for preparing and processing the thin films. We are also indebted to Peer Zalm, Dick van Oers, and Thuy...
Dao for the RBS characterization, Monique Vervest and Hetty de Barse for the SEM photographs, Harry Wondergem and René Bakker for the XRD measurements, and Robbert Weemaes, Marcel Verheijen, and Monja Kaiser for the FIB preparation and TEM characterization. In addition, we thank Bert Hintzen (TU Eindhoven) for useful comments. This work has been financially supported by the Dutch SenterNovem Foundation.

Eindhoven University of Technology assisted in meeting the publication costs of this article.

References