



# On the electrophoretic and sol–gel deposition of active materials on aluminium rod current collectors for three-dimensional Li-ion micro-batteries



Gabriel Oltean\*, Mario Valvo, Leif Nyholm, Kristina Edström

Uppsala University, Department of Chemistry – Ångström Laboratory, Box 538, 75121 Uppsala, Sweden

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## ABSTRACT

Electrophoretic deposition of titanium oxide particles, as well as sol–gel synthesis of thin films of TiO<sub>2</sub> employing a titanium isopropoxide precursor solution, were studied as possible deposition routes for the coating of aluminium pillar current collectors intended for three-dimensional Li-ion micro-batteries. While electrophoresis of TiO<sub>2</sub> particles was homogeneously covering the two-dimensional aluminium substrates, it was difficult to conformally coat the three-dimensional current collectors with this technique. The sol–gel approach, on the other hand, gave rise to thin and amorphous TiO<sub>2</sub> layers on the Al rod based current collectors. The latter could be cycled for 100 cycles indicating that such straightforward sol–gel approaches may be used for the manufacturing of 3D electrodes for Li-ion micro-batteries.

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## 1. Introduction

The development within the microelectronics industry is advancing at a very rapid pace. Micro–electromechanical systems, such as sensors and actuators, are readily available in small sizes, in the range of square millimetres. In 2004, Long et al. [1] identified the rapid advancements in the miniaturisation of microelectronic devices as compared to the relative slow down-scaling of batteries as a major problem and proposed that batteries should rely on a three dimensional (3D) rather than a two dimensional (2D) architecture in order to enable autonomous powering of such small microelectronic devices. Lithium-ion batteries are perfect candidates for three dimensional cell architectures, as they possess the highest energy and power densities among commercially available rechargeable battery systems. The research within 3D Li-ion batteries is at present mainly focused on the coating of active materials (negative or positive) onto three-dimensional current collectors, as well as on the deposition of polymer electrolytes on the resulting electrodes [2–15]. The main techniques that have been employed to manufacture these three-dimensional electrodes so far include: electrodeposition [2–6,9–11,16], anisotropic etching [17], lithography [18], sol–gel synthesis [19,20], atomic layer deposition [7], spray coating [8] and a floating catalyst method followed by chemical reduction [14,15].

Despite these achievements, only a few complete 3D Li-ion batteries have been described so far [16,18–20]. Pikul and co-workers [16]

presented a structure containing NiSn alloy and MnO<sub>2</sub> electrodeposited in the pores of nickel foams. The nickel foams were deposited on an interdigitated array substrate by an inverse opal method. Although the battery showed a very good power capability, the energy density of the cell was rather low (i.e., 2.5 μWh cm<sup>−2</sup> μm<sup>−1</sup> at a 0.5 C rate). Min et al. [18] constructed a battery consisting of interdigitated arrays of carbon and dodecylbenzenesulfonate-doped polypyrrole posts. The cycling of the cell was, however, terminated after merely three cycles, most likely due to an electrical short circuit between the anode and cathode arrays. Kotobuki and co-workers [19] reported the injection of LiCoO<sub>2</sub> (used as the cathode material) and Li<sub>4</sub>Mn<sub>5</sub>O<sub>12</sub> (used as the anode material) into the voids of a Li<sub>0.35</sub>La<sub>0.55</sub>TiO<sub>3</sub> (LLT) honeycomb structure. The low discharge capacity of this cell, which was 7.3 μAh cm<sup>−2</sup>, was likely due to the long lithium diffusion paths within the micrometre large holes and the low ionic conductivity of the LLT structure. Finally, Ergang et al. [20] coated a three dimensionally ordered porous carbon anode with a polymer and filled the rest of the space with a V<sub>2</sub>O<sub>5</sub> gel cathode. This cell, however, lost its capacity after ten cycles, an effect that was ascribed to the poor electronic conductivity of the V<sub>2</sub>O<sub>5</sub> gel electrode.

Electrochemical methods are well suited for the deposition of electrode materials, as these techniques are relatively straightforward and cost effective. Edström et al. [21] thus showed that electrodeposition is a suitable technique for the fabrication of three dimensional current collectors, as well as subsequent deposition of layers of materials for 3D Li-ion cells. Within this field, the electrochemical syntheses of 3D copper current collectors [2] and 3D aluminium current collectors [22, 23] were the first studied topics. Taberna et al. [2] also investigated

\* Corresponding author. Tel.: +46 184713773; fax: +46 18513548.  
E-mail address: [gabriel.oltean@kemi.uu.se](mailto:gabriel.oltean@kemi.uu.se) (G. Oltean).

the electrodeposition of Fe<sub>3</sub>O<sub>4</sub> on 3D copper current collectors, whereas the electrodeposition of NiSn alloy [3], Bi [4], Sn [5] and Sb [6] on the same type of 3D current collector was reported subsequently. We are, however, not aware of any previous reports on the electrodeposition of active materials on aluminium pillars. Only a few depositions of active materials on 3D aluminium current collectors have in fact been reported based on the use of atomic layer deposition of TiO<sub>2</sub> [7] and spray coating of LiCoO<sub>2</sub> [8], respectively. There is consequently a need for further evaluation of methods that straightforwardly may be used for the deposition of active materials on aluminium current collectors.

Titanium dioxide is an inexpensive, abundant and non-toxic material that can intercalate lithium ions and offers improved safety as compared to graphite, since TiO<sub>2</sub> operates at a higher potential. This material also exhibits structural stability over many charge–discharge cycles and the most intensively used polymorph of titania in Li storage is anatase. The electrochemical reaction that takes place upon its discharge and charge is:



For bulk anatase, it has been shown that the maximum amount of lithium ions that can be reversibly inserted is 0.5 Li<sup>+</sup> per formula unit [24–27]. Nevertheless, it was demonstrated that by nano-texturing the anatase particles, the cycling performance of TiO<sub>2</sub> electrodes could be improved [27] and that by reducing the size of the particles below 20 nm, the amount of lithium ions that may be inserted could be further increased to about 0.8 Li<sup>+</sup> per formula unit [28]. Titanium dioxide in the form of thin films can be synthesized for use in Li-ion batteries by a number of techniques including atomic layer deposition [7], electrochemical deposition [29], sol–gel synthesis [30] and anodisation of titanium foils [31]. As a result of this, titanium oxide should be a good model compound when evaluating different methods for the deposition of active materials on aluminium current collectors.

Electrophoretic deposition is an electrochemical technique that offers advantages compared to conventional electrodeposition since it enables the deposition of non-conductive particles from a solution. It should, however, be pointed out that electrophoretic deposition may in fact be regarded as an electrodeposition process in which charged particles (e.g. non-conductive materials) migrate towards one of the electrodes to form a deposit there under the influence of an applied electric field. Charged particles dispersed in a colloidal suspension can hence be deposited in this direct and simple way [32]. The electrophoretic deposition of titanium dioxide particles has been studied for the manufacturing of films with controlled thickness for ceramic coatings [33–35] and for use in dye sensitized solar cells [36–38]. In the above-mentioned reports, the titanium dioxide particles were deposited electrophoretically on carbon fibres, stainless steel, titanium and conductive glass substrates, respectively. The use of electrophoretic deposition for the manufacturing of 3D electrodes for Li-ion micro-batteries has, however, not yet been investigated. Although electrophoresis is relatively simple and effective for depositions on two-dimensional substrates, the complex 3D morphology of the aluminium rods could, however, complicate the deposition process.

Sol–gel synthesis, which is another straightforward and versatile technique, has likewise been extensively used in the preparation of electrode materials for Li-ion batteries [39,40]. Different sol–gel routes based on a titanium isopropoxide precursor have thus been utilised for the synthesis of titanium dioxide for applications including electroluminescent devices [41], photocatalytic devices [42], solar cells [43, 44] and Li-ion batteries [45–47]. The sol–gel deposition of TiO<sub>2</sub> using titanium isopropoxide as precursor may, for example, provide an approach to conveniently obtain a conformal TiO<sub>2</sub> coating on high aspect ratio aluminium rods.

In the present work, the deposition of TiO<sub>2</sub> particles on planar and 3D aluminium current collectors, using both electrophoresis and sol–

gel synthesis techniques, is investigated with the scope of investigating the suitability of these methods with respect to a straightforward and cost-effective coating of active materials on aluminium rod current collectors for three dimensional Li-ion micro-batteries.

## 2. Experimental

### 2.1. Materials

TiO<sub>2</sub> anatase (99.7%), Butvar B 98, 1-methyl-2-pyrrolidone (NMP, 99.5%), titanium isopropoxide (titanium diisopropoxide bis(acetylacetonate) 75 wt.% in isopropanol), and dichloromethane were purchased from Sigma-Aldrich. 1-Ethyl-3-methyl imidazolium chloride (EMICl, >99%) and aluminium chloride (AlCl<sub>3</sub>, 99.999%, anhydrous) were acquired from Alfa Aesar whereas polycarbonate membranes (Cyclopore, 20 μm thick, 1 and 2 μm pore diameters) and glass fibre separators (260 μm thick) were obtained from Whatman. TiO<sub>2</sub> P25 was purchased from Degussa, lithium perchlorate (LiClO<sub>4</sub>) from GFS, propylene carbonate (Puro-lite) from Ferro, ethanol (99.5%) from Solveco and aluminium plates (99.999%) from Goodfellow. Phospholan PE 169 was kindly provided by Akzo Nobel. All chemicals were used as received, without any further purification.

### 2.2. Electrodeposition

Three-dimensional aluminium current collectors were obtained by galvanostatic electrodeposition within an argon filled glove-box (O<sub>2</sub> and H<sub>2</sub>O < 2 ppm) using a previously described approach [22]. In this configuration, a commercial porous polycarbonate (PC) membrane (Cyclopore, Whatman) and a glass fibre separator (Whatman) were sandwiched between two 1 cm<sup>2</sup> aluminium plates. This arrangement was then clamped between two teflon plates with the aid of stainless steel clamps and subsequently immersed in an ionic liquid electrolyte (EMICl/AlCl<sub>3</sub> 1:2 molar ratio). The galvanostatic deposition was performed using a pulsed current protocol described earlier [23]. After the deposition, the PC membrane was dissolved in dichloromethane for 10 min at room temperature to obtain the resulting three-dimensional aluminium current collector.

### 2.3. Electrophoresis

The electrophoretic deposition experiments were carried out using an ethanol based electrolyte containing titanium dioxide nano-particles, PE169 as a dispersant and Butvar as a binder, respectively. Two different types of TiO<sub>2</sub> particles were used: P25 (containing 80% anatase and 20% rutile) and pure anatase, respectively. The titania (2 g of P25 or 0.665 g of anatase), dispersant (250 μL) and binder (0.11 g) were added in this order to 50 mL of ethanol and the solution was then stirred for at least 2 h. The solution was then sonicated for 20 min and used straight away for the electrophoretic depositions. The latter was performed by means of a power supply (Delta Elektronika, SM 3004-D) providing the necessary voltage, with a planar aluminium electrode or an aluminium 3D current collector as the working electrode (cathode) and a stainless steel plate as the counter electrode. The applied voltage between the two electrodes was set to 10 V for the suspensions containing P25 particles and 50 V for the ones containing pure anatase particles, respectively. In both cases, the time of electrophoresis was varied between 60 and 120 s.

### 2.4. Sol–gel

The sol–gel route involved impregnation of the aluminium substrates with a titanium precursor solution in a controlled atmosphere. In this case, the titanium dioxide deposit was obtained using a 0.1 M solution of titanium isopropoxide in NMP. Different volumes of this precursor solution (10 and 15 μL) were placed onto

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