Continuous and Conformal Lithium Titanate Spinel Thin Films by Solid State Reaction

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In this work, we report on the fabrication of continuous and uniform thin films by a solid state reaction. The fabrication of spinel Li4Ti5O12 thin films was demonstrated by solid state reaction between TiO2 and Li2CO3 stacked-layer upon thermal annealing. The TiO2 layer was prepared by physical vapor deposition or atomic layer deposition, whereas the Li2CO3 layer was deposited by chemical solution deposition or atomic layer deposition. The solid state reaction and obtained material properties were investigated on planar substrates. It was found that continuous films with crystalline and stoichiometric Li4Ti5O12 can be formed by solid state reaction at temperatures higher than 650 °C. The prepared films exhibited Li-ion intercalation characteristics for Li4Ti5O12 spinel with the typical flat plateau at 1.55 V (vs Li+/Li) for both charging and discharging. The theoretical capacity of 612 mAh cm3 was obtained at slow charging rate of 0.1 C with still 45% capacity attainable at 20 C. Interestingly, it was found that the kinetics is strongly dependent on the current collector substrate used. A TiN substrate provided faster Li4Ti5O12 electrode kinetics than a Pt substrate, despite a thin anatase interlayer at the TiN/TiO2/Li4Ti5O12 interface, showing the importance of interface or work function matching for high rate lithiation/delithiation performance. In addition, the potential of conformal Li4Ti5O12 thin films on high aspect ratio structures was demonstrated.

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conversion technique using conformal coated amorphous TiO₂ and Li₂CO₃, both deposited by ALD.

**Experimental**

**Fabrication of TiO₂ thin films on planar substrate.**—100 nm of Pt were deposited by DC sputtering on top of 30 nm thick TiN layer grown by atomic layer deposition (ALD). The TiN is deposited on a 30 nm SiO₂ layer grown by thermal oxidation of a 200 nm silicon wafer. The Pt layer serves as a current collector whereas the TiN interlayer is used as an adhesion layer and a diffusion barrier. On top of the Pt layer, 30 nm of Ti were deposited using DC magnetron sputtering with a sputter rate of 1 nm min⁻¹. The samples are then subject to thermal oxidation at 600°C under O₂ atmosphere for 10 min resulting in the formation of 50 nm thick TiO₂ layer.

**Fabrication of TiO₂ thin films on TiN 3D micropillar substrate.**—This substrate consists of 40 nm of TiO₂ film deposited on top of 60 nm of TiN both grown by ALD. The TiO₂/TiN stacked layers were deposited on a 30 nm SiO₂ grown by CVD on a 200 nm silicon wafer. In such a configuration, the TiN layer is used as a current collector instead of Pt.

**Fabrication of TiO₂ thin films on TiN 3D micropillar substrate.**—The 3D substrate consists of a silicon micropillar arrays where the Si pillars were fabricated by photolithography patterning and reactive ion etching (RIE). As such, 1cm by 1cm pillar Si arrays were fabricated in Si wafer; the dimensions of the Si pillars were: 50 μm in height, 2 μm pillar diameter and 2 μm inter-pillar spacing between the edges of two neighboring pillars (see fig. S4). Then, a nominal thickness of 23 nm TiN layer was deposited by atomic layer deposition (ALD) on the Si substrate using a plasma based process. Due to the plasma process the TiN film is expected to be somewhat thinner than the nominal 23 nm on the sidewalls and especially near the bottom of the pillars. Even though the exact thickness conformity of the TiN film was not measured, uniform TiN coverage over the whole pillar array was confirmed by electrochemical deposition experiments. The TiN layer is used as a current collector and a diffusion barrier for silicon at the same time. Next, a 100 nm amorphous TiO₂ film was conformally deposited on the TiN coated 3D substrate. Spatial ALD was used for the TiO₂ deposition with TiCl₄ and H₂O as deposition precursors. The water most probably is due to water taken up by the hygroscopic ALD precursors.

**Li₂CO₃ coating on planar substrates.**—For the Li₂CO₃ layer, an aqueous citrate based lithium precursor was developed using lithium hydroxide (LiOH ≥ 98%, Sigma-Aldrich), citric acid (C₆H₈O₇, 99%, Sigma-Aldrich) and concentrated ammonia (NH₄OH extra pure, 32%, Merck) as starting compounds. Precursors of 0.25 M and 0.42 M Li concentrations were prepared with a pH equal to 7.

Before the Li₂CO₃ deposition, the substrate was exposed to UV-ozone treatment for 30 min at 50°C. The Li₂CO₃ was deposited by spincoating at 3000 rpm for 30 s, followed by a thermal treatment on a hot plate at 110°C for 1 min to remove the water residue then at 280°C and 520°C for 2 min each to decompose the organic compounds present within the deposited layer as revealed by thermogravimetric analysis (TGA) (data is shown in the Supplementary Information figure S2).

To prepare the TiO₂/Li₂CO₃ stack for solid-state reaction, Li₂CO₃ was spincoated from the 0.42 M precursor solution (Li₂CO₃ equivalent film thickness = 11 nm). To increase the amount of Li₂CO₃, an intermediate solid-state reaction step is done. The double spincoating and annealing experiments are as follows: first a Li₂CO₃ layer is spincoated followed by the thermal treatment steps for drying and curing (110°C for 1 min, 280°C for 2 min and 520°C for 2 min), then the sample is annealed at 750°C for 20 min to start the solid-state reaction. Next, a second layer of Li₂CO₃ is spincoated on the same sample again followed by drying and curing and a second annealing at 750°C for 20 min to complete the solid-state reaction.

**Li₂CO₃ coating on 3D micropillar substrate.**—Li₂CO₃ thin-film deposition was done on the 3D TiO₂ coated substrate by atomic layer deposition (ALD). The deposition precursors are Li-tet butoxide, H₂O and CO₂. The deposition process is composed of 4500 cycles. Each cycle is composed of precursor pulsing and purging steps as follow: Li-tet butoxide pulsing for 5 s (at 140°C) followed by 15 s purge, then 5 s H₂O pulsing followed by 15 s of purging and 7.5 s of CO₂ pulsing followed by 15 s purging.

**Annealing.**—For thermal treatments, two types of oven were used. For the thin-film solid state reactions, a high temperature tube furnace (Nabertherm) was used. The annealing experiments were carried out at 750°C for 20 min (heating rate = 10°C min⁻¹; cooling rate = 4°C min⁻¹) at ambient atmosphere or under vacuum with a pressure of 5 × 10⁻⁶ mBar.

The second oven (Heat pulse 410, AG Associates) allows us to do a rapid thermal annealing (RTA). The heating rate was 100°C min⁻¹ and the cooling rate was 20°C min⁻¹. This oven was used for the thermal oxidation of the Ti layers at 600°C for 20 min under an O₂ atmosphere and for drying the 3D LTO samples after the water soaking at 350°C for 120 min in air.

**Material characterization.**—The film morphology was investigated by Scanning Electron Microscopy (SEM) using SEM Nova 200 and Philips SEM XL30 microscopes. To prove the crystalline structure, X-ray diffraction (XRD) measurements were performed using X'Pert PRO PANalytical system with Cu Kα radiation. A Grazing incidence mode was used in a 2θ scan range between 15 deg and 65 deg with a step size of 0.07 deg and a scan speed of 0.009 deg s⁻¹. For elemental analysis, including lithium, elastic recoil detection measurements were performed using a home-made ERD system using an 8 MeV beam energy and a C²⁺ ion. A substrate of Si₃N₄ (70 nm) on Si is used for this kind of measurement. X-ray photoelectron spectroscopy (XPS) was carried out on a nonmonochromatized Al Kα X-ray source (1486.6 eV) with a spot size of 400 μm. Rutherford Backscattering Spectrometry (RBS) measurements were performed using a 1.523 MeV He⁰ beam, a tilt angle of 11 deg and a scatter angle of 170 deg.

**Electrochemical characterization.**—The electrochemical performance of the prepared LTO layers was evaluated using a three-electrode configuration with lithium metal foil as a counter and a reference electrode. The three electrodes were separated in a tefelon cell by a liquid electrolyte of 1 M of LiClO₄ (99.99%, Sigma-Aldrich) in propylene carbonate (anhydrous, 99.7%, Sigma-Aldrich) solvent. The setup was connected to an Auto-lab PGSTAT 5 potentiotstat controlled by Nova 1.10 software. The electrochemical measurements were performed at room temperature in an argon filled glove-box (Pl-HE-46B-1800, Innovative Technology). Capacity, rate performance and cyclability were determined using cyclic voltammetry and galvanostatic lithiation and delithiation measurements.

**Results and Discussion**

**Characterization of the spincoated Li₂CO₃ films.**—Lithium carbonate films were deposited by chemical solution deposition from an aqueous mixture of LiOH, citric acid and ammonia. The precursor solution was spincoated at 3000 rpm for 30 s. After spincoating, the liquid precursor film was cured by heating in air (three thermal steps of 100°C for 1 min, 280°C for 2 min, and 520°C for 2 min) to form the Li₂CO₃ film. For the purpose of chemical characterization, Li₂CO₃ films were fabricated on Si₃N₄ substrates. Table I gives the stoichiometry measured with ERD of the spincoated and cured films obtained from a 0.25 M and 0.42 M LiOH precursor solutions. In both cases, the stoichiometry of the deposited film is close to the theoretical stoichiometry of Li₂CO₃. The presence of hydrogen indicates that water is present in the film. Indeed, when correcting for 2.25% of water, the atomic concentration becomes very close to stoichiometric Li₂CO₃.

The water most probably is due to water taken up by the hygroscopic Li₂CO₃ from the air even though we cannot exclude crystal water or remnants from the precursor solution.
Table I. Atomic percentage of the elements in the prepared Li2CO3 as determined by ERD with and without correction for 2.25% of H2O. The Li2CO3 film was spincoated at 3000 rpm for 30 s from 0.25 M and 0.42 M precursor solutions followed by 3 thermal treatment steps at 100°C (1 min), 280°C (2 min) and 520°C (2 min).

| Element | At. Percentage [%] | Corrected at. Percentage [%] | Li atomic concentration [at cm²] | Equivalent Li2CO3 thickness [nm] |
|---------|--------------------|-------------------------------|----------------------------------|---------------------------------|
| Li      | 30.1               | 31.7                         | 2.05 × 10¹⁶                   | 6                               |
| C       | 15.7               | 16.8                         | 3.82 × 10¹⁶                   | 11                              |
| O       | 49.7               | 48.2                         |                                 |                                 |
| H       | 4.5                | 4.5                          |                                 |                                 |

*Atomic percentage corrected for 2.25% of H2O.

Table II. Li2CO3 film thickness resulting from different precursor concentrations. Each Li2CO3 coating was deposited by spincoating at 3000 rpm for 30 s on top of Si3N4 substrate and followed by thermal treatments at 110°C for 1 min, 280°C for 2 min and at 520°C for 2 min.

| Precursor concentration [M] | Number of Li2CO3 spincoats | Li atomic concentration [at cm²] | Equivalent Li2CO3 thickness [nm] |
|----------------------------|-----------------------------|----------------------------------|---------------------------------|
| 0.25                       | 1                           | 2.05 × 10¹⁶                   | 6                               |
| 0.42                       | 1                           | 3.82 × 10¹⁶                   | 11                              |

The equivalent film thicknesses of the Li2CO3 coatings were calculated using ERD data and considering a dense film (density of crystalline Li2CO3 = 2.11 g cm⁻³). Table II summarizes the different Li2CO3 film thicknesses resulting from using two precursor concentrations for single and multiple coatings. Li2CO3 films with equivalent thickness of 6 nm and 11 nm were obtained from a single spincoating from 0.25 M and 0.42 M Li+ precursor solutions, respectively. Interestingly, sequential spincoatings of Li2CO3 layers with the three thermal treatment steps in-between did not lead to thicker Li2CO3 films. On the contrary, it gave even slightly thinner layers. For example, using a 0.42 M precursor, an 8.4 nm thick Li2CO3 layer was obtained in case of 2 coatings and 8.7 nm in case of 3 coatings. This means that the first deposited layer dissolves when spincoating fresh precursor solution on top of it as a result of the use of aqueous solutions.

In summary, we can increase the Li2CO3 film thickness by increasing the Li+ concentration in the precursor, but not by applying multiple spincoatings with aqueous solutions.

For the rest of the work the precursor of 0.42 M will be used for the Li2CO3 deposition (Li2CO3 thickness = 11 nm). To increase the amount of Li2CO3, an intermediate solid-state reaction step is done after each Li2CO3 layer deposition during the LTO fabrication process.

Fabrication and characterization of Li4Ti5O12 thin films by solid state reaction on planar substrate.—Fabrication procedure.—Li4Ti5O12 thin films were prepared by solid state reaction between Li2CO3 and TiO2 films deposited on Pt and TiN coated substrates. The TiO2 was obtained by oxidation of 30 nm Ti film on Pt or from ALD of 40 nm TiO2 on TiN coated substrates. Using the Pt coated substrate, the prepared Li2CO3/TiO2 stack was annealed under ambient atmosphere to trigger the solid state reaction between the two materials. Figure 1 shows a schematic diagram of the different steps in order to produce the Li4Ti5O12 layer over a Pt substrate. The steps of Li2CO3 coating and solid state reaction were repeated in order to fully convert the TiO2 films into LTO. The main conversion conditions are summarized in Table III. It is worth to mention that the Li4Ti5O12 films could also be fabricated directly using a Ti layer; i.e. without doing the extra oxidation step (step 1) to transform it to TiO2. The LTO films prepared with such a procedure show a similar performance in comparison to the LTO films prepared using an oxidized Ti layer.

Figure 1. Process steps to prepare Li4Ti5O12 thin films. (1) Transformation of 30 nm of sputtered Ti into TiO2 by thermal oxidation at 600°C for 10 min in oxygen atmosphere. (2) Spincoating and cure of Li2CO3 film on top of the TiO2 film; (3) Synthesis of LTO thin film by a solid state reaction between the TiO2 and Li2CO3 layers by thermal annealing at 750°C for 20 min in air.

Table III. Specifications and fabrication conditions of the samples mainly used for the preparation of Li4Ti5O12.

| Condition | substrate | Li2CO3 thickness [nm] | TiO2 thickness [nm] | Post annealing: temperature [°C]; time [min] | Post annealing ambient | Number of Li2CO3 coating and post annealing |
|-----------|-----------|-----------------------|---------------------|---------------------------------------------|------------------------|---------------------------------------------|
| Pt0       | Pt        | 11                    | 50                  | 750; 20                                     | air                    | 1                                           |
| Pt1       | Pt        | 11                    | 50                  | 750; 20                                     | air                    | 2                                           |
| Pt2       | Pt        | 11                    | 100                 | 750; 20                                     | air                    | 2                                           |
| TiN1      | TiN/TiO2  | 11                    | 40                  | 750; 20                                     | vacuum                 | 1                                           |

*Thickness for a single coating as evaluated from the ERD data assuming a density of 2.11 g cm⁻³ for Li2CO3. This thickness is evaluated for Li2CO3 deposited on a Si3N4 substrate; it may be different when the Li2CO3 is deposited on TiO2 (case of TiN1, Pt1 and Pt2).

bThicknesses as-found by SEM.
Note, however, that the UV-ozone treatment step oxidizes at least a fraction of the Ti film. To assure proper control of the Ti oxidation, all further experiments were done with the extra Ti oxidation step.

In case of the TiN(60 nm)/TiO2(40 nm) substrate, a Li2CO3 layer was deposited after which the sample was annealed under vacuum (5 x 10^-6 mbar) in order to prevent the further oxidation of the TiN current collector layer. The anneal was similarly for Pt substrate also done at 750 °C for 20 min. Even though the annealing was performed under vacuum, partial oxidation of TiN still occurred (further details in the Structure and morphology section).

The LTO layer is the result of a solid state reaction between the Li2CO3 and TiO2 films. This process can be described by the following reaction (Equation 1):

$$\text{Li}_2\text{CO}_3(s) + \frac{5}{2}\text{TiO}_2(s) \rightarrow \frac{1}{2}\text{Li}_4\text{Ti}_5\text{O}_{12}(s) + \text{CO}_2(g) \quad [1]$$

The thickness of the LTO layer formed using condition Pt1 was estimated at 54 nm based on the Ti atomic concentration measured using RBS (125.8 x 10^15 atoms cm^-2 on Si3N4 substrate) assuming a dense Li4Ti5O12 film (d = 3.5 g cm^-3). From stoichiometric conversion of 50 nm of TiO2 (as determined from SEM) a 69 nm LTO film is expected according to Equation 1 assuming dense materials. The observed difference is then explained by a lower density for the oxidized Ti phase and the incertitude in TiO2 thickness extracted from the SEM images (40 nm expected for 54 nm LTO). Conversely, 29 nm of Li2CO3 would be required to form a 54 nm LTO film based on Equation 1 which is close the 22 nm of Li2CO3 assumed for a double coating. In the case of Li1CO3, the ERD equivalent film thickness was calculated for single coatings on Si3N4 substrates which can be slightly different for coatings directly on TiO2 or partially converted TiO2 (as in this case of the LTO fabrication in two conversion steps). Later we will show that 2 cycles of Li2CO3 deposition are indeed sufficient with even a slight excess.

Structure and morphology.—To check the temperature at which crystalline LTO is formed by SSR, a series of ex-situ XRD measurements were performed on samples with 50 nm TiO2 and a single Li2CO3 coating (~11 nm) on Pt substrates. The annealing was carried out for 20 min in ambient air in all cases, but at different temperatures: 550°C, 650°C and 750°C. The LTO diffraction peaks were detected only for the sample annealed at 750°C. Hence, thermal treatment at a temperature higher that 650°C is needed to obtain a crystalline LTO. Temperatures above 650°C are also reported for the crystallization of amorphous LTO thin-films.15-17

Figure 2 shows the XRD patterns for the different prepared samples summarized in Table III. For sample Pt1 (pattern (a) in Figure 2), only intense peaks characteristic for LTO are detected next to the Pt substrate, indicating that a pure phase LTO is indeed formed as a result of the solid state reaction (SSR). In this case, the complete conversion of the 50 nm TiO2 was achieved using double SSR sequence (~22 nm Li2CO3). From XRD, we cannot exclude the possibility of amorphous phases and crystalline impurities below the detection limit.

Also, the XRD patterns of the samples fabricated with conditions Pt2 and Pt0 (patterns (b) and (c) in Figure 2) show intense peaks for LTO. In this case, however, additional TiO2 rutile diffraction peaks are detected indicating that the amount of Li2CO3 involved in the reaction was insufficient: 50 nm TiO2 with 11 nm Li2CO3 (single SSR) in case of Pt0 and 100 nm TiO2 with 22 nm Li2CO3 (double SSR) in case of Pt2.

Also for sample TiN1, both LTO and TiO2 diffraction peaks are present in the XRD pattern (c) in Figure 2. In this case, however, both anatase and rutile peaks are detected, with anatase being the most intense of the two. From the electrochemical results below, it will be shown that at least part of the TiO2 originates from partial oxidation of the TiN current collector.

Figure 3 shows SEM top view and cross-sectional images of the sample Pt1 (case of full conversion). The top view image exhibits granular morphology of the prepared LTO consistent with a crystalline LTO as found by XRD. The SEM cross-sectional image displays continuous and uniform layers of Li4Ti5O12. No remaining Li2CO3 residue can be seen on the surface.

Film chemical composition.—ERD depth profile analysis was used to determine the chemical composition of the LTO films. For this type of measurements, the LTO films were grown on Si3N4 coated silicon substrate instead of platinum or TiN as the signals originating from the current collectors (Pt and TiN) interfere with that of LTO. The full conversion Pt1 conditions were used. Figure 4 shows the corresponding atomic concentrations depth profiles. The top layer (between dotted lines) shows uniform distribution of Li, Ti and O with a ratio close to the theoretical composition of spinel Li4Ti5O12 (see Table IV). As Si3N4 is not an ideal diffusion barrier, some intermixing is seen at the interface with formation of lithiated silicon oxynitride.23

Figure 5 shows XPS spectra measured on Pt1 samples before and after SSR. Before thermal treatment, the O 1s spectrum exhibits only a peak at 532 eV for oxygen in lithium carbonate (Li2O-CO3).23 After SSR, the intensity of this 532 eV peak significantly decreased and an intense peak appears at 530 eV for oxygen in Li4Ti5O12 (Li-Ti-O). The XPS spectrum of the C 1s for the sample before the thermal treatment exhibits a peak at 290 eV that can be attributed to the lithium carbonate. The peak at 284 eV is attributed to the surface carbon contamination as a result of exposure of the film to the ambient atmosphere.23 After annealing, the peak at 290 eV almost disappears indicating that the Li2CO3 is nearly completely consumed by the reaction.
Figure 4. Atomic concentrations-depth profiles from ERD measurement for 54 nm LTO film prepared with the condition of Pt1 on a Si3N4 substrate. The average concentration of the elements in the film is determined in the area between the two dashed lines.

For the Li 1s spectrum, before thermal treatment, the peak around 55.5 eV corresponds to lithium atoms in lithium carbonate. After thermal treatment, the peak shifts toward lower energies for lithium atoms in a LTO phase.24–26

These results confirm that the thermal treatment of the Li2CO3/TiO2 stacked layers results in an intermixing of elements with the formation of crystalline Li4Ti5O12 material. The ERD depth profile shows that the carbon (Li2CO3) is present only on the surface. The measured elements concentrations of the formed film are close to the theoretical stoichiometry of Li4Ti5O12 and a homogenous element distribution exists throughout the thin film. A small amount of Li2CO3 remains on the surface, confirming that sufficient lithium precursor was provided for the stoichiometric Reaction1.

Table IV . Concentrations of different elements of an as-prepared Li4Ti5O12 film and the theoretical element concentrations of the spinel Li4Ti5O12. The LTO sample was fabricated by a solid state reaction at 750 °C for 20 min in air between 22 nm of Li2CO3 and 50 nm of TiO2 on Si3N4. The average concentration is determined in the area between the two dashed lines in Figure 4.

| Element | Elements ratio [%] | Theoretical elements ratio [%] |
|---------|--------------------|--------------------------------|
| Li      | 17.5               | 19                             |
| Ti      | 26.2               | 24                             |
| O       | 56.3               | 57                             |

Figure 5. XPS surface spectra of a sample prepared with the condition Pt1 before thermal treatment (green solid line) and after thermal treatment (red dashed line).

Electrochemical analysis.—Cyclic voltammetry measurements.—Cyclic voltammetry was carried out in a solution of 1 M lithium perchlorate (LiClO4) and 1 M propylene carbonate (PC) on the samples prepared with the conditions listed in Table III within a voltage window of 0.8–2.8 V vs. Li+/Li at a scan rate of 10 mV s⁻¹. The corresponding cyclic voltammograms are shown in Figure 6.

All curves show a pair of sharp redox peaks centered around 1.55 V vs. Li+/Li which is the typical signature of spinel Li4Ti5O12. The cathodic peak at about 1.50 V vs. Li+/Li corresponds to the insertion of Li ions in the spinel Li4Ti5O12 upon reduction of Ti(IV) to Ti(III). The anodic peak around 1.68 V vs. Li+/Li is attributed to the process of Li-ion extraction from the LTO as a result of the re-oxidation of Ti(III) to Ti(IV).8,9,6 The electrode reaction is expressed as follows (Equation 2):

\[
\text{Li}_4\text{Ti}_5\text{O}_{12} + x\text{e}^- + x\text{Li}^+ \leftrightarrow \text{Li}_{4+x}\text{Ti}_5\text{O}_{12} \quad (0 \leq x \leq 3) \quad [2]
\]

In the case of a sample prepared with the condition TiN1, the cyclic voltammogram shows an additional couple of smaller redox peaks located around 1.8 V vs. Li+/Li attributed to the lithium ion insertion/extraction in/from anatase TiO2.9 The corresponding electrode reaction can be expressed by the following equation (Equation 3):

\[
\text{TiO}_2 + x\text{e}^- + x\text{Li}^+ \leftrightarrow \text{Li}_x\text{TiO}_2 \quad (0 \leq x \leq 1) \quad [3]
\]
The presence of TiO\textsubscript{2} redox peaks confirms that after thermal treatment the sample contains TiO\textsubscript{2} leftover (from unreacted TiO\textsubscript{2} and/or oxidation of TiN substrate) as found previously by XRD. The XRD results indeed showed intense anatase and also smaller rutile peaks next to the LTO phase in the film. In contrast, no clear anatase TiO\textsubscript{2} peaks for samples Pt1 and Pt2 were detected. In the case of Pt2, however, a larger amount of unreacted rutile TiO\textsubscript{2} is still present as only half of the Li\textsubscript{2}CO\textsubscript{3} precursor needed for complete reaction was provided (see the Fabrication procedure section). Note that rutile TiO\textsubscript{2} is known to be a poor Li-ion insertion material. Therefore, we expect the same intensity for the LTO redox peaks and/or oxidation of TiN substrate) as found previously by XRD. The XRD results indeed showed intense anatase and also smaller rutile peaks next to the LTO phase in the film. In contrast, no clear anatase TiO\textsubscript{2} peaks for samples Pt1 and Pt2 were detected. In the case of Pt2, however, a larger amount of unreacted rutile TiO\textsubscript{2} is still present as only half of the Li\textsubscript{2}CO\textsubscript{3} precursor needed for complete reaction was provided (see the Fabrication procedure section). Note that rutile TiO\textsubscript{2} is known to be a poor Li-ion insertion material. Hence, the incomplete solid state reaction results an electrochemically inactive rutile fraction on Pt2, whereas the oxidized TiN forms active anatase TiO\textsubscript{2} (TiN1 case).

Samples Pt1 and Pt2 are expected to have the same amount of Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} as we provided the same amount of Li\textsubscript{2}CO\textsubscript{3} with Pt1 a pure phase LTO (54 nm) and Pt2 a mixed phase with significant rutile TiO\textsubscript{2} fraction. Therefore, we expect the same intensity for the LTO redox peaks. However, this is not the case; the voltammogram of sample Pt2 shows much lower peak intensities compared to sample Pt1. It implies that the unreacted rutile TiO\textsubscript{2} phase also inhibits the LTO kinetics as the sample Pt2 has an electrochemically inactive rutile phase.

**Galvanostatic lithiation-delithiation measurements.**—Figure 7a shows the curves of the second lithiation/delithiation cycle of the Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} film prepared with the condition Pt1, at 1 C-rate corresponding to 3.37 × 10\textsuperscript{-6} A cm\textsuperscript{-2} (calculated for 54 nm LTO), in a potential window between 1.0 and 2.0 V vs. Li\textsuperscript{+}/Li. During lithiation, the initial potential drop from 2.0 V to 1.6 V corresponds to the initial Li-ion insertion reaction in the Li\textsubscript{4+6}Ti\textsubscript{5}O\textsubscript{12} phase (<x<0.03). The flat potential plateau at 1.55 V vs Li\textsuperscript{+}/Li is typical for LTO and corresponds to the Li-ion insertion reaction (0.03<x<3) for the Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} and Li\textsubscript{7}Ti\textsubscript{5}O\textsubscript{12} bi-phase. The second potential drop from 1.5 and 1.0 V corresponds to nearly completed lithiation into the single phase of Li\textsubscript{4+4}Ti\textsubscript{5}O\textsubscript{12} (x~3). The opposite is true for the delithiation reaction with a potential plateau at 1.56 V vs. Li\textsuperscript{+}/Li. The difference between the lithiation and delithiation capacities can be explained by the slower Li-ion diffusion kinetic through Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} with higher x values for higher lithiated state.

Figure 7b shows lithiation and delithiation curves of the sample TiN1. The measurement was performed at 1 C-rate corresponding to 2.82 × 10\textsuperscript{-6} A cm\textsuperscript{-2} (for 50 nm LTO formed out of 40 nm TiO\textsubscript{2}). As this film contains both LTO and anatase TiO\textsubscript{2} known to be electrochemically active, two potential plateaus are observed for the lithiation and delithiation curves (as for the two peaks in the cyclic voltammograms of Figure 6). The shorter plateaus at 1.70 V and 2.05 V correspond to the Li-ion insertion/extraction reactions for anatase TiO\textsubscript{2}. The longer plateaus at 1.54 V and 1.55 V are for LTO. During lithiation a capacity of 4.11 μAh cm\textsuperscript{-2} is reached where 1.35 μAh cm\textsuperscript{-2} (33%) comes from the Li-ion insertion in the anatase TiO\textsubscript{2} and 2.76 μAh cm\textsuperscript{-2} (67%) from the Li-ion insertion in the LTO.

**Effect of current collector and impurity phases on Li-ion intercalation kinetics.**—To better understand the Li-ion intercalation behavior for the different films, we have summarized in Table V the different crystalline phases observed in the film together with the starting precursor quantities and targeted LTO thickness. Note that the diffraction peak ratios are only given as a relative indication of the amount of each phase present, it is not quantitative.

The Sample TiN1 contains anatase and a small fraction of rutile next to the bulk LTO phase. The ratio of (101) anatase/(111) LTO and (110) rutile/(111) LTO peak intensities of 1.6 and 0.4, respectively, indicate that the presence of the anatase phase is more significant compared to the rutile one. As TiN1 was made from an anatase precursor film, the rutile residues are expected to be formed during the conversion process.

Samples Pt1 and Pt2 were made from a TiO\textsubscript{2} precursor film on Pt obtained from oxidation of Ti at 600 °C. No distinct diffraction peaks

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**Figure 6.** Cyclic voltammograms (the second scan) of Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} thin films synthesized by solid state reaction between a TiO\textsubscript{2} film and Li\textsubscript{2}CO\textsubscript{3} layer with conditions of: sample Pt1 (solid black line), sample Pt2 (solid gray line), and sample TiN1 (dashed black line); with a scan rate of 10 mV s\textsuperscript{-1}.

**Figure 7.** Potential versus Li-ion capacity curves during galvanostatic lithiation and delithiation of Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} films. 7a 2nd cycle of an LTO film prepared with conditions Pt1 at 1 C-rate (3.37 × 10\textsuperscript{-6} A cm\textsuperscript{-2}). 7b 2nd cycle at 1 C-rate (2.82 × 10\textsuperscript{-6} A cm\textsuperscript{-2}) of sample prepared with conditions TiN1.
60–70% of the total material was addressed. Note that the time of the 54 nm LTO was reached. At 1 C-rate still 32–39 nm or from the galvanostatic measurement at 0.1 C-rate the full capac-
city that can be reached for anatase TiO₂ (Li₀.₅TiO₂). In the cal-
culations, dense materials with densities for LTO (3.43 g cm⁻³), rutile (4.23 g cm⁻³), TiO₂ and anatase (3.78 g cm⁻³) were detected after annealing either. For the sample Pt2, additional rutile peaks were detected from the XRD pattern with a (110) rutile/(111) LTO ratio of 2.2. In this case the rutile originates from (further) crystallization of the unreacted fraction.

From the charges under the redox peaks in the cyclic voltam-
mograms and the potential plateaus in the lithiation and delithiation curves (provided in the supplementary information, Table S1), the effective (or minimum) LTO and TiO₂ film thicknesses contributing to the Li-ion insertion/extraction reactions were calculated (see Table VI). For the thickness calculations, 612 mAh cm⁻³ as the maximum capacity that can be reached for TiO₂ (x = 0.5).

Table V. Summary of the conditions used for the preparation of samples TiN₁, Pt1 and Pt2 and the different phases in the film. The (110)rutile/(111)LTO and (101)anatase/(111)LTO ratios are calculated from the XRD diffraction peak intensities.

| Sample | TiO₂ precursor thickness [nm] | TiO₂ precursor type | Estimated Li₂CO₃ thickness [nm] | TiO₂ residues after LTO formation | Ratio (110)rutile/(111)LTO | Ratio (101)anatase/(111)LTO | LTO thickness (RBS) [nm] |
|--------|-----------------------------|--------------------|--------------------------------|-------------------------------|--------------------------|---------------------------|--------------------------|
| TiN₁   | 40                          | Anatase by ALD     | 11                             | Anatase, rutile               | 0.4                      | 1.6                       | –                        |
| Pt₁    | 50                          | TiO₂ from oxidized Ti | 22                             | –                             | –                        | 54                        | –                        |
| Pt₂    | 100                         | TiO₂ from oxidized Ti | 22                             | –                             | 2.2                      | –                        | –                        |

*The thickness is calculated for a Li₂CO₃ deposited on a Si₃N₄ substrate, it can be different when the Li₂CO₃ is deposited on TiO₂ (case of TiN₁, Pt1 and Pt2).

| Sample | Thickness cathodic [nm] | Thickness anodic [nm] | Thickness cathodic [nm] | Thickness anodic [nm] |
|--------|------------------------|-----------------------|-------------------------|-----------------------|
| TiN₁   | 43                     | 38                    | 16                      | 16                    |
| Pt₁    | 40                     | 38                    | N.A*                    | N.A                   |
| Pt₂    | 22                     | 21                    | N.A*                    | N.A                   |

*NNo signal detected.

for anatase or rutile were detected for the pre-oxidized film (see Figure S1 for XRD of oxidized Ti film). For the sample Pt1, no anatase or rutile TiO₂ diffraction peaks were detected after annealing either. For the sample Pt2, additional rutile peaks were detected from the XRD pattern with a (110) rutile/(111) LTO ratio of 2.2. In this case the rutile originates from (further) crystallization of the unreacted fraction.

First, sample Pt1 which is the pure phase LTO material will be discussed. From RBS, we know that at least 54 nm of dense LTO film is present. From the cyclic voltammogram, an equivalent of 38–40 nm LTO was determined or about 70% of the total material. From the galvanostatic measurement at 0.1 C-rate the full capacity of the 54 nm LTO was reached. At 1 C-rate still 32–39 nm or 60–70% of the total material was addressed. Note that the time for LTO lithiation and delithiation in the voltammogram at 10 mV s⁻¹ was 60 s and 36 s, respectively; which corresponds to C-rates of about 60 and 100 C, respectively. Still the effective capacity is higher for the voltammograms compared to lithiation/delithiation at 1 C. The difference is that the charging and discharging steps happen initially slower in the potentialdynamic mode which is apparently beneficial for Li-ion intercalation especially in the delithiation step. As LTO is initially a poor electronic conductor, lithiation occurs close to the current collector giving a bottom-up like filling of the film. When a sudden current is applied (1 C) the film is forced to charge quickly forming a lithium rich layer near the electrolyte interface blocking further lithiation. The same holds for delithiation.

For the sample TiN₁, an equivalent of 43/38 nm of dense LTO film contributed to the Li-ion insertion and extraction processes during the cyclic voltammogram measurement. As this sample also contains anatase, an additional equivalent of 16/16 nm of TiO₂ was also determined from the peaks in the voltammogram. From the galvanic lithiation and delithiation measurement at 1 C, 45/26 nm of LTO and 41/40 nm of TiO₂ were measured. Hence, the sample contains at least an equivalent of 45 nm of LTO and 41 nm of TiO₂. In the fabrication process of this sample, we started with 40 nm of TiO₂ on 60 nm of TiN. This indicates that at least the TiO₂ precursor film was fully converted to LTO (40 nm TiO₂ gives 49 nm of LTO) and that the anatase results from the oxidation of TiN current collector (at least 32 nm of TiN was consumed). The presence of rutile TiO₂ diffraction peaks in the XRD pattern of the sample TiN₁ (curve d in Figure 2) suggests that more than 32 nm TiN was oxidized and that some of the TiN was converted to rutile TiO₂. The amount of the rutile TiO₂ can however not be quantified from the CV as done for the anatase as it is known to have a poor electrochemical activity. This will be confirmed later when discussion the cyclic voltammogram of the sample Pt2.

Note that equivalent thickness obtained from cyclic voltammetry and from galvanostatic measurements is quite different for anatase whereas it is comparable for the LTO phase. During the cyclic voltammogram measurement, the potential sweep limits the time provided to the Li-ion insertion/extraction processes to occur. For TiO₂ the time for Li-ion insertion (between 2 V and 1.6 V) is limited to only 24 s (comparable to 144 C). For comparison, the time for LTO lithiation during the potential scan in the voltammogram was 52 s (70 C).

For the sample Pt2, which has a rutile phase underneath the LTO film as a result of excess TiO₂ precursor, only 22 nm and 21 nm of LTO contributed to the Li-ion insertion and extraction reactions, respectively as determined from cyclic voltammetry. However, this sample should contain at least 54 nm of LTO similarly to the sample Pt1 as the same amount of Li₂CO₃ precursor was provided for the SSR. This confirms that the presence of the underlying untreated rutile considerably slows down the lithiation kinetics of the LTO film. Importantly, the TiN₁ sample (TiN/anatase/LTO) shows faster Li-ion intercalation/extraction kinetics than the phase pure Pt1.
Figure 8. Schematic band diagrams of the Pt/LTO and TiN/TiO2(anatase)/LTO junctions without taking into account the band bending, i.e. how the bands would be before the materials are brought in contact with each other. The dotted line indicates the upper range of valence band edge energies from literature (Table S2).

sample (Pt/LTO). We believe that the improved kinetics of the TiN/anatase/LTO is a result of better electronic contact as the work function of TiN (3.4–4.4 eV) is well aligned with the conduction band edges of both anatase (3.6–4.4 eV) and Li4Ti5O12 (3.6 eV). Platinum, on the other hand, has a work function (6.3 eV) in the middle of the LTO bandgap and thus relies on the many electronic states in the LMO bandgap for the electron transfer at the Pt/LTO interface, which is less efficient than the direct electron exchange at the conduction band. The band diagram is shown schematically in Figure 8 according to the metal work function, conduction band edge energies and bandgap summarized in Table S2.30–34 Indeed, as the electrode materials are semiconductor materials, a proper ohmic contact between metal current collector and semiconductor is important and often overlooked. Interestingly, for LTO the band edges shift down in energy during lithiation (reduction of Ti(IV) to Ti(III)) while maintaining similar bandgap energy. For the fully lithiated Li7Ti5O12 form, the band edges have shifted down with about 3 eV.35 Hence, in this case also the Pt valence band gives proper overlap with the LTO conduction band. This means that the delithiation process would be easier than the lithiation process for Pt as current collector for LTO. Indeed, from Table VI it followed that the rate difference between TiN and Pt was mainly in the lithiation step. For the delithiation step, Pt seemed to be even slightly faster.

Cyclability and rate performance.—The cyclability and rate performance of the phase-pure LTO film (Pt1) was tested in the voltage range between 1 V and 2 V vs. Li+/Li. First the stability of the lithiation/delithiation capacity at 1 C-rate was checked over 100 continuous cycles (Figure S3). Initially, a drop in lithiation capacity of about 20% is observed during the first 10 cycles (from 521 mAh cm\(^{-3}\) to 411 mAh cm\(^{-3}\); i.e. from 85% to 67% of the theoretical capacity). After the 10\(^{th}\) cycle, the film capacity becomes stable reaching 395 mAh cm\(^{-3}\) at the 100\(^{th}\) cycle (65% of the theoretical capacity). The initial drop is due to the uninterrupted cycling, i.e. without waiting period for equilibration between the lithiation and delithiation steps, evolving to a steady-state behavior after about 10 cycles. For the delithiation, only a small drop in capacity of about 4% is found during the 10 first cycles (from 364 mAh cm\(^{-3}\) to 350 mAh cm\(^{-3}\); i.e. from 59% to 57% of the theoretical capacity), reaching 338 mAh cm\(^{-3}\) at the 100\(^{th}\) cycle (55% of theoretical capacity). In both cases, the LTO film retains 96% of the 10\(^{th}\) cycle capacity at the 100\(^{th}\) cycle confirming the typical good cycling ability of Li4Ti5O12. The delithiation capacity is consistently about 10% lower, indicating a loss in capacity which we cannot explain at this point.

Next, the C-rate performance was measured between 0.1 C and 20 C. Figure 9a shows the corresponding lithiation and delithiation curves at different C-rates. At the lowest C-rate of 0.1 C, extremely flat operational plateaus at 1.557 V for lithiation and at 1.567 V for delithiation are observed during the first 10 cycles from 364 mAh cm\(^{-3}\) to 350 mAh cm\(^{-3}\); i.e. from 59% to 57% of the theoretical capacity). After the 10\(^{th}\) cycle, the film capacity becomes stable reaching 395 mAh cm\(^{-3}\) at the 100\(^{th}\) cycle (65% of the theoretical capacity). The initial drop is due to the uninterrupted cycling, i.e. without waiting period for equilibration between the lithiation and delithiation steps, evolving to a steady-state behavior after about 10 cycles. For the delithiation, only a small drop in capacity of about 4% is found during the 10 first cycles (from 364 mAh cm\(^{-3}\) to 350 mAh cm\(^{-3}\); i.e. from 59% to 57% of the theoretical capacity), reaching 338 mAh cm\(^{-3}\) at the 100\(^{th}\) cycle (55% of theoretical capacity). In both cases, the LTO film retains 96% of the 10\(^{th}\) cycle capacity at the 100\(^{th}\) cycle confirming the typical good cycling ability of Li4Ti5O12. The delithiation capacity is consistently about 10% lower, indicating a loss in capacity which we cannot explain at this point.

Figure 9. Lithiation and delithiation performance of Li4Ti5O12 film prepared with condition Pt1. 9a Potential-capacity curves for galvanostatic lithiation and delithiation between 1V and 2V at different C-rates (0.1, 1, 2, 5, 10 and 20 C corresponding to 3.37 \times 10^{-5}, 3.37 \times 10^{-4}, 6.73 \times 10^{-4}, 1.68 \times 10^{-3}, 3.37 \times 10^{-3}, 6.73 \times 10^{-3} A cm\(^{-2}\)). 9b Lithiation capacity extracted from 8a in function of C-rate.
delithiation are found in the potential capacity curves. With increasing C-rates, the plateau values shift due to IR drop and the plateaus become shorter due to kinetic limitations. By increasing the C-rate, the plateau potential shifts from 1.556 at 1 C to 1.539 V at 20 C during lithiation and from 1.567 V at 1 C to 1.592 V at 20 C for the delithiation process. From this IR-shift a film resistivity of $0.63 \times 10^8 \Omega \text{cm}$ and $0.57 \times 10^8 \Omega \text{cm}$ for lithiation and delithiation, respectively, is calculated. This high film resistivity indicates that the low rate capability of the LTO film is due to its low electronic conductivity and not to a Li-ion diffusion limitation as we are working with thin film.

Figure 9b shows the lithiation capacity in function of the C-rate. At 0.1 C, the theoretical capacity is reached. By increasing the C-rate, the lithiation capacity at 1 V drops from 410 mAh cm$^{-2}$ at 1 C to 275 mAh cm$^{-2}$ at 20 C (drop of 33%) because of the kinetic limitations. But still at 20 C the film reaches 45% of its theoretical capacity. For the application of 3D thin film batteries such high C-rates are sought to enable quick recharge of the footprint limited micro-batteries.

**Fabrication and characterization of Li$_4$Ti$_5$O$_12$ thin films by solid state reaction on 3D micropillar substrate.**—Figure 10 shows the SEM images of the as-deposited TiO$_2$ and Li$_2$CO$_3$ film conformally coated over the pillar array by ALD. First, an amorphous TiO$_2$ thin-film with nominal thickness of 100 nm was deposited by spatial ALD over the TiN coated silicon pillar array. The conformality of the Titania process was about 80% with 102 nm on the top of the pillars, 90 nm on the middle of the pillars and 80 nm on the bottom. Next, a Li$_2$CO$_3$ thin-film with nominal thickness of 163 nm was deposited by thermal ALD. This process resulted in the deposition of a film with a Li$_2$CO$_3$ thickness of 350 nm on the top of the pillars, 260 nm on the middle of the pillars and 250 nm on the bottom. The Li$_2$CO$_3$ film has a pyramidal-like morphology due a CVD-like component as a result of water absorption in the layer also known as the reservoir effect. To convert the TiO$_2$/Li$_2$CO$_3$ stack to Li$_4$Ti$_5$O$_12$, the sample was annealed at 750$^\circ$C for 20 min in vacuum. XRD patterns of: 11a as-deposited TiO$_2$ on the 3D pillar array. 11b the TiO$_2$/Li$_2$CO$_3$ on the 3D pillar array after annealing (750$^\circ$C for 20 min in vacuum). 11c the TiO$_2$/Li$_2$CO$_3$ on the 3D pillar array after annealing (750$^\circ$C for 20 min in vacuum), soaking (in water for 24h) and drying (350$^\circ$C for 120 min in air).

**Conclusions**

Li$_4$Ti$_5$O$_12$ thin films were successfully synthesized by a solid state reaction between stacked TiO$_2$ and Li$_2$CO$_3$ thin-films. XRD patterns show the characteristic LTO peaks and the SEM images show a uniform morphology of a continuous film. The ERD analyses indicate that the fabricated film has a stoichiometry close the theoretical Li$_4$Ti$_5$O$_12$ stoichiometry (Li: O: Ti = 17.5%; 26.2%; 56.3%) and a homogenous distribution of Li, Ti and O throughout the film. An annealing temperature higher than 650$^\circ$C is needed to form the crystalline spinel material.

The Li$_4$Ti$_5$O$_12$ films formed by solid state reaction are electrochemically active around 1.55 V vs. Li$^+$/Li. The theoretical capacity of 612 mAh cm$^{-2}$ is reached at low charging rate of 0.1 C.

The type of the current collector material used affects the composition and the performance of the prepared LTO film. In case of using a Pt current collector, a pure phase LTO film can be formed when sufficient amount of Li$_2$CO$_3$ precursor is provided (in one or more SSR steps). In case of excess TiO$_2$, the remaining TiO$_2$ after the SSR has the rutile phase. It was found that this rutile residue inhibits the
kinetics of Li-ion intercalation/extraction in the LTO film and as such lower the effective Li-ion capacity.

In case of a TiN current collector, an anatase TiO₂ interlayer is formed between the TiN and the LTO. Surprisingly, the kinetics of the TiN/anatase/LTO stack had significantly better rate performance (effective Li-ion capacity) than the Pt/LTO stack due to the better band alignment for the TiN/anatase/LTO stack compared to the Pt/LTO contact.

High aspect ratio silicon pillar arrays coated with 125 nm Li₄Ti₅O₁₂ were fabricated using our thin film solid-state conversion technique. In this case, conformal TiO₂ and Li₂CO₃ superposed layers were deposited by ALD. Unfortunately, as all the thin ALD TiN current collector coating was completely consumed in the process, the 3D LTO electrodes were not electrochemically active. To remedy this issue and maintain sufficient TiN on the pillars as current collectors, fast cooldown of the samples by e.g. rapid thermal anneal (RTA) process should be implemented instead. Nevertheless, the results show that it is indeed possible to form continuous and uniform film conformal over high aspect ratio structures using the SSR technique. The fabricated thin-film LTO coatings on the silicon micron pillar arrays could potentially be used as 3D electrode for thin film micro-batteries. In addition, our technique could also be used for the fabrication of conformal and continuous protective coatings around active electrode particles to improve their electrode performance. Thin-films of LTO up to a few tens of nanometer thick are of interest as dual conducting shell coatings as around cathode active materials as they are sufficiently conductive, both for Li-ions and electrons. Its chemical inertness can protect materials against dissolution and parasitic reaction with the electrolyte. In this case, the complete consumption of TiN, which can be applied as a diffusion barrier, could even be used as an advantage.

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