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Superior Electrochemical Performance of Electropolymerized Self-Organized TiO2 Nanotubes Fabricated by Anodization of Ti Grid

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Author contribution statement

VA S performed experiments, analyzed the experimental results and wrote the manuscript. VA S, AG, APK, FV and TD discussed experimental results. FV and TD supervised the works. All the authors contributed to the reading of paper and gave advice on the revision of the manuscript.

Keywords

Anode, microbatteries, polymer electrolyte, Ti grid, TiO 2 nanotubes

Abstract

Word count: 136

Self-organized TiO2 nanotubes grown on Ti grid acting as anode for Li-ion microbatteries were prepared via an electrochemical anodization. By tuning the anodization time, the morphology and length of the nanotubes were investigated by scanning electron microscope. When the anodization time reached 1.5 h, the TiO2nts/Ti grid anode showed a well-defined nanotubes, which are stable, well adherent -90 nm with a length of 1.88 µm. Due to their high surface utilization, surface area and material loading per unit area, TiO2nts /Ti grid anode using polymer electrolyte exhibited a high areal capacity of 376 µAh cm-2 at C/10 rate and a stable discharge plateau at 1.8 V without using a polymer binder and conductive additive. The storage capacity of the TiO2nts/Ti grid after 10 cycles is fifteen times higher compared to previous reports using planar Ti foils.

Contribution to the field

Dear Professor Galstyan In this work, we report thefabrication of self-organized TiO2 nanotubes grown on Ti grid by anodization. By tuning the anodization time, well-defined nanotubes could be obtained, which are stable and well adherent. Due to their high surface utilization, surface area and material loading per unit area, TiO2nts /Ti grid anode using polymer electrolyte exhibited a high areal capacity of 376 µAh cm-2 at C/10 rate and a stable discharge plateau at 1.8 V without using a polymer binder and conductive additive. More remakbaly, the storage capacity of the TiO2nts/Ti grid after 10 cycles is fifteen times higher compared to previous reports using planar Ti foils. >considering the outstanding performance, we believe that the results could attract the interest of the scientists interested in the development of Li-ion batteries and we hope you can consider the mansucript for potential publication in Frontiers in Physics.

Ethics statements

Studies involving animal subjects Generated Statement: No animal studies are presented in this manuscript.

Studies involving human subjects

Generated Statement: No human studies are presented in this manuscript.

Inclusion of identifiable human data

Generated Statement: No potentially identifiable human images or data is presented in this study.

Data availability statement

Generated Statement: The datasets generated for this study are available on request to the corresponding author.



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- 15
- 16 Abstract

17	Self-organized TiO ₂ nanotubes grown on Ti grid acting as anode for Li-ion microbatteries were
18	prepared via an electrochemical anodization. By tuning the anodization time, the morphology and
19	length of the nanotubes were investigated by scanning electron microscope. When the anodization time
20	reached 1.5 h, the TiO2nts/Ti grid anode showed a well-defined nanotubes, which are stable, well
21	adherent ~90 nm with a length of $1.9 \pm 0.1 \ \mu$ m. Due to their high surface utilization, surface area and
22	material loading per unit area, TiO2nts /Ti grid anode using polymer electrolyte exhibited a high areal
23	capacity of 376 μ Ah cm ⁻² at C/10 rate and a stable discharge plateau at 1.8 V without using a polymer
24	binder and conductive additive. The storage capacity of the TiO2nts/Ti grid after 10 cycles is fifteen
25	times higher compared to previous reports using planar Ti foils.

26 **1. Introduction**

Due to their high energy density, no memory effect and long cycle life, rechargeable Li-ion batteries 27 28 (LIBs) have been extensively used as power sources for many electronic devices [1–4]. More recently, 29 all-solid-state microbatteries have attracted intense attention for powering miniaturized electronics 30 such as wireless sensors and a wide range of applications for the Internet of Things (IoT) [5-8]. 31 Titanium dioxide (TiO_2) is an attractive and versatile material that is used in many technologies due to 32 its unique properties such as high surface area, electronic properties, biocompatibility, and 33 environmental well-being [9,10]. Particularly, synthesis of nanostructured TiO_2 such as nanotubes, 34 nanowires and nanofibers has raised interest lately compared to the conventional microstructures due to their high surface-to-volume ratio [11–13]. The first reports on the formation of self-organized 35 36 nanotubes on titanium by Assefpour-Dezfuly et al. in 1984 [14] where Ti metal was firstly etched in 37 alkaline peroxide, then anodized in chromic acid and later by Zwilling et al. in 1999 [15] reported on 38 the formation of nanoporous anodized TiO₂ nanotubes in a fluoride containing electrolyte. Since then, 39 TiO₂ nanotubes have been extensively explored in various fields, such as photocatalysis [16], 40 sensors [17], dye sensitized solar cells [18] and energy storage device [19].

41 Various approaches, such as sol-gel, hydrothermal treatment, template assisted method, 42 electrospinning and electrochemical anodization have been employed to prepare one-dimensional TiO₂ 43 nanostructures [20]. However, self-organized TiO₂nts formed by anodization method is preferred 44 owing to their simplicity, better control over the nanotube morphology and low-cost [19,21]. Thus, 45 pristine as well as chemically modified TiO₂nts obtained by anodization have been used as negative 46 electrodes for high performance Li-ion batteries [22-24]. Most studies on self-organized TiO₂nts are 47 focused on the planar surface, for instance Ti foil. The utilization of Ti grid as the substrate to 48 synthesize the TiO₂nts has been extensively studied owing to its flexibility and unique geometry 49 [25,26]. Much attentions have been paid on the fabrication of the TiO₂nts on Ti grid as photoanode,

50 possessing an enhanced performance in terms of photon absorption and electron collection efficiency 51 compared to anodized Ti foil [27-29]. Previous studies have shown the use of TiO₂nts /Ti grid in Dye 52 Sensitized Solar Cells (DSSCs) can effectively improve the charge collection efficiency of 53 approximately 3.15% [27]. Liu et al. fabricated vertically oriented TiO₂ nanotube arrays with 54 controllable lengths on Ti grids by electrochemical anodization in ethylene glycol-based electrolyte 55 and investigated their potential application as flexible electrodes for DSSCs [30]. The work reported 56 by Motola et al. showed a high photocatalytic, antimicrobial and antibioflm activities of the TiO_2 57 nanotube layers grown on Ti grid [31,32].

Despite a large number of reports published on the fabrication of self-organized TiO₂nts and their 58 59 applications, the use of TiO2nts /Ti grid as anode material has never been investigated with a polymer 60 electrolyte to achieve the fabrication of all-solid-state microbatteries. To improve the performance of 61 the TiO₂nts anodes for Li-ion microbatteries, self-organized TiO₂nts grown on Ti grid is considered as 62 a great choice owing to its large aspect ratio of length to diameter, higher surface area and high Ti 63 conversion into TiO₂nts [33,34]. Hence, the self-organized TiO₂nts anode provides more easily access 64 for the Li ions, which improves the electrochemical performance of the microbatteries. Herein, we 65 report the fabrication of a liquid-free microbattery using self-organized TiO₂nts/Ti grid filled by an 66 electropolymerized electrolyte. The effect of the anodic oxidation time on the formation of the TiO2nts 67 were investigated by scanning electron microscopy and the electrochemical performances of the 68 electropolymerized TiO₂nts was also studied by cyclic voltammetry and galvanostatic 69 charge/discharge cycling. Compared to planar Ti surfaces (i.e. foil and thin film), we confirm that the 70 discharge capacity values obtained from TiO₂nts supported on a Ti grid are strongly enhanced.

71

73 2. Experimental

2.1. Synthesis of TiO₂ nanotubes 74

75 The TiO₂nts anodes were fabricated by the electrochemical anodization of a titanium grid (Good 76 Fellow 0.57 mm thickness, 0.23 mm wire diameter). Before anodization, the Ti grids were cut to 1.3 x 1.3 cm² in size and cleaned via sonication in acetone, isopropanol and methanol for 10 min each in 77 78 order to remove any surface impurity. After drying the grids with compressed air, TiO₂nts were grown 79 by the anodization of Ti grid in an organic electrolyte containing 96.7 wt. % glycerol, 1.3 wt. % NH₄F 80 and 2 wt. % water [35]. All the anodization experiments were carried out at room temperature in a two-81 electrode system with a Ti grid as a working electrode and platinum (Pt) foil as a counter electrode. 82 The working electrode was pressed against an O-ring of the electrochemical cell leaving approximately 83 0.63 cm² exposed to the electrolyte. The distance between the working and counter electrodes was set 84 to 2 cm and the anodization was performed at room temperature without stirring of the electrolyte 85 during anodization. A constant voltage of 60 V was applied to the two-electrode electrochemical cell 86 using a generator (ISO-TECH IPS-603) for 1, 1.5, 2.5 and 3 h, respectively. After anodization, the 87 samples were dipped in 0.5 vol. % HF solution for 30 seconds in order to remove the residue of the 88 electrolyte, washed with distilled water and dried using compressed air. The as-formed TiO₂nts were 89 annealed at 450 °C in air for 3 h with a heating rate of 5 °C min⁻¹ in order to obtain anatase phase.

90

2.2. Electrochemical polymerization

91 In order to achieve the electrodeposition of PMMA-PEG (poly methyl ether methacrylate-polyethylene 92 glycol) polymer electrolyte, cyclic voltammetry was performed on the TiO_2nts in a three-electrode 93 system using a VersaSTAT 3 potentiostat (Princeton Applied Research), Ag/AgCl as the reference and 94 Pt electrode as the counter electrode in an aqueous solution composed of 0.5 M of 95 bis(trifluoromethanesulfone)imide (LiTFSI) and 0.5 M MMA-PEG (methyl ether methacrylate-

96 polyethylene glycol) with an average molecular weight of 500 g mol⁻¹. Prior to electropolymerization, 97 the aqueous solution containing the polymer electrolyte was purged with Argon gas for 10 min to 98 remove dissolved oxygen. The cyclic voltammetry experiments were carried out for 100 cycles at the 99 scan rate of 10 mV s⁻¹ in the potential window of -0.35 V to -1V vs. Ag/AgCl (saturated) [20,36].

100 **2.3. Characterizations**

101 The crystallinity of the synthesized samples was examined by X-ray diffraction (XRD). The XRD 102 pattern was recorded at room temperature using a Siemens D5000 diffractometer equipped with copper 103 anticathode (Cu K_{α} radiation of 0.1506 nm wavelength was used with graphite monochromator). The 104 diffractogramms were analyzed by comparing with the JCPDS-ICDD database (Joint Committee on 105 Powder Diffraction Standards International Centre for Diffraction Data). The morphology of TiO₂nts 106 was investigated by scanning electron microscopy (SEM) using a Carl Zeiss AG - ULTRA 55 SEM 107 using an electron beam energy of 15 kV. The chronoamperometric test took place in a two-electrode 108 electrochemical cell with Ti grid and Pt foil as a working and counter electrode, respectively, using 109 PARSTAT 2273.

The Swagelok test cells were assembled in an Ar-filled glove box. In the half-cell system, TiO₂nts electrodes were assembled against metallic Li foil using the gel electrolyte of the LiTFSI and MMA-PEG. The Li foil was cut in a circular shape with the diameter of 9 mm and 2 circular sheets (10 mm in diameter) of the gel electrolyte in the Whatman paper were used as separator. The cells were galvanostatically charged and discharged in the potential window of 1 - 3 V vs. Li/Li⁺ at different current densities and cyclic voltammetry was performed at a scan rate of 0.1 mV s⁻¹ using a VMP3 potentiostat-galvanostat (Bio Logic).

117

119 **3. Results and Discussion**

120 In this work, the growth of TiO₂ nanotubes was carried out by a low-cost and simple electrochemical 121 anodization of Ti grid at different anodization time in a glycerol electrolyte containing fluoride ions 122 and small amounts of water. Figure 1a shows the actual size of Ti grid used in the experiments and 123 the inset shows the SEM image of the Ti grid. It can be seen Ti grid consist of many thin and radial Ti 124 filaments which increase the surface area of the substrate. Figure 1b shows the chronoamperometric 125 curve of Ti grid anodized at 60 V for 3 h. As seen, after a minor increase at the beginning of the 126 anodization, the current density dropped with time due to the presence of an electrical barrier formed 127 by the compact oxide layer. The minor increase in current density at the early stage of anodization 128 might be attributed to the exposure of surface area that was not covered with the electrolyte due to the 129 nature of the Ti grid structure. Self-organized TiO₂nts starts to form as the result of the competition 130 between electrochemical oxide formation and chemical dissolution of the oxide layer by fluoride ions 131 according to Equations 1 and 2, respectively. Finally, steady current density was achieved when 132 equilibrium was established between the growth and dissolution of the oxide layers [11].

$$133 \quad Ti + 2 H_2 0 \rightarrow Ti O_2 + 4 H^+ + 4 e^- \tag{1}$$

134
$$TiO_2 + 4H^+ + 6F^- \rightarrow TiF_6^{-2} + 2H_2O$$
 (2)

135

The crystallinity of the TiO₂nts was examined by XRD, as represented in **Figure 1c**. Immediately after growth the TiO₂nts the tubes are amorphous and the formation of the anatase phase is obtained after annealing treatment. The presence of new peaks at about 25.3° and 47.9° correspond to the reflections of anatase phase (JCPDS file no. 21-1272). The Ti peaks observed on the XRD analysis are Ti substrate due to the direct growth of TiO₂nts on the Ti grid. The residual Ti grid is directly used as the current collector.



Figure 1 a) Ti grid (inset: SEM image of Ti grid), b) chronoamperometric curve for the anodized Ti
grid at applied potential of 60 V, and c) XRD patterns of TiO₂nts annealed in air at 450 °C for 3 h.

145

In this work, effects of anodization time on the formation of TiO₂nts arrays have been investigated.
Figure 2a-d illustrates how the morphology and length of the anodized layer evolve with the anodizing
time. The SEM images show the top surface and cross-section morphologies of TiO₂nts anodized at 60
V for different durations of 1, 1.5, 2.5, and 3 h, respectively.



Figure 2 SEM images of TiO₂ nanotube arrays formed by electrochemical anodization of the Ti grid
at 60 V for 1 h (a), 1.5 h (b), 2.5 h, (c), and 3 h (d). Insets show the cross-sectional views.

153

As seen, some changes can be observed with the increasing anodization time. For the shortest duration (1 h), the nanotubes are clearly visible and the length of the nanotubes is ca. $1.75 \pm 0.1 \,\mu\text{m}$ (Figure 2a). However, the nanotube tops are not enough homogenous and smooth to ensure the conformal deposition of the polymer electrolyte. In Figure 2b, the SEM images showed the nanotubes anodized

158 for 1.5 h has an open-top structure without any bundle formation. The anodized Ti grid had 159 comparatively longer and well-defined nanotubes, which are stable, well adherent to the grid substrate 160 with a tube length of $1.9 \pm 0.1 \,\mu$ m. Comparatively, 1.5 h and 1 h anodization does not show any bundle 161 formation, yet, 1 h anodization showed shorter nanotubes than 1.5 h anodization. Indeed the collapse 162 due to over dissolution of the top surface of nanotubes becomes very significant after 1.5 h. As a 163 consequence, a substantial change in the morphology will affect the electrochemical performance of 164 the electrodes. It is also observed that the length of the TiO_2nts varies with the anodization time. The length of the TiO₂nts increases as the anodization time increases from 1 h to 1.5 h, afterwards the length 165 does not continue to increase with longer anodization time. 166

After longer anodization time (2.5 and 3 h), the nanotubes have closed-top structure and the bundled formation is found covering the entire top surface of the nanotubes. The thickness of the nanotubes layer after 2.5 h and 3 h anodization are $1.8 \pm 0.2 \mu m$ and $1.5 \pm 0.2 \mu m$, respectively. Some studies showed that in long-duration anodization experiments, tubes can have inhomogeneous structures due to etching of the top [37]. The bundles on the tube tops might be formed due to the formation of needlelike morphologies as the walls may become too thin to support their own weight [11,38]. This bundle morphology is also described as nanograss or nanospike [39,40].

174 Nevertheless, when the anodization time is decreased, the bundle formation is disappeared. So, an 175 appropriate oxidation time is the essential condition for the fabrication of highly ordered TiO_2 nanotube 176 arrays onto Ti grid. These findings are in good agreement with the previous report. Mor et al. reported 177 that the nanotubes can grow longer by extending the anodization time, however the top of the nanotubes 178 are gradually destroyed after extended anodization. The partial collapse of the nanotubes occurred due 179 to an over dissolution reaction of the tubes top during the prolonged anodization, leading to the 180 formation of bundled nanotubes [41,42]. Also, Zeng et al. reported that TiO₂ nanotubes grown on Ti grid showing a well-defined nanotubular structure after 20 minutes anodization, however the tubes top 181

- 182 become fuzzy after prolonging the anodization time to 40 minutes [25]. Liu et al. [43] investigated the
- 183 effect of the anodization time on the growth of TiO₂ nanotubes onto Ti grid at 60 V for 1-16 h and
- 184 reported that the nanotube arrays grew uniformly after 3 h anodization. Additionally, as seen in Figure
- 185 2, several fissures and bundling on the surfaces of the nanotubes could alsobe attributed to van der
- 186 Waals attraction and capillary forces during drying [11,26,34].
- Indeed, compared to Ti foils substrate, the intertwined structure of the Ti grid had more promising results in terms of surface area. As a result, the electrolyte can penetrate easily to the entire surface of the nanotubes that are radially grown in a 3-D array on the Ti grid [43,44]. Therefore, to further study the electrochemical performance of the self-organized TiO₂nts/Ti grid, the TiO₂nts/Ti grid anodized for 1.5 h was selected to be studied as anode for all-solid-state Li-ion microbatteries using PMMA-PEG polymer electrolyte.

193 After growing the TiO₂nts on Ti grid substrate, the conformal electrodeposition of the electrolyte into 194 nanotubes was achieved by the cyclic voltammetry (CV) technique. This approach is highly valuable 195 to fully exploit the large surface area offered by the nanotubes through the formation of an augmented 196 electrode/electrolyte interface [45–49]. Figure 3 shows the cyclic voltammogram of the 197 electropolymerization of the polymer electrolyte on the TiO₂nts. The window of the applied cathodic 198 potential was selected between the H₂ bubbling and the beginning of the proton reduction (-1 V < E <199 $E(H^+/H_2) = -0.551$ V vs. Ag/AgCl calculated from the Nernst equation) [46]. From cyclic 200 voltammograms (CVs), as seen in Figure 3a, the absolute value of the cathodic current at -1 V vs. 201 Ag/AgCl drops gradually with the increasing of cycles. The fading in the current can be explained by 202 the successive deposition of the thin polymer layers that passivated the TiO₂nts electrode. Additionally, the redox peaks of Ti^{4+}/Ti^{3+} are not observed and it is expected that there is no irreversible change in 203 204 the oxidation states of Ti during the electropolymerization reaction. By using the same 205 electrodeposition technique on the TiO₂nts/Ti foil, Plylahan et. al.[47] reported that after 5 cycles CV,

the growth of a polymer layer occurred inside and outside of each nanotube walls. Indeed, after 10 cycles CV, the inter-tube spaces are filled with the polymer and the nanotube walls become significantly thicker compared to the sample obtained after 5 cycle of CV. After 100 cycles, the polymer fills the inter-tube spaces and coats top surfaces of the TiO₂nts/Ti grid (**Figure 3b**).



Figure 3 a) Cyclic voltammograms of TiO₂nts electrode in 0.5M LiTFSI + 0.5M MMA-PEG500. The curves were recorded in the potential window of -0.35 to -1 V vs. Ag/AgCl (3M) at the scan rate of 10 mV s⁻¹, b) SEM images of the bare TiO₂nts for 1.5 h and electropolymerized TiO₂nts (inset).

214

The CV experiments were performed to investigate the redox potential of TiO_2nts electrodes. The CV curves were recorded at the scan rate of 0.1 mV s⁻¹ between 1 and 3 V vs. Li/Li⁺. **In Figure 4a**, the two curves exhibit well-defined cathodic and anodic peaks at 1.75 and 1.98 V vs. Li/Li⁺, respectively, corresponding to lithium insertion/extraction potentials in anatase TiO₂nts. The Li insertion/extraction process is reversible as seen in the unchanged shape of the CV curves upon cycling. The consecutive decrease in the absolute cathodic current indicates the slight discharge capacity fading upon cycling. **Figure 4b** shows the galvanostatic charge/discharge profiles of the anatase TiO₂nts. The profiles of

222 each sample show flat plateaus of charge at 1.77 V vs. Li/Li⁺ and discharge 1.88 V vs. Li/Li⁺ which



223 are typical profiles for the anatase TiO_2nts .



Figure 4. a) Cyclic voltammogram of anatase phase TiO_2nts recorded at a scan rate of 0.1 mV s⁻¹ in the potential window of 1 V–3 V vs. Li/Li⁺, b) Galvanostatic charge/discharge profiles of the polymercoated TiO₂nts electrode, c) Capacity vs. cycle number of the polymer-coated TiO₂nts electrode and d) Coulombic efficiency (%) the polymer-coated TiO₂nts electrode.



233	cell cycled between 1 and 3 V vs Li/Li ⁺ delivers an average capacity of ~376 μ Ah cm ⁻² at C/10 and
234	~350 μ Ah cm ⁻² at C/5. The initial charge and discharge capacities of the electrodes are 375 μ Ah cm ⁻²
235	and 580 μ Ah cm ⁻² , corresponding to a relatively low initial coulombic efficiency of 64.7%. A large
236	irreversible capacity observed at the first cycles is attributed to the side reaction of Li^+ and the presence
237	of residual water at the surface of TiO2nts and in the polymer electrolyte. Additionally, some Li ions
238	are trapped inside the TiO_2 lattice structure after the first Li^+ insertion, thereby reducing the capacity
239	of the cell [35]. Nevertheless, for the subsequent cycles the capacities can be stabilized, the discharge
240	capacity values recorded in the 2nd and 3rd cycles are 382 and 380 μ Ah cm ⁻² with improved coulombic
241	efficiency of 98.4 % and 98.7%, respectively. The cycling retention continuously enhanced after first
242	cycle and the coulombic efficiency approaches 100%.
243	The electrochemical performances of TiO ₂ nts grown on Ti grid and Ti foil are summarized in Table

1. After 10 cycles, the storage capacity of the TiO₂nts/Ti grid is fifteen times higher compared to our previous report with Ti foils [14]. Calculated using a microbattery voltage of 1.8 V, the obtained areal energy and power density of the TiO₂nts/ Ti grid anode are 677 μ Wh cm⁻² and 67.7 μ W cm⁻², respectively.

Electrodes	Areal Capacity at C/10 rate after 10 cycles (µAh cm ⁻²)	Vcell (V)	Energy density (µWh cm ⁻²)	Power density (µW cm ⁻²)
TiO2nts/ Ti foil [20]	25	1.7	43	4.3
TiO2nts/ Ti grid	376	1.8	677	67.7

248 **Table 1.** Electrochemical performances of the microbatteries using PMMA-PEG polymer electrolyte

249

250

252 **4.** Conclusion

To sum up, Ti grid is used as a 3D substrate to form self-organized TiO₂ nanotubes. The anodization 253 254 time shows a significant influence on the morphological properties of the nanotubes. Well-defined 255 nanotubes without bundle formation with a tube length of 1.9 ± 0.1 µm can be obtained after 1.5 h 256 anodizing a Ti grid. Due to its radial and intertwined structure, Ti grid supplies much larger area than 257 a Ti foil for a same footprint area. Actually, Ti grid showed much higher areal capacity in comparison 258 to Ti foil at the same kinetics (C/10 and C/5). The main reason is because self-supported nanotubes are 259 successfully formed within a very large surface area increasing the amount of the active material and the battery performance. After 10 cycles, the storage capacity of the TiO₂nts/Ti grid is fifteen times 260 261 higher compared to our previous report with Ti foils. 262

263 Author Contribution

VA S performed experiments, analyzed the experimental results and wrote the manuscript. VA S, AG,
 APK, FV and TD discussed experimental results. FV and TD supervised the works. All the authors
 contributed to the reading of paper and gave advice on the revision of the manuscript.

267 Conflict of Interest Statement

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

270

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Figure 3.TIF











