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Galvanostatic electrodeposition of aluminium nano-rods for Li-ion three-dimensional micro-battery current collectors

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ABSTRACT

Constant current and pulsed current electrodeposition of aluminium nano-rods, for use as threedimensional (3D) Li-ion micro-battery current collectors, have been studied using an ionic liquid electrolyte (1-ethyl-3-methylimidazolium chloride/aluminium chloride) and a template consisting of a commercial alumina membrane. It is shown that the homogeneity of the height of the rods can be improved significantly by inclusion of a short (i.e. 50 ms) potential pulse prior to the controlled current deposition step. The latter potential step increased the number of aluminium nuclei on the aluminium substrate and the best results were obtained for a potential of -0.9 V vs. Al/Al³⁺. The obtained nanostructured surfaces, which were characterized using electron microscopy and X-ray diffraction, consisted of parallel aligned aluminium nano-rods homogeneously distributed over the entire surface of the substrate. A narrower height distribution for the rods was obtained using a pulsed galvanostatic approach then when using a constant current, most likely due to the less favourable diffusion conditions in the latter case. The results also indicate that depletion and iR drop effects within the nano-pores result in a more homogeneous height distribution. It is concluded that the height distribution of the nano-rods is controlled by a combination of the nucleation probability in each pore at the start of the experiment, and the homogeneity of the diameters of the pores within the commercial alumina membranes employed as the electrodeposition template.

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1. Introduction

The advances that have been made in the field of miniaturization of electronics have far outpaced the corresponding development within the battery field. Today's thin film Li-ion battery technology can consequently not provide the power per footprint area required by devices such as micro-electrochemical systems (MEMS), sensors, actuators and in vivo medical devices. Long et al. [1] have shown that in order to have enough energy and power density to supply the latter devices, the Li-ion battery technology has to move from two-dimensional to three-dimensional (3D) systems. The latter type of systems can provide higher energy and power densities per footprint area, larger contact areas between the current collector and the active material, and larger power capabilities (if the active material can be deposited as sufficiently thin layers on the current collectors) than the corresponding two-dimensional devices. There is therefore a great interest in the manufacturing of three-dimensional Li-ion batteries [1-4].

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As discussed by Long et al. [1], several approaches can be employed in the development of three-dimensional microbatteries, including the use of interdigitated cylindrical anodes and cathodes, interdigitated plate arrays of anodes and cathodes, and aperiodic or "sponge-like" architectures. The interdigitated architectures are generally considered to be more straightforward to manufacture, although a sequential layer by layer deposition needs to be carried out to achieve the final three-dimensional micro-battery. Most of the work up to now has, however, been focused on the development of three-dimensional anodes and cathodes rather than complete devices. Golodnitsky et al. [5] used a perforated silicon or glass substrate on which a nickel current collector and molybdenum oxysulfide cathodes were deposited. Using a porous alumina template, Taberna et al. [6] electrodeposited vertically aligned copper nano-rods on which Fe₃O₄ was then electrodeposited to yield a three-dimensional anode. Based on the 3D architectured copper current collector approach described by Taberna et al. [6], electrodes based on electrodeposited NiSn alloy [7], Bi [8] and Sn [9] have likewise been investigated. Perre et al. [10] analogously deposited Sb on Cu-rods and could show that a subsequent heat-treatment gave rise to a nanostructured Cu₂Sb electrode which could be cycled for at least 100 cycles. In all of the reports cited above, the obtained 3-dimensional electrodes

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exhibited improved capacity and cycling behaviour when compared to the corresponding thin film electrodes. Recently, Cheah et al. [11] synthesised a vertically aligned current collector composed of aluminium nano-rods, which then was coated with TiO₂ by atomic layer deposition (ALD), thus giving rise to a 3D architectured cathode. An order of magnitude increased discharge capacity was reported compared to the capacity for the corresponding planar electrode. Some attempts of building full 3D micro-batteries have been made, but the obtained prototypes have generally not been very successful [2–4]. Ergang et al. [2] constructed a 3D cell consisting of a three-dimensionally ordered carbon anode and a polymer electrolyte and V₂O₅ ambigel cathode coated inside the pores of the anode. The cell could, however, only be cycled for about 10 cycles before losing all the capacity, probably due to the low electronic conduction of the cathode material. Min et al. [3] constructed an interdigitated cell consisting of a carbon anode and polypyrrole cathode, but short-circuits occurred between the arrays of cathodes and anodes while cycling the battery. Another interdigitated approach was described by Kotobuki et al. [4], in which the holes of a honeycomb structured ceramic electrolyte (Li_{0.35}La_{0.55}TiO₃) were filled with LiCoO₂ and Li₄Mn₅O₁₂ as the cathode and anode materials, respectively. The cycling behaviour of the cell was unfortunately found to be poor, probably due to the large honeycomb holes leading to too long diffusion paths for Li ions.

Although the electrodeposited copper nanostructures obtained by Taberna et al. [6] are well-defined geometrically, such current collectors cannot be used on the cathode side, as the operating voltages of the cathode (~4V vs. Li/Li⁺) would result in oxidation of the copper in contact with the electrolyte. For the latter reason, aluminium is the most commonly used current collector material for cathodes in Li-ion batteries, due to its excellent corrosion resistance. Aluminium in the form of rods, whiskers or wires has been fabricated by electron beam evaporation [12,13], physical vapour deposition [14,15], ultra high vacuum deposition [16], and electrodeposition [17-21]. Pang et al. [17] synthesized aluminium nanowire arrays by electrodeposition of Zn into the pores of an aluminium membrane and a subsequent replacement of Zn in an AlCl₃ solution. Pomfret et al. [18] electrodeposited aluminium into the pores of a polycarbonate template, while Sing et al. [19] electrodeposited aluminium into the pores of an alumina membrane. In the latter two studies, the aluminium rods were, however, not free standing on the silver conductive layers utilized in both cases. Perre et al. [20,21] were the first to study the direct electrodeposition of aluminium nano-rods on an aluminium substrate, using a pulsed potentiostatic technique. Although the obtained aluminium deposit was homogeneous, covering the entire surface of the substrate, the heights of the rods were unfortunately not as uniform as for the corresponding copper nanostructured current collectors described by Taberna et al. [6].

Electrodeposition of aluminium from AlCl₃ has to be carried out in aprotic solvents, as AlCl₃ is not stable in aqueous solutions. Extensive research has been performed on electrodeposition of aluminium from room temperature ionic liquids [22–26], consisting of melts of aluminium chloride and alkylpyridinium or dialkylimidazolium salts. It has been shown that dialkyl-imidazolium chloroaluminate ionic liquids have a more negative cathodic potential limit than the alkylpyridinium counterparts [22,23], making the former more suitable for aluminium electrodeposition.

As it is evident from the reports cited above, electrodeposition is a frequently employed technique for the manufacturing of three-dimensional current collectors for Li-ion micro-batteries. As the electrodeposition generally can be carried out either potentiostatically or galvanostatically, involving either a constant potential or current, or a potential or current varying with time, electrodeposition offers excellent possibilities for control of the properties of the deposited material. The main advantage with the galvanostatic approach is that the rate of the deposition can be precisely controlled, while the control of the deposition potential, which is an important factor determining the morphology of the deposit, naturally, is better in the potentiostatic mode. During the electrodeposition of nano-rods employing an alumina template, there will generally be significant depletion of the solution within the alumina pores. To account for this, pulse deposition approaches have been proposed [6,9-11,20,21] in which re-equilibration or growth pulses were employed in between deposition or nucleation pulses, respectively. While Perre et al. [20,21] and Cheah et al. [11] used a pulsed potentiostatic approach for the deposition of aluminium nano-rods, there has, to the best of our knowledge, not been any publications dealing with the galvanostatic deposition of aluminium nano-rods. There is consequently very little information regarding the influence of the current density, and the use of pulsed vs. constant current conditions, on the homogeneity of aluminium nano-rods electrodeposited within alumina porous templates. In this context, it is particularly interesting to study if the problem with non-homogeneous pillar heights, reported by Perre et al. [20,21] and Cheah et al. [11] can be circumvented employing pulsed galvanostatic conditions in the absence and presence of an initial short nucleation pulse.

In the present work, different galvanostatic approaches have been utilized for the electrodeposition of aluminium on an aluminium substrate through the pores of an alumina membrane using 1-ethyl-3methylimidazolium chloride/aluminium chloride ionic liquid electrolyte. The influence of the use of an initial potentiostatic nucleation pulse, prior to the galvanostatic growth of the aluminium nano-rods, on the homogeneity of the deposit and the height of the aluminium nano-rods will be characterized employing SEM and XRD.

2. Experimental

The experiments, including the preparation of the ionic liquid, were performed in an argon filled glove box (O₂ and $H_2O < 2 ppm$) at room temperature using an Autolab PGSTAT30 potentiostat/galvanostat and a two-electrode setup for the deposition of aluminium nano-rods, consisting of a 1 cm² aluminium plate (Goodfellow 99%) working electrode covered with a porous alumina membrane (Anodisc 13, Whatman), a glass separator and a 1 cm² aluminium plate combined counter and reference electrode. The latter items were all stacked in between two stainless steel clamps and immersed in an ionic liquid electrolyte (1-ethyl-3methylimidazolium chloride/aluminium chloride 1:2 molar ratio). The 1-ethyl-3-methylimidazolium chloride (98.5%, Fluka) and the aluminium chloride (99.99%, Sigma-Aldrich) were used as received and the ionic liquid was prepared by slowly adding the aluminium chloride to the stirred 1-ethyl-3-methylimidazolium (EMIm) chloride. As the reaction is highly exothermic, extra caution needs to be taken in order to avoid decomposition of the ionic liquid. Prior to being used as electrodes, the aluminium plates were treated in an acid bath, consisting of HNO₃ (52.5%), H₃PO₄ (85%) and H₂SO₄ (98%) in the proportion of 5:70:25 (v/v/v), and the plates were subsequently degreased for 15 min in ethanol.

The galvanostatic electrodeposition of the aluminium nano-rods was performed using either a constant current of -1 mA, or a pulsed current sequence involving -5 mA pulses with a duration of 0.2 s separated by 2 s rest periods (i.e. zero current periods) for between 5000 and 7000 cycles. Prior to the deposition, potentiostatic pulses of -0.7, -0.8 and -0.9 V vs. Al/Al³⁺, respectively, were applied for 50 ms to facilitate the aluminium nucleation and growth process. After the galvanostatic electrodeposition experiments were performed, free standing aluminium nano-rods were obtained by



Fig. 1. Low (a) and high (b) magnification SEM micrographs of aluminium nano-rods using a constant current of -1 mA for 9600 s.

dissolving the alumina membrane in a chromic bath, consisting of an aqueous solution of CrO_3 (1.8 wt.%) and H_3PO_4 (6 wt.%), at room temperature during 12 h.

Scanning electron micrographs were obtained by using a Leo 1550 scanning electron microscope, while X-ray diffraction experiments were performed using a Siemens 5000D diffractometer with CuK α radiation.

3. Results and discussion

The commercial alumina membrane used for the template electrodeposition of the aluminium nano-rods had a porosity of 50-65%, with pores having a mean diameter of 200 nm and a length of 60 μ m. The shape of the pores was not uniform with respect to the whole thickness of the membrane. On one side of the membrane, the pores were parallel aligned while on the other side the pores were less ordered. The ordered surface of the membrane was selected to be in contact with the aluminium working electrode.

In Fig. 1, SEM micrographs of the aluminium nano-rods obtained after electrodeposition in the ionic liquid using a constant current of -1 mA for 9600 s are depicted. Prior to the deposition experiment, the surface of the aluminium working electrode was covered by a native oxide layer but since a reduction of aluminium was carried out on this electrode, this oxide layer should have been reduced to aluminium at the start of the deposition. From the low magnification SEM image (Fig. 1a) it can be seen that the deposit covered the surface of the aluminium plate, but the high magnification SEM image (Fig. 1b) clearly shows that the heights of the nano-rods varied over the surface. These results, which are analogous to those previously obtained by Perre et al. [20,21] by pulsed potentiostatic deposition in the same electrolyte, suggest that the rate of electrodeposition of aluminium within the alumina pores differs from pore to pore.

In Fig. 2, the chronopotentiogram for the deposition of aluminium nano-rods depicted in Fig. 1 is presented. As is seen from the graph, the potential initially rapidly attained a value of approximately -0.5 V vs. Al/Al³⁺, a potential compatible with the reduction of Al₂Cl₇⁻ in an ionic liquid consisting of [EMIm]Cl and AlCl₃ in 1:2 molar ratio [25]. After almost 1 h, a sudden drop to about -2.3 V vs. Al/Al³⁺ was observed, followed by a continuous drift to more negative potentials. According to the reduction reaction of Al₂Cl₇⁻ anion (i.e. $4\text{Al}_2\text{Cl}_7 + 3\text{e}^- = \text{Al} + 7 \text{AlCl}_4^-$)[22], there will be an excess of AlCl₄⁻ in the pores of the membrane. The reduction of Al₂Cl₇-[22,23]. The drastic change in the potential after about 1 h can therefore be ascribed to the onset of electrolyte reduction, followed by reduction of AlCl₄⁻, once the diffusion rate of Al₂Cl₇⁻ into the pores becomes insufficient to maintain the imposed current.

As is seen in Fig. 3, experiments were also carried out under pulsed galvanostatic conditions, in which -5 mA deposition pulses with a duration of 200 ms were separated by 2 s long rest periods without any applied current. The rest periods, which mainly were included to allow diffusion of new aluminium species (i.e. Al₂Cl₇anions [20,21]) into the depth of the alumina pores between current pulses, most likely also reduced problems due to the reduction of the EMIm cations of the ionic liquid. The excess of AlCl₄- generated within the pores should render the ionic liquid basic rather than acidic which should impede the deposition of aluminium. A reduction of the EMIm cation could explain the decrease in current efficiency found by Perre [21] when depositing aluminium on a gold coated quartz crystal electrode employing a current density of $-5 \,\mathrm{mA}\,\mathrm{cm}^{-2}$, as well as the black powder within the alumina membrane and cellulose separator obtained by Perre [21] during potentiostatic deposition at -1 V vs. Al/Al³⁺. The latter hypothesis is supported by the fact that the reduction of the EMIm cation in a basic (i.e. AlCl₄⁻ rich) ionic liquid has been reported [22] to take place at about -1 V vs. Al/Al³⁺.

As is seen in Fig. 3c, the deposition into the pores of an alumina membrane using 7000 pulsed current cycles, however, resulted in an inhomogeneous deposit, with the nano-rods growing in an island manner and the aspect of the deposit resembling a "cauliflower". When the experiment was repeated for 5000 (Fig. 3a) and 6000 cycles (Fig. 3b), respectively, it was found that the result in terms of the coverage was worse. The micrograph for the 5000



Fig. 2. Chronopotentiogram recorded for the deposition of aluminium nano-rods employing a constant current of -1 mA for 9600 s.



Fig. 3. SEM micrographs of aluminium nano-rods deposited using -5 mA pulses for 0.2 s and rest periods of 2 s for: (a) 5000, (b) 6000 and (c) 7000 cycles, respectively.

cycle deposition (see Fig. 3a) clearly shows some Al islands on specific spots of the aluminium substrate, but a very low overall degree of coverage. After 6000 cycles, more islands have been formed and the coverage was consequently higher, while most of the substrate was covered after 7000 cycles. However, the islands were still not connected to each other giving rise to an inhomogeneous deposit of nano-rods. This result is in good agreement with the previous potentiostatic result obtained by Perre et al. [20] and Cheah et al. [11], featuring aluminium nano-rods of uneven heights. The latter authors proposed that the problem was coupled to either the nucleation process on the aluminium substrate or to the inhomogeneous distribution of pores in the commercial alumina membranes employed.

To further investigate the nucleation hypothesis, experiments, in which a short (i.e. 50 ms) potentiostatic nucleation pulse was used prior to the pulsed galvanostatic deposition, were carried out. It is well known that the number of nuclei on an electrode surface increases with increasing overpotential [27] and for this reason short voltage pulses of -0.7, -0.8 and -0.9 V vs. Al³⁺/Al, respectively, were employed. Pulses to even more negative potentials were not attempted due to the fact that EMIm cation has been reported to undergo reduction at approximately -1 V vs. Al/Al³⁺ [22]. To verify this onset potential of the reduction of the EMIm cation, cyclic voltammetry experiments were carried out in the ionic liquid. However, as the current was found to be a linear function of the potential between 0 and -1 V vs. Al/Al³⁺, the current was clearly limited by the resistance of the electrolyte, and the onset potential could hence not be determined (analogous voltammograms were incidentally also obtained by Perre et al. [20,21]).

The low sampling rate required with the long deposition times in the pulsed galvanostatic deposition (including pulses of -5 mA and 0 mA, respectively) made it very difficult to monitor the potential during each deposition cycle. It was, nevertheless, found that the potential varied between approximately -2 and 0 V vs. Al/Al³⁺ throughout the deposition, indicating that the same deposition potential was reached during all cycles when using the rest current periods. This is in contrast to the situation during the constant current deposition, since the latter should be significantly affected by depletion effects within the pores, whose magnitude should increase with increasing deposition time.



Fig. 5. High magnification SEM micrograph of aluminium nano-rods deposited using -5 mA pulses for 0.2 s and rest periods of 2 s for 7000 cycles with an initial 50 ms nucleation potential step to -0.9 V vs. Al/Al³⁺.

In the pulsed galvanostatic experiments, the length of the nucleation pulses was set as short as 50 ms to minimise the influence of any decomposition of the electrolyte. It should also be pointed out that the nucleation pulse was only used once, before the start of the pulsed galvanostatic deposition, as the purpose of this pulse was to generate nuclei which then should grow under controlled current conditions. The present approach is therefore significantly different from the approach utilized by Perre et al. [20,21] and Cheah et al. [11], who employed one nucleation pulse within each cycle of their pulsed potentiostatic deposition. In Fig. 4 it is clearly seen that the coverage of the substrate was improved when the nucleation potential was made more negative. With a nucleation of -0.9 V vs. Al/Al³⁺, a good homogeneity of the nano-pillar deposit was thus obtained (Fig. 4c). The latter is even more clearly seen in Fig. 5, depicting a high magnification SEM micrograph of the deposit obtained with an initial voltage of -0.9 V vs. Al/Al³⁺.

As the influence of the nucleation pulse should be most clearly seen early in the deposition process, the pulsed galvanostatic deposition was also carried out with a smaller number of cycles (i.e. 5000



Fig. 4. SEM micrographs of aluminium nano-rods deposited using -5 mA pulses for 0.2 s and rest periods of 2 s for 7000 cycles with 50 ms initial nucleation potential step to: (a) -0.7, (b) -0.8 and (c) -0.9 V vs. Al/Al³⁺, respectively.



Fig. 6. SEM micrographs of aluminium nano-rods deposited using -5 mA pulses for 0.2 s and rest periods of 2 s for 5000 cycles with an initial 50 ms nucleation potential step to -0.9 V vs. Al/Al³⁺.



Fig. 7. X-ray diffraction patterns for (a) the aluminium substrate and (b) the aluminium nano-rods on the aluminium substrate.

cycles). From a comparison of the low magnification SEM micrograph seen in Fig. 6a and the micrograph in Fig. 3a, it is clearly seen that the coverage was good in the presence of the nucleation pulse and poor in its absence. A closer look at the high-resolution micrographs in Figs. 5 and 6b, however, still indicates that the heights of the nano-rods differed within the deposit. The fact that the height distribution was narrower after 7000 cycles than after 5000 cycles suggests that the deposition process involved an inherent levellingout effect. We ascribe this to the formation of AlCl₄⁻ within the electroactive pores, as discussed above. This suggests that an even narrower rods height distribution could be obtained if a higher number of pulses were used. However, when depositions involving more than 7000 cycles were attempted, it became evident that the nano-rods grew so tall (i.e. around $8 \mu m$) that they collapsed under their own weight. The latter problem can possibly be circumvented employing alumina membranes with larger pore diameters (the larger the diameter, the higher the rods can be grown) and larger distances between the pores (the larger the pitch between the rods, the more space for further deposition of material), but such membranes are unfortunately not readily commercially available. It is also highly likely that even better nano-rods deposits can be deposited employing more well-defined alumina membranes. The commercially available membranes are generally not as welldefined geometrically as the membranes manufactured in house, although the commercial membranes are more straightforward to use.

The nano-rods were also studied by X-ray diffraction to confirm that the nano-rods were indeed made of aluminium and to determine the preferred growth orientation. As is seen from the X-ray diffractogram in Fig. 7a, the aluminium substrate exhibited a strong (200) orientation, while the orientation for the nano-rods coated substrate (see diffractogram in Fig. 7b) was less straightforward to determine. As the height of the nano-rods was around 6μ m, there was a significant contribution also from the substrate in the diffractogram. Nevertheless, by comparing the relative intensities of the peaks corresponding to the (200) and (111) planes for the aluminium substrate and the aluminium nano-rods, it can be concluded that for the aluminium nano-rods, the contribution of the peak corresponding to the (111) plane is about seven times stronger than for the aluminium substrate itself. This indicates that the aluminium nano-rods grow with a preferred (111) orientation, in good agreement with previous results [15,17].

4. Conclusions

Constant current and pulsed galvanostatic deposition of aluminium nano-rods through the pores of a commercial alumina membrane employing a 1-ethyl-3-methylimidazolium chloride/aluminium chloride ionic liquid has been studied. It has been shown that the homogeneity of the deposits, which were characterized by SEM and XRD, can be improved significantly by the inclusion of a short (i.e. 50 ms long) initial potentiostatic nucleation pulse prior to the galvanostatic deposition. Constant current deposition resulted in a homogeneous deposit, but with uneven heights of the nano-rods. In the absence of the nucleation pulse, the pulsed current deposition resulted in an inhomogeneous deposit of the aluminium nano-rods, with islands of nano-rods forming on different parts of the substrate. The size of the island could be increased by extending the deposition time, but the nano-rods did still not cover the entire surface of the substrate even after 7000 deposition cycles. This problem was circumvented by nucleation potential pulse prior to the deposition, as this pulse increased the

number of the initial nucleation sites on the surface of the aluminium substrate. With a nucleation potential of $-0.9 V \text{ vs. Al/Al}^{3+}$, a homogeneous deposit of aluminium nano-rods on the surface of the substrate was found both for longer (7000 cycles) and shorter (5000 cycles) deposition times. For longer deposition times, the heights of the nano-rods were not perfectly even, but the distribution of heights was found to be significantly more uniform than for the deposits obtained with the constant current technique. Finally, it was demonstrated by x-ray diffraction that the aluminium nano-rods exhibited a (111) preferred growth direction. It is concluded that the present nano-rods should be well-suited for use as current collectors in three-dimensional Li-ion microbatteries.

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