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# ALD Al<sub>2</sub>O<sub>3</sub>-Coated TiO<sub>2</sub> Nanotube Layers as Anodes for Lithium-Ion Batteries

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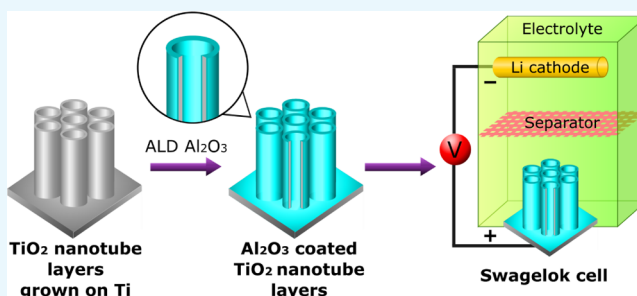
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## S Supporting Information

**ABSTRACT:** The utilization of the anodic TiO<sub>2</sub> nanotube layers, with uniform Al<sub>2</sub>O<sub>3</sub> coatings of different thicknesses (prepared by atomic layer deposition, ALD), as the new electrode material for lithium-ion batteries (LIBs), is reported herein. Electrodes with very thin Al<sub>2</sub>O<sub>3</sub> coatings (~1 nm) show a superior electrochemical performance for use in LIBs compared to that of the uncoated TiO<sub>2</sub> nanotube layers. A more than 2 times higher areal capacity is received on these coated TiO<sub>2</sub> nanotube layers (~75 vs 200 μAh/cm<sup>2</sup>) as well as higher rate capability and coulombic efficiency of the charging and discharging reactions. Reasons for this can be attributed to an increased mechanical stability of the TiO<sub>2</sub> nanotube layers upon Al<sub>2</sub>O<sub>3</sub> coating, as well as to an enhanced diffusion of the Li<sup>+</sup> ions within the coated nanotube layers. In contrast, thicker ALD Al<sub>2</sub>O<sub>3</sub> coatings result in a blocking of the electrode surface and therefore an areal capacity decrease.



## INTRODUCTION

During the last decade, TiO<sub>2</sub> nanomaterials have widely been studied as an alternative electrode material for lithium-ion batteries (LIBs).<sup>1–15</sup> TiO<sub>2</sub> has a higher lithiation potential (~1.6 V vs Li/Li<sup>+</sup>) compared to that of the negative electrodes, such as graphite (~0.1 V vs Li/Li<sup>+</sup>), and therefore enhances safety of the cells and provides a good capacity retention on cycling and a low self-discharge.<sup>1–4</sup> Furthermore, TiO<sub>2</sub> shows low volume changes of less than 4% upon reversible insertion and extraction of Li<sup>+</sup> in the lattice. However, TiO<sub>2</sub> also has a poor electrical conductivity and shows limited Li<sup>+</sup> uptake and slow Li<sup>+</sup> insertion kinetics.<sup>1–4</sup> To overcome these drawbacks, nanostructured TiO<sub>2</sub>, such as mesoporous microspheres,<sup>5</sup> nanowires,<sup>6,7</sup> nanoparticles,<sup>8</sup> nanoflakes,<sup>9</sup> or TiO<sub>2</sub> nanotubes,<sup>1–4,10</sup> produced via different methods have been considered as anodes due to the larger specific surface area. Although most of these structures are randomly oriented and have to be deposited on the back contact of the electrode, self-organized TiO<sub>2</sub> nanotube layers produced by electrochemical anodization of the Ti substrates consist of straight and vertically aligned nanotubes in direct electrical contact with the underlying Ti substrate.<sup>16</sup> Another advantage of the vertically aligned nanotube layers is a direct diffusion path for the Li<sup>+</sup> ions, resulting in a superior electrochemical performance.<sup>11</sup>

To further increase the capacity and conductivity of the TiO<sub>2</sub> nanotubes for their use in LIBs, they have been decorated or coated with other metals and metal oxides, with higher conductivities and capacities, for example, Ag,<sup>17</sup> Cu<sub>6</sub>Sn<sub>5</sub>,<sup>18</sup> Fe<sub>2</sub>O<sub>3</sub>,<sup>19</sup> SnO,<sup>20</sup> SnO<sub>2</sub>,<sup>21,22</sup> or ZnO.<sup>23</sup> Another advantage of these composite structures is that due to their hollow tubular architecture they can bear volume variations upon battery cycling without mechanical failure.

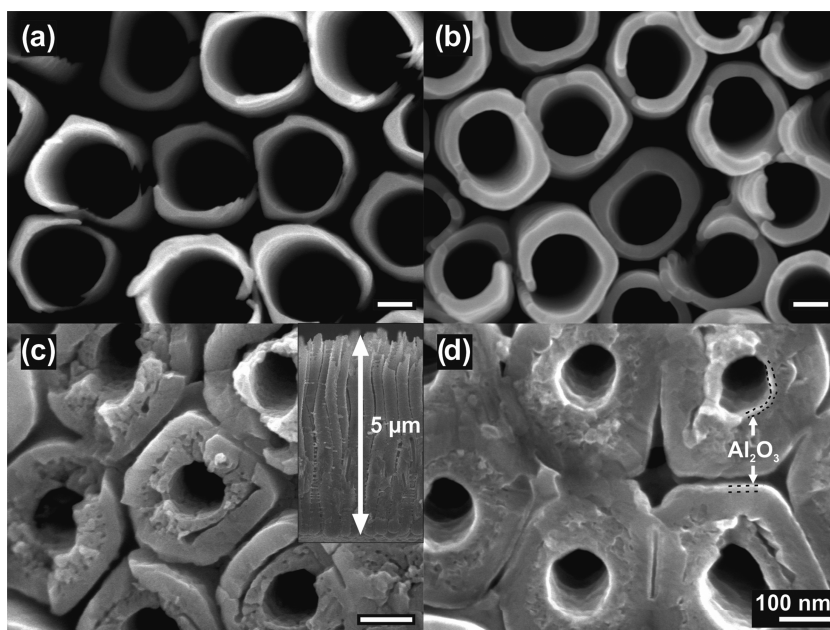
Among the various methods that can be used for the coating and decoration of the TiO<sub>2</sub> nanotube layers, atomic layer deposition (ALD) has been the only method that creates uniform coatings of the nanotube walls from inside as well as outside, with a precise control of the coating thickness according to the deposition cycles.<sup>24–26</sup> However, although several reports can be found on utilization of the ALD coatings of different materials to modify the electrodes for lithium-ion battery application,<sup>27–33</sup> only one publication reports on the use of ALD to coat an anode prepared from an anodic TiO<sub>2</sub> nanotube layer with ZnO.<sup>23</sup>

Usually, passivation layers on the electrode surfaces (solid electrolyte interphase (SEI)) are formed via decomposition of

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**Figure 1.** SEM images of the top (a, b) and bottom parts (c, d) of the uncoated  $\text{TiO}_2$  nanotube layer (a, c) and 10 nm ALD  $\text{Al}_2\text{O}_3$ -coated  $\text{TiO}_2$  nanotube layer (b, d). The inset in (c) shows an illustrative image of the whole  $\text{TiO}_2$  nanotube layer, revealing a thickness of  $\sim 5 \mu\text{m}$ .

the electrolyte and are necessary to prevent further electrolyte decomposition that often leads to unsafe operation conditions.<sup>34</sup> However,  $\text{Li}^+$  ions are consumed for SEI formation, reducing the overall capacity of the electrode. Thin layers of  $\text{Al}_2\text{O}_3$  can suppress the SEI formation and undesirable side reactions. Several reports demonstrated the beneficial effect of the  $\text{Al}_2\text{O}_3$  coatings on electrodes prepared from different materials for passivation of the electrode surfaces.<sup>35–43</sup> At the same time,  $\text{Al}_2\text{O}_3$  acts as a substitute for the SEI layer due to the formation of  $\text{Li-Al-O}$  in the first few cycles, which is a good ionic conductor, blocking the electron transfer efficiently.<sup>39,40,43</sup>

In this work, for the first time, the vertically aligned  $\text{TiO}_2$  nanotube layers prepared by anodization were coated with thin  $\text{Al}_2\text{O}_3$  layers of different thicknesses by ALD (i.e., 0.2, 1, 2, 5, and 10 nm corresponding to of 2, 9, 18, 46, and 92 ALD cycles, respectively) and examined as potential anodes for LIBs. The results were compared to that of the uncoated  $\text{TiO}_2$  nanotube layers.

## EXPERIMENTAL SECTION

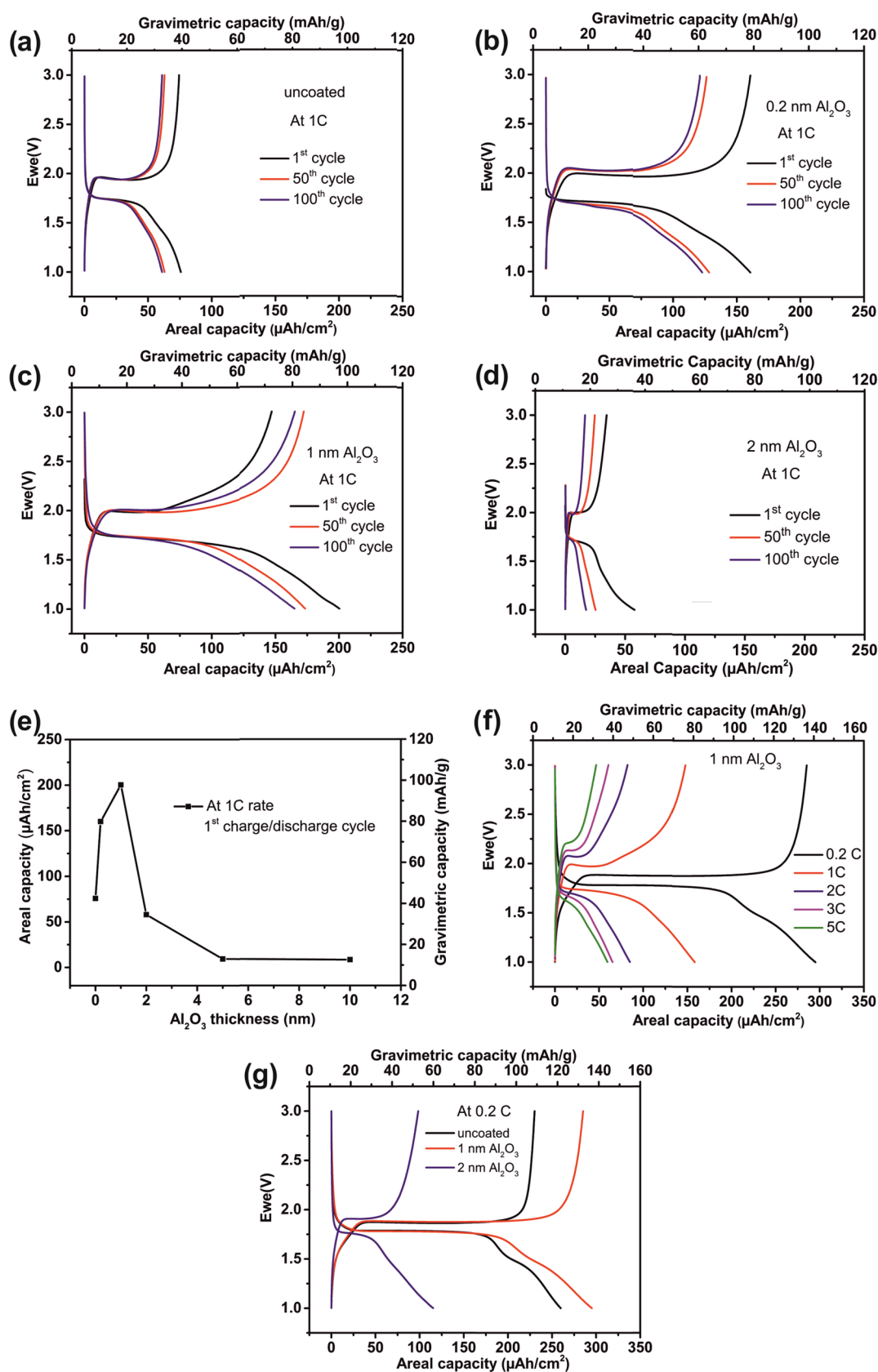
$\text{TiO}_2$  nanotube layers, with a thickness of  $\sim 5 \mu\text{m}$  and a diameter of  $\sim 230 \text{ nm}$ , were prepared according to the previously published work.<sup>44</sup> In brief, Ti foils (Sigma Aldrich, 0.127 mm thick, 99.7% purity) were degreased in isopropanol and acetone and afterwards anodized in an ethylene glycol-based electrolyte containing 150 mM  $\text{NH}_4\text{F}$  and 10 vol %  $\text{H}_2\text{O}$  at 100 V for 4 h. The electrochemical cell consisted of a high-voltage potentiostat (PGU-200V; Elektroniklabor GmbH) in a two-electrode configuration, with a Pt foil as the counter electrode and Ti foil as the working electrode. After anodization, the nanotube layers were sonicated in isopropanol and dried in air. Before further use, all of the  $\text{TiO}_2$  nanotube layers were annealed in a muffle oven at  $400^\circ\text{C}$  to receive a crystalline anatase phase.

The prepared  $\text{TiO}_2$  nanotube layers were coated with  $\text{Al}_2\text{O}_3$  layers of different thicknesses using an ALD tool (thermal ALD, TFS 200, Beneq). Trimethylaluminum (TMA, Strem, elec.

grade, 99.999+%) and deionized water ( $18 \text{ M}\Omega$ ) were used as aluminum and oxygen precursors, respectively. Under these deposition conditions, one ALD  $\text{Al}_2\text{O}_3$  growth cycle was defined by the following sequence: TMA pulse (100 ms)– $\text{N}_2$  purge (2 s)– $\text{H}_2\text{O}$  pulse (100 ms)– $\text{N}_2$  purge (3 s). All processes were carried out at a temperature of  $200^\circ\text{C}$ , using  $\text{N}_2$  (99.9999%) as the carrier gas, at a flow rate of 400 sccm.  $\text{Al}_2\text{O}_3$  coatings of different thicknesses were deposited within the  $\text{TiO}_2$  nanotube layers. The number of cycles required for the different  $\text{Al}_2\text{O}_3$  thicknesses was estimated from the growth per cycle value of the  $\text{Al}_2\text{O}_3$  process at  $200^\circ\text{C}$  ( $\sim 1.1 \text{ \AA/cycle}$ ). Thus, ALD processes of 2, 9, 18, 46, and 92 cycles led to nominal  $\text{Al}_2\text{O}_3$  coating thicknesses of 0.2, 1, 2, 5, and 10 nm, respectively.

The structure and morphology of the  $\text{TiO}_2$  nanotube layers were characterized by a field-emission electron microscope (FE-SEM JEOL JSM 7500F). Dimensions of the nanotubes were measured and statistically evaluated using proprietary Nanomeasure software.

The electrochemical performance of the ALD  $\text{Al}_2\text{O}_3$ -coated  $\text{TiO}_2$  nanotube layers was studied using Swagelok-type cells. The  $\text{TiO}_2$  nanotube layers were assembled with metallic Li (Aldrich) as the counter electrode, with a glass fiber (Whatman) used as a separator. The electrolyte consisted of a solution of 1 M  $\text{LiPF}_6$  in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1, in w/w) (Sigma Aldrich). The cells were assembled in an argon-filled glovebox (MBraun, Germany), with  $<0.5 \text{ ppm H}_2\text{O}$  and  $<0.5 \text{ ppm O}_2$  atmosphere. Galvanostatic tests were carried out using a VMP3 potentiostat (Bio Logic, France). The cells were cycled at 1C ( $\sim 1 \text{ h charge/discharge}$ ) in a potential window of 1–3 V. The current was applied considering the mass of the  $\text{TiO}_2$  nanotube layers and was calculated considering a density of  $4.23 \text{ g/cm}^3$  and porosity of 76%. The porosity calculation is based on the amount of the  $\text{TiO}_2$  nanotubes per  $\text{cm}^2$ . The volume occupied by the  $\text{TiO}_2$  nanotubes was calculated by subtracting the inner tube area from outer tube area.



**Figure 2.** Galvanostatic cycling at 1C rate of the (a) uncoated (0 cycles), (b) 0.2 nm (2 cycles), (c) 1 nm (9 cycles), and (d) 2 nm (18 cycles) ALD  $\text{Al}_2\text{O}_3$ -coated  $\text{TiO}_2$  nanotube layers, (e) the discharge capacity of the first charge/discharge cycle of the  $\text{TiO}_2$  nanotube layers coated with  $\text{Al}_2\text{O}_3$  of different thicknesses at 1C rate, (f) galvanostatic discharge/charge curves of the first reversible cycle of the 1 nm  $\text{Al}_2\text{O}_3$ -coated  $\text{TiO}_2$  nanotube layer at different C rates, and (g) galvanostatic discharge/charge curves of the first reversible cycle of the uncoated, and the 1 and 2 nm ALD  $\text{Al}_2\text{O}_3$ -coated  $\text{TiO}_2$  nanotube layer at C/5.



The chronoamperometric (CA) tests were conducted in a three-electrode Swagelok cell. The uncoated and the 1 and 2 nm ALD  $\text{Al}_2\text{O}_3$ -coated  $\text{TiO}_2$  nanotube layer electrodes were assembled against one Li foil serving as a counter electrode and another Li foil as a reference electrode. Two separators were placed between each electrode soaked in a solution of 1 M  $\text{LiPF}_6$  in EC/DEC (1:1, in w/w) obtained from Sigma Aldrich. The CA tests were performed by applying a constant potential of 1.7 V for 80 s using a VMP3 potentiostat–galvanostat (Bio Logic).

For electrochemical impedance spectroscopy (EIS) measurements, the nanotube layers were assembled in a three-electrode system, with separate Li foils as the reference and counter electrodes, using Whatman paper as the separator. EC/DEC with 1 M  $\text{LiPF}_6$  was used as the electrolyte. The cells were kept for 24 h at open circuit potential (OCP) to get stabilized. The AC impedance measurements were carried out using a VMP3 Biologic Potentiostat at OCP in a frequency range of 100 kHz to 10 mHz at amplitude of 10 mV. The obtained spectra were fitted by “Z-fit” in the EC-Lab software (Bio Logic).

## RESULTS AND DISCUSSION

Figure 1 shows SEM images of the top (a, b) and bottom parts (c, d) of the uncoated  $\text{TiO}_2$  nanotube layer and the 10 nm  $\text{Al}_2\text{O}_3$ -coated  $\text{TiO}_2$  nanotube layer. As can be seen, the wall thickness on top of the nanotube layers increased from the uncoated to 10 nm ALD  $\text{Al}_2\text{O}_3$ -coated  $\text{TiO}_2$  nanotube layers. At the bottom parts, thin layers of  $\text{Al}_2\text{O}_3$  could be observed on the inside as well as outside of the nanotube walls. The thin layers were visible due to the different mass contrasts between  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$ . In line with our previous work, the ALD  $\text{Al}_2\text{O}_3$  coatings on the  $\text{TiO}_2$  nanotube layers were very uniform and homogeneous.<sup>26</sup>

It has to be noted that the double-walled structure that can be seen at the bottom parts of both the uncoated and coated nanotube layers is an intrinsic feature of the  $\text{TiO}_2$  nanotube layers prepared in ethylene glycol-based electrolytes and is well known from the literature.<sup>45</sup>

Figure 2a–d shows the charge/discharge profiles obtained by chronopotentiometry in the potential range of 1.0–3.0 V for the uncoated  $\text{TiO}_2$  nanotubes (taken as reference), 0.2 nm  $\text{Al}_2\text{O}_3$ , 1 nm  $\text{Al}_2\text{O}_3$ , and 2 nm ALD  $\text{Al}_2\text{O}_3$ -coated  $\text{TiO}_2$  nanotube layers recorded at 1C. In all of the cases, the presence of two plateaus is attributed to the reversible insertion of  $\text{Li}^+$  into crystalline anatase  $\text{TiO}_2$ . In the discharge profile, the plateau at  $\sim 1.75$  V corresponds to the accommodation of  $\text{Li}^+$ , according to a reduction reaction. In the charge profile, the plateau at  $\sim 1.95$  V was induced by the extraction of  $\text{Li}^+$ , according to an oxidation reaction. The reversible insertion reaction of  $\text{Li}^+$  in anatase  $\text{TiO}_2$  is given by eq 1<sup>1</sup>



As can be seen in Figure 2a–d, the presence of  $\text{Al}_2\text{O}_3$  coating clearly had a strong influence on the electrochemical performance of the  $\text{TiO}_2$  nanotube electrodes. Indeed, the areal and gravimetric capacities grew with increasing  $\text{Al}_2\text{O}_3$  thickness until a maximum value for the 1 nm  $\text{Al}_2\text{O}_3$ -coated  $\text{TiO}_2$  nanotube layers and then decreased for the  $\text{TiO}_2$  nanotube layers with thicker coatings. The gravimetric capacities were calculated on the basis of an estimated porosity of 76%. It must be noted that the porosity of the nanotube layers is just an estimated value and therefore the gravimetric capacities are not

as accurate as the areal capacities. The theoretical capacity of  $\text{TiO}_2$  is 336 mAh/g for 1 mol of Li-ion insertion. For the fully reversible reaction,  $\text{TiO}_2$  inserts a maximum of 0.5 mol Li ions, giving a theoretical capacity of 168 mAh/g.<sup>1</sup> Thus, the theoretical capacity is not reached for 1 nm coatings, according to our porosity calculation. However, the calculated gravimetric capacity for the nanotube layers with 1 nm coating was 149 mAh/g for the first cycle at a C rate of C/5 (Figure 2f,g), which is very close to the theoretical value of 168 mAh/g, especially taking the above mentioned accuracy into account.

Figure 2e shows dependence of the first discharge capacity delivered by the  $\text{TiO}_2$  nanotube layers coated by  $\text{Al}_2\text{O}_3$ , using various coating thicknesses. After being coated with 1 nm  $\text{Al}_2\text{O}_3$ , the areal capacity was more than 2 times higher compared to that of the reference ( $\sim 200$  vs  $\sim 75$   $\mu\text{Ah}/\text{cm}^2$ , respectively), whereas for thicker  $\text{Al}_2\text{O}_3$  coatings, the areal capacity decreased significantly. More remarkably, after the charge/discharge tests, the capacity remained almost 3 times higher than that for the reference ( $\sim 164$  vs  $\sim 60$   $\mu\text{Ah}/\text{cm}^2$ , respectively).

Reasons for the enhancement of capacity on the  $\text{Al}_2\text{O}_3$ -coated  $\text{TiO}_2$  nanotube layers are at least 2-fold. At first, an inhibition of the significant volume changes of the  $\text{TiO}_2$  nanotubes during Li insertion due to an improved mechanical stability should be considered. An improved mechanical and chemical stability of the ALD  $\text{Al}_2\text{O}_3$ -coated  $\text{TiO}_2$  nanotube arrays was recently reported by the Macak group,<sup>46</sup> showing that already thin  $\text{Al}_2\text{O}_3$  coatings of 1 nm have a beneficial effect. Moreover, it was reported that an addition of  $\text{Al}_2\text{O}_3$  can stabilize the mesoporous anatase  $\text{TiO}_2$  structures upon Li insertion.<sup>47</sup> However, SEM analyses of the electrodes was carried out after 100 charge/discharge cycles, presented in Figure 2. All of the nanotube layers preserved their architecture (see Figure S1) without any noticeable change or damage.

The second reason for the enhanced capacity is a better diffusion of the  $\text{Li}^+$  ions within the  $\text{Al}_2\text{O}_3$ -coated  $\text{TiO}_2$  nanotube layers, which might be explained by changes in the  $\text{Al}_2\text{O}_3$  layer upon galvanostatic experiments. Xiao et al.<sup>41</sup> found that the structure of the ultrathin  $\text{Al}_2\text{O}_3$  changes to  $\text{Al}_2\text{O}_3/\text{AlF}_3$  during cycling, providing a better  $\text{Li}^+$ -ion conductivity and formation of  $\text{LiAlO}_2$  on the surface that can promote Li insertion by reducing the associated energy barrier.

However, on the basis of Figure 2, a suppression of the SEI layer due to  $\text{Al}_2\text{O}_3$  coatings can be excluded, even though  $\text{Al}_2\text{O}_3$  coatings are typically discussed in the literature<sup>39,40,43</sup> as inhibitors of SEI formation. It is also known that on the  $\text{TiO}_2$  anodes only very thin SEI layers are formed when electrochemical cycling experiments are performed at potentials higher than 1 V.<sup>2,11,48</sup> Indeed, from Figure 2 it is clear that the capacity loss during the first charge/discharge cycle (when SEI typically forms) was very low for the uncoated  $\text{TiO}_2$  nanotube layer, suggesting that only a very thin SEI layer was formed. In contrast, the capacity loss during the first charge/discharge cycle was much more pronounced for the  $\text{Al}_2\text{O}_3$ -coated  $\text{TiO}_2$  nanotube layers. This high irreversible capacity of the ALD  $\text{Al}_2\text{O}_3$ -coated  $\text{TiO}_2$  nanotube layers might be caused by Li-containing  $\text{Al}_2\text{O}_3$  phase formation.<sup>39</sup> It is believed that the insulating  $\text{Al}_2\text{O}_3$  layers cause a potential drop and also slow down Li diffusion during the first cycle. Thereafter,  $\text{Al}_2\text{O}_3$  reacts with the electrolyte and forms  $\text{AlF}_3$ , which facilitates the charge transfer.<sup>39</sup> It was also suggested that lithiation of the  $\text{Al}_2\text{O}_3$  coating layer proceeds until a thermodynamically stable phase is reached (corresponding to  $\text{Li}_{3.4}\text{Al}_2\text{O}_3$ ).<sup>49</sup> The extra  $\text{Li}^+$  ions

then overflow into the electrode passing through the coating layer. If the  $\text{Al}_2\text{O}_3$  coating layer is too thick, a longer time would be needed until the thermodynamically stable phase is reached.<sup>49</sup> This explains that thicker  $\text{Al}_2\text{O}_3$  coatings blocked Li diffusion into  $\text{TiO}_2$  and therefore the areal capacity decreased for the thicker  $\text{Al}_2\text{O}_3$  coatings within the  $\text{TiO}_2$  nanotube layers, as can be seen in Figure 2e. Furthermore, a higher amount of  $\text{Li}^+$  from the electrolyte is needed to build a thermodynamically stable phase  $\text{Li}_{3.4}\text{Al}_2\text{O}_3$  for the thicker  $\text{Al}_2\text{O}_3$  layers, reducing the charge/discharge capacities.

Additionally, calculations of the diffusion coefficients using chronoamperometry and the Cottrell equation were carried out after cycling the cell for three cycles at 1C rate to facilitate formation of the Li–Al–O phase (see Figure S2). The diffusion coefficients calculated for the uncoated (0 cycles ALD) and 1 nm (9 cycles) ALD  $\text{Al}_2\text{O}_3$ -coated  $\text{TiO}_2$  nanotube layers were  $1 \times 10^{-16}$  and  $1.44 \times 10^{-16} \text{ cm}^2 \text{ s}^{-1}$ , respectively, which shows the positive influence of  $\text{Al}_2\text{O}_3$  on  $\text{Li}^+$  diffusion. For the 2 nm (18 cycles) ALD  $\text{Al}_2\text{O}_3$ -coated  $\text{TiO}_2$  nanotube layers, the diffusion coefficient was estimated to be  $9 \times 10^{-17} \text{ cm}^2 \text{ s}^{-1}$ , suggesting that at a higher  $\text{Al}_2\text{O}_3$  thickness  $\text{Li}^+$  diffusion is hindered.

Lindstrom et al.<sup>50</sup> have reported an  $\text{Li}^+$  diffusion coefficient of  $1 \times 10^{-17} \text{ cm}^2 \text{ s}^{-1}$  for nanoporous anatase  $\text{TiO}_2$  using chronoamperometry. Apart from the positive influence of the thin  $\text{Al}_2\text{O}_3$  coating on the  $\text{TiO}_2$  nanotubes shown for our samples, the higher  $\text{Li}^+$  diffusion also indicates that one-dimensional nanomaterials (like the vertical aligned nanotubes) could help promote better charge diffusion compared with nanoporous films.

These results are also in agreement with findings reported in the literature. Lipson et al.<sup>43</sup> observed for an ALD  $\text{Al}_2\text{O}_3$ -coated MnO electrode that  $\text{Li}^+$  was unable to diffuse through the thick  $\text{Al}_2\text{O}_3$  films and thus the thick ALD  $\text{Al}_2\text{O}_3$  films blocked the electrode surface. Ultrathin  $\text{Al}_2\text{O}_3$  films (9 Å thick), however, inhibited SEI formation without blocking the electrode surface.

Considering the superior performance for the 1 nm  $\text{Al}_2\text{O}_3$ -coated  $\text{TiO}_2$  nanotube layer at 1C, cycling tests at faster kinetics have been explored to study the rate capability of this coating in more detail. As shown in Figure 2f, the discharge capacities of the first reversible cycle were  $\sim 295$ ,  $\sim 158$ ,  $\sim 84$ ,  $\sim 65$ , and  $\sim 59 \mu\text{Ah}/\text{cm}^2$  for C/5, 1C, 2C, 3C, and 5C, respectively. As expected, the areal capacity decreased with an increased C rate due to the higher applied current density. Figure 2g shows the galvanostatic discharge/charge curves of the first reversible cycle of the uncoated and the 1 and 2 nm ALD  $\text{Al}_2\text{O}_3$ -coated  $\text{TiO}_2$  nanotube layer at 0.2C. As can be seen, the theoretical gravimetric capacity was just reached in the case of the 1 nm ALD  $\text{Al}_2\text{O}_3$ -coated  $\text{TiO}_2$  nanotube layer, taking accuracy of the porosity calculation into account. It can be pointed out that these high capacity values obtained for the 1 nm ALD  $\text{Al}_2\text{O}_3$ -coated  $\text{TiO}_2$  nanotube layer were only obtained by the uncoated  $\text{TiO}_2$  nanotube layers at very slow kinetics (C/10).

The coulombic efficiencies (CEs) for the first charge/discharge cycles for the uncoated and 1 nm ALD  $\text{Al}_2\text{O}_3$ -coated  $\text{TiO}_2$  nanotube layers are given in Table 1. As expected, the CE for the uncoated  $\text{TiO}_2$  nanotube layer was very high from the first charge/discharge cycle. The CE of the 1 nm ALD  $\text{Al}_2\text{O}_3$ -coated  $\text{TiO}_2$  nanotube layer, however, is comparably lower during the first 10 cycles. This is probably due to the formation of the Li–Al–O phase during the first charge/discharge cycles.

Figure 3a depicts the discharge capacities of the uncoated  $\text{TiO}_2$  nanotube layer and the 1 nm  $\text{Al}_2\text{O}_3$ -coated  $\text{TiO}_2$  nanotube layer for the 100 charge/discharge cycles at 1C.

**Table 1. CEs for the First Charge/Discharge Cycles for the Uncoated and 1 nm ALD  $\text{Al}_2\text{O}_3$ -Coated  $\text{TiO}_2$  Nanotube Layers**

charge/discharge cycle no.	CE of the uncoated $\text{TiO}_2$ nanotube layer (%)	CE of the 1 nm ALD $\text{Al}_2\text{O}_3$ -coated $\text{TiO}_2$ nanotube layer (%)
1	92.2	73.2
2	98.85	93.03
3	98.35	93.80
5	99.05	95.67
10	99.13	97.54

After an initial decrease of the capacity during the initial discharge cycle, more than 2 times higher capacity was attained for the 1 nm  $\text{Al}_2\text{O}_3$ -coated  $\text{TiO}_2$  nanotube layer compared to that of the reference. However, a very slight decrease of the discharge capacity could be seen for the uncoated nanotube layer, whereas for the 1 nm  $\text{Al}_2\text{O}_3$ -coated  $\text{TiO}_2$  nanotube layer, an increase of the discharge capacity was clearly visible during the first cycles. This increase might be explained with an increase in conductivity of the  $\text{Al}_2\text{O}_3$  coating during the electrochemical cycling, as explained above. All in all, the 2-fold difference was preserved even after extensive cycling.

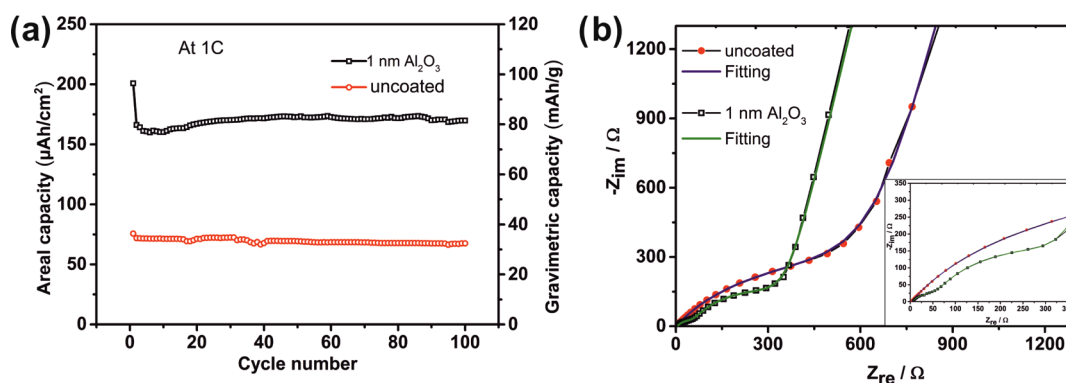
EIS measurements were performed to further elucidate the effect of the  $\text{Al}_2\text{O}_3$  coatings on  $\text{TiO}_2$  nanotube layers. Figure 3b shows the overlaid impedance spectra of both samples and their fittings at OCP. The figure demonstrates the excellent agreement between the experimental and fit data. The equivalent circuit for the EIS spectra of the uncoated  $\text{TiO}_2$  nanotube layer is represented by  $[R_e + R_{CT}/Q_{CT} + Q]$ , shown in Figure 4a, where  $R$  represents resistors and  $Q$  constant phase elements (CPEs).  $R_e$  represents essentially the resistance of the electrolyte. The depressed semicircle at the medium frequency and the sloped line at low frequencies represent the charge-transfer impedance ( $R_{CT}/Q_{CT}$ ) of the lithium intercalation process and the capacitive effect ( $Q$ ), respectively. From the fit data of the EIS spectra,  $R_{CT}$  for the uncoated  $\text{TiO}_2$  nanotube layer was 692.2  $\Omega$ .

The EIS spectrum for the  $\text{Al}_2\text{O}_3$ -coated  $\text{TiO}_2$  nanotube layer consists of two semicircles. The first depressed semicircle at high frequency is attributed to the impedance due to the  $\text{Al}_2\text{O}_3$  coating on the nanotube layer<sup>51</sup> and the second semicircle in the medium frequency range to the impedance due to the charge transfer resistance. The equivalent circuit shown in Figure 4b for the 1 nm  $\text{Al}_2\text{O}_3$ -coated  $\text{TiO}_2$  nanotube layer is  $[R_e + R_{\text{Al}_2\text{O}_3}/Q_{\text{Al}_2\text{O}_3} + R_{CT}/Q_{CT} + Q]$ . From the fit data,  $R_{\text{Al}_2\text{O}_3}$  and  $R_{CT}$  were calculated to be 56.07 and 289.1  $\Omega$ , respectively. The exponent for the last CPE was 0.8 for both samples, which suggests largely a capacitive effect. The lower  $R_{CT}$  for the 1 nm ALD  $\text{Al}_2\text{O}_3$ -coated  $\text{TiO}_2$  nanotube layer revealed a positive influence of the  $\text{Al}_2\text{O}_3$  coating in enhancing the electronic conductivity of the  $\text{TiO}_2$  nanotube layer.

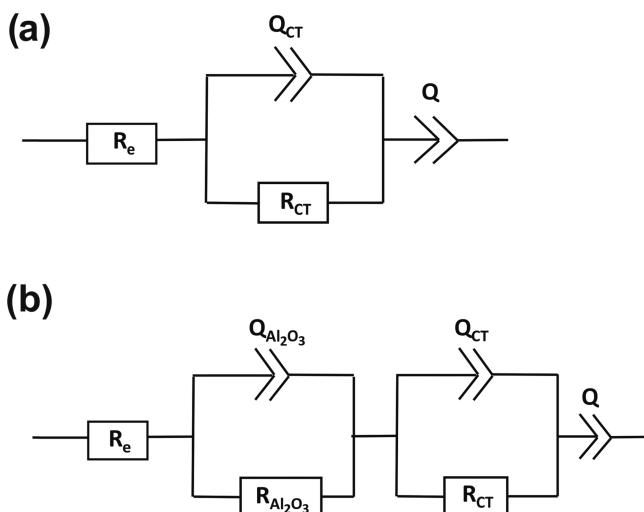
Another advantage of the  $\text{Al}_2\text{O}_3$  coating is that it can also prevent the electrolyte side reactions with  $\text{TiO}_2$  during the charge/discharge process, thereby suppressing any passivation layer on the surface of the  $\text{TiO}_2$  nanotube layer.

## CONCLUSIONS

In summary, it was demonstrated that the ALD coating of the  $\text{TiO}_2$  nanotube layers, with thin layers ( $\leq 1$  nm) of  $\text{Al}_2\text{O}_3$ , have a beneficial effect on the areal capacity and cycling behavior of the  $\text{TiO}_2$  nanotube layers. This is due to an increased



**Figure 3.** Discharge capacity as a function of the discharge cycle number of the cells at 1C rate (a) and Nyquist plots (at OCP vs  $\text{Li/Li}^+$ ) (b) for the uncoated and 1 nm ALD  $\text{Al}_2\text{O}_3$ -coated  $\text{TiO}_2$  nanotube layers. The inset in (b) shows a higher magnification of the first semicircle.



**Figure 4.** Equivalent circuits for the EIS plots of the (a) uncoated and (b) 1 nm ALD  $\text{Al}_2\text{O}_3$ -coated  $\text{TiO}_2$  nanotube layers.

mechanical stability of the nanotube layers upon  $\text{Al}_2\text{O}_3$  coating and a better diffusion of the  $\text{Li}^+$  ions within the  $\text{Al}_2\text{O}_3$ -coated  $\text{TiO}_2$  nanotube layers. On the other hand,  $\text{Al}_2\text{O}_3$  coatings with thickness  $>2$  nm show a reduced capacity. The approach presented in this work is important for future applications of the  $\text{TiO}_2$  nanotube layers, where a thin and highly conformal coating of the secondary material can significantly enhance the performance of the  $\text{TiO}_2$  nanotube layers and explore these composite nanotube layers for new applications, previously unfeasible for the uncoated (bare)  $\text{TiO}_2$  nanotube layers.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00463.

Postcycling SEM images; chronoamperometric plots (PDF)

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## Notes

The authors declare no competing financial interest.

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