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Tuning three-dimensional TiO₂ nanotube electrode to achieve high utilization of Ti substrate for lithium storage

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Abstract

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Keywords

substrate, three, lithium, dimensional, storage, achieve, tio₂, ti, nanotube, utilization, high, electrode, tuning

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Tuning three-dimensional TiO₂ nanotube electrode to achieve high utilization of Ti substrate for lithium storage

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Abstract

Three-dimensional (3D) TiO₂ nanotube arrays grown on Ti mesh were prepared via the anodization process. The diameters of the Ti and TiO₂/Ti wires and the length of the TiO₂ nanotubes have linear relationships with the anodization processing time. When the anodization processing time is 600 min, the TiO₂/Ti mesh anode materials showed good capacity retention and high specific area capacity, without the need for a current collector or binder, due to their high surface area, high substrate utilization, and large active material loading rate per unit area. At the current density of 50 μA cm⁻², TiO₂/Ti mesh with 600 min anodization processing time has a stable discharge platform at 1.78 V, and the specific area capacity is 1745.5 μAh cm⁻² over 100 cycles. By tuning the geometric parameters of the TiO₂/Ti mesh and the anodization processing time, we can pave the way to finding TiO₂/Ti mesh electrodes for lithium-ion batteries with high capacity per unit area and outstanding mechanical behaviour.

Key words: TiO₂/Ti mesh, anodization, anode materials, lithium-ion batteries

1. Introduction

Rechargeable lithium-ion batteries (LIBs) have been widely used as power sources for portable electronic devices due to their high energy-storage density, high voltage, long cycle life, and operation at ambient temperature [1-3]. Most of the commercial LIBs use graphitic carbon as the anode material. There are safety concerns about this material, however. Graphite electrode is prone to growing lithium dendrites after repetitive charge-discharge, resulting in irreversible damage to the lithium ion battery. Compared to graphite, TiO_2 has a higher lithium intercalation potential (1.75 V vs. Li^+/Li), enabling it to avoid the deposition of metallic lithium, and it has higher capacity for Li^+ intercalation/de-intercalation [4, 5]. These properties make TiO_2 suitable for large-scale energy storage, when coupled with high-voltage cathode materials (LiMn_2O_4 , $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_4$, etc.) [6-9]. Moreover, TiO_2 is non-toxic, low-cost, abundant in nature, and has good electronic properties, as well as stable physical and chemical properties [10, 11].

Nanostructured TiO_2 anodes have been successfully used to improve cycling stability and high rate capability over those of their bulk counterparts. Compared with nanoparticles, nanowires, and nanoribbons, self-organized TiO_2 nanotube arrays possess larger specific surface areas and faster Li^+ transport [12-14]. The traditional TiO_2 nanotube arrays, however, only have a low surface area and a small aspect ratio of length to diameter, because they are grown on Ti foil by electrochemical anodization and the length of TiO_2 nanotube is only around 500 nm, so the traditional TiO_2/Ti foil electrode shows low area capacity [5, 15]. Moreover, the use of Ti foil is expensive and wasteful. Liao et al. reported that only around 2 wt% of the Ti was converted into TiO_2 nanotubes [16]. TiO_2 nanotube array electrode grown on Ti mesh is a good choice to avoid these disadvantages. The TiO_2 nanotubes extend radially in a 3D array on a grid of fine Ti wires, so the TiO_2/Ti mesh electrode has high surface area, a large aspect ratio, and a high Ti conversion rate ($M_{\text{Ti-1}}$ (Ti converted into TiO_2

nanotubes)/ $M_{\text{Ti-O}}$ (Ti mesh substrate)) [17-19]. Meanwhile, the 3D TiO_2 nanotube arrays allow Li^+ to more easily access the TiO_2 surface from the electrolyte [20, 21]. Some reports have shown real benefits from the 3D electrode design, such as in LIBs using Sn/graphene in a 3D multilayer structure and 3D ordered porous Sn-Ni alloy as anode to improve the specific area capacity, conductivity, and cycling stability [22, 23]. The benefits for lithium ion batteries associated with 3D nanotube arrays of TiO_2 grown on Ti mesh, however, have not been studied to date.

Here, TiO_2/Ti mesh as a new type of anode material was prepared by the electrochemical anodization method. TiO_2/Ti mesh can be applied directly as an electrode material in a test cell without the need for a current collector or binder. 3D TiO_2 radial nanotube arrays with different lengths were grown on Ti mesh by controlling the anodization time. The special architecture of the 3D nanotube arrays with large surface area can provide effective contact between the active materials and the electrolyte, and shorten the lithium diffusion length. Moreover, the thin Ti wires at the centre of the nanotubes can maintain good conductivity. In this work, we tested the properties of TiO_2/Ti mesh electrodes with different anodization processing times. When the anodization processing time was 600 min, the investigated TiO_2/Ti mesh electrode possessed both high electrochemical performance and good mechanical behaviour.

2. Experimental

3D TiO_2 nanotube arrays on Ti mesh were prepared following our previous method [24]. A polished piece of Ti mesh ($30 \times 55 \text{ mm}^2$, 100 mesh, 0.1 mm thick, purity 99.5 wt%) was anodized in organic electrolyte consisting of ammonium fluoride (NH_4F , 0.25 wt%) and ethylene glycol (EG; $(\text{HOCH}_2)_2$, 98 vol%; H_2O , 2 vol%). The potential was supplied by a laboratory DC power supply (TPR-6405, LWDQGS). The nanotube length could be

increased by increasing the anodization time of the Ti mesh at 20 V in organic electrolyte. The as-prepared TiO₂/Ti meshes were annealed at 500 °C under ambient air for 3 h to induce TiO₂ crystallization. The TiO₂/Ti meshes were analysed by X-ray diffraction (XRD; GBC MMA) with Cu K α radiation, as well as by field emission scanning electron microscopy (FESEM; JEOL 7500).

The TiO₂/Ti mesh electrodes were cut to 1 × 1 cm² in size and then dried at 80 °C in a vacuum oven for 24 h. CR 2032 coin-type cells were assembled in an Ar-filled glove box (Mbraun, Unilab, Germany), using lithium metal foil as the counter electrode. The electrolyte was 1 M LiPF₆ in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 by volume, provided by MERCK KGaA, Germany). The cells were galvanostatically charged and discharged in the range of 3.0-1.0 V at different current densities using a computer-controlled charger system manufactured by Land Battery Testers. A Biologic VMP-3 electrochemical workstation was used to perform cyclic voltammetry (CV; scanning rate 0.1 mV s⁻¹).

3. Results and discussion

Fig. 1 shows the XRD patterns of the 3D TiO₂ nanotube arrays on Ti mesh prepared by anodization in organic electrolyte over periods ranging from 60 min to 720 min, with the samples designated as TiO₂/Ti-*t* mesh (*t* = 0, 60, 180, 420, 600, 720 min; the different anodization time intervals were used to obtain more comprehensive results and are also mentioned in our previous report) [24]. After annealing at 500 °C, the TiO₂ nanotubes on Ti mesh (JCPDS 44-1294) are mainly anatase phase (JCPDS 21-1272). Some weak peaks related to the rutile phase (JCPDS 44-1276) appear in the XRD patterns of the TiO₂/Ti-*t* mesh samples, but the nanotubes are mostly still composed of anatase phase [16]. Varghese et al. reported that rutile phase mainly existed in the barrier layer underlying the TiO₂ nanotube

arrays [25]. With increasing anodization processing time, the intensity of the rutile phase peaks decreases, while the intensity of the anatase phase peaks increases because the weight percentage of TiO₂ nanotubes is increased.

FESEM images of the anodic TiO₂ nanotubes on the Ti mesh substrates are presented in Fig. 2. Fig. 2 shows that the diameter of the TiO₂/Ti wire increases with prolonged anodization processing time. When the anodization processing time is 60 min, the morphology of the TiO₂/Ti-60min mesh has only slightly changed compared with the Ti mesh, because the additional diameter of the TiO₂/Ti wire is only around 10 μm, while the diameter of the bare Ti wire is 90.2 μm [Fig. 2(a, b)]. With increasing anodization processing time, the TiO₂ nanotube arrays are interspaced with fissures at irregular intervals [Fig. 2(c-f)]. This can be attributed to van der Waals attraction and capillary forces during drying [16-18]. Meanwhile, we can see from the Fig 2(b-f) insets that the TiO₂ nanotube arrays and the Ti wire substrates have been separated at their interfaces due to the stress when the TiO₂/Ti mesh was cut down during the FESEM characterization. From Fig. 2, we can measure the diameters of the Ti and TiO₂/Ti wires and the length of the TiO₂ nanotubes. Fig. 3(a) shows the geometric parameters of the TiO₂/Ti mesh obtained by anodization in organic electrolyte. The diameters of the Ti and TiO₂/Ti wires and the length of the TiO₂ nanotubes have a linear relationship with the anodization processing time [Fig. 3(b)]. The Ti mesh did not react with the organic electrolyte when t was 0 min, so the intercepts for the TiO₂/Ti wire diameter and the Ti wire diameter have the same value (90.2 μm, the diameter of the Ti wire before anodization), and the intercept for the TiO₂ nanotube length is 0. The linear fit results can be written as the following equations

$$D = k_1 \times t + B \quad (1)$$

$$d = -k_2 \times t + B \quad (2)$$

$$h = k_3 \times t \quad (3)$$

where D is the diameter of the TiO₂/Ti wire (μm), d is the diameter of the Ti wire (μm), h is the length of the TiO₂ nanotubes (μm), t is the anodization processing time (min), k_1 , k_2 , k_3 is the growth rate with processing time of the TiO₂/Ti wire diameter, the Ti wire diameter, and the TiO₂ nanotube length, respectively, and B is the TiO₂/Ti wire and Ti wire diameter intercept ($B = 90.2 \mu\text{m}$). From the linear fit results, the absolute values of the slopes have similar values ($|K| \approx 0.08$; $k_1 = 0.081 (\pm 0.007)$, $k_2 = -0.079 (\pm 0.004)$, $k_3 = 0.080 (\pm 0.005)$). Therefore, the relationship between D and d can be written as in the following equation

$$D = |K| \times t + B \quad (4)$$

For the Ti mesh used here, the distance between two adjacent Ti wires ($a_{\text{Ti-Ti}}$) is $257.1 \mu\text{m}$ for Ti mesh. There will be no void regions between two adjacent TiO₂/Ti wires in the TiO₂/Ti mesh when D approaches $257.1 \mu\text{m}$. That is to say, the void regions in the Ti mesh will be fully filled with TiO₂ nanotube arrays, so that the TiO₂/Ti mesh shows the highest specific surface area. Meanwhile, the electrolyte can penetrate to the entire surface of the TiO₂ nanotubes due to the nanotube arrays that are radially grown on the Ti wires [Fig. 3(a, c-e)]. For the TiO₂/Ti mesh samples, however, the TiO₂ nanotube arrays are easily detached from the Ti mesh when t is 720 min, because the length of the TiO₂ nanotubes ($h_{\text{TiO}_2} = 61.4 \mu\text{m}$) is around two times the diameter of the Ti wire ($d_{\text{Ti}} = 30.1 \mu\text{m}$; Fig. 2(f)). The TiO₂/Ti-720min mesh electrode shows poor mechanical behavior. Fig. 2(e) shows that the TiO₂/Ti mesh with 600 min anodization processing has been uniformly covered with TiO₂ nanotubes, and the ratio of $h_{\text{TiO}_2}/d_{\text{Ti}}$ is 1.2 ($h_{\text{TiO}_2} = 50.5 \mu\text{m}$, $d_{\text{Ti}} = 43.6 \mu\text{m}$). The Ti conversion rate can be calculated from the masses of the Ti mesh and the TiO₂/Ti-600min mesh for 1 cm^2 electrode area (18.1 mg and 11.56 mg, respectively). The Ti conversion rate is 22 wt%, much higher than that previously reported (2 wt%) [16]. Therefore, the TiO₂/Ti-600min mesh electrode is

the most promising electrode, as it has high surface area, good mechanical behavior, and a high Ti conversion rate. Furthermore, by controlling the distance between two adjacent Ti wires and controlling the anodization processing time, we can obtain higher surface area and better mechanical behavior in TiO₂/Ti mesh electrode for lithium-ion batteries.

In order to compare TiO₂/Ti mesh electrode prepared over a short time (60 min) and a longer time (600 min), we conducted FESEM using high magnification. FESEM images of anodic TiO₂ nanotubes on the Ti mesh substrates are presented in Fig. 2(b, e), and high magnification FESEM images are presented in Fig. 4(a, b). After the 60 min anodization process, the mesh retained sufficient void regions, and the TiO₂ nanotubes grew perpendicularly to the surface of the Ti wire and covered the entire wire uniformly [Fig. 2(b)]. The Ti wires act as the current collector during LIB testing. The length and inner diameter of the TiO₂ nanotubes are ~4.9 μm and ~100 nm, respectively [Fig. 2(b) and Fig. 4(a)]. The length and inner diameter of the TiO₂ nanotubes are ~50.5 μm and ~100 nm, respectively, when the anodization processing time is 600 min [Fig. 2(e) and Fig. 4(b)].

The TiO₂/Ti-60min mesh electrode and TiO₂/Ti-600min mesh electrode were selected to test their performance in LIBs. Fig. 5(a, b) shows cyclic voltammograms of TiO₂/Ti mesh for the first five cycles at the scan rate of 0.1 mV s⁻¹. In the first cycle, the TiO₂/Ti-60min mesh electrode presents a pair of cathodic/anodic peaks centred at 1.65 V and 2.10 V (vs. Li/Li⁺), corresponding to lithium insertion/extraction into/from the anatase TiO₂ lattice, respectively, while the TiO₂/Ti-600min mesh electrode's cathodic/anodic peaks are centred at 1.55 V and 2.15 V (vs. Li/Li⁺). In the following cycles, however, both the TiO₂/Ti-60min mesh and the TiO₂/Ti-600min mesh electrodes show a single pair of cathodic/anodic peaks at about 1.70 V and 2.05 V (vs. Li/Li⁺), consistent with a two-phase redox reaction of $x\text{Li}^+ + xe^- + \text{TiO}_2 \leftrightarrow \text{Li}_x\text{TiO}_2$ ($x \approx 0.5$) [4, 26]. A similar observation has been previously reported, and it has been ascribed to an activation effect during the initial cycling of the TiO₂ nanotubes [27].

It should be noted that there is a pair of broad and low cathodic/anodic peaks that appear around 1.4 V and 1.6 V (vs. Li/Li⁺) [Fig. 5(a, b)]. These peaks correspond to lithium insertion/extraction into/from the rutile TiO₂ lattice, respectively [1]. These cathodic and anodic peaks are in accordance with the plateaus in the discharge/charge curves. Fig. 5(c, d) displays typical discharge/charge curves for the TiO₂/Ti-60min mesh and TiO₂/Ti-600min mesh electrodes at different current densities from 50 to 1000 μA cm⁻². The TiO₂/Ti-60min mesh electrode starts to show sloping discharge curves from 250 μA cm⁻², whereas the TiO₂/Ti-600min mesh electrode still shows a flat plateau, even at 500 μA cm⁻². Those results suggest that the kinetic properties of the TiO₂/Ti mesh electrode have remained stable with increasing length of the TiO₂ nanotubes.

Fig. 5(e) shows the cycling performances of the TiO₂/Ti-60min mesh and TiO₂/Ti-600min mesh electrodes at 50 μA cm⁻². The TiO₂/Ti-60min mesh electrode shows an initial discharge capacity of 720.9 μA h cm⁻². After the second cycle, the capacity retention remains stable at around 600 μA h cm⁻². After 30 cycles, however, the discharge capacity continuously decreases to 388.9 μA h cm⁻². The capacity retention after 100 cycles is around 54% of the initial discharge capacity. In comparison, the TiO₂/Ti-600min mesh electrode shows great enhancement of the capacity retention. The TiO₂/Ti-600min mesh electrode shows an initial discharge capacity of 2249.9 μA h cm⁻², and after 100 cycles, it was measured to be 1745.5 μA h cm⁻², which is around 78% of the initial discharge capacity. For comparing specific capacity with other reported nanostructured TiO₂ anodes, the specific capacity of the TiO₂/Ti-600min mesh (1 cm⁻²) based on its mass (11.56 mg) was calculated. The initial discharge capacity and the discharge capacity after 100 cycles were 195.3 mAh g⁻¹ and 151.5 mAh g⁻¹, respectively, and the discharge current density was 4.3 mA g⁻¹, similar to other reports in the literature (where the capacity is between 100 mAh g⁻¹ and 170 mAh g⁻¹ after 100 cycles at 20 mA g⁻¹ [1, 2, 4, 12, 28]). Fig. 5(f) shows the specific capacity retention

rate as a function of current density for lithium cells containing the TiO₂/Ti-60min mesh and TiO₂/Ti-600min mesh electrodes. As shown in Fig. 5(f), the specific capacity retention rate of the TiO₂/Ti-600min mesh electrode decreases much more slowly with increasing discharge rate than that of the TiO₂/Ti-60min mesh electrode. Although the 3D TiO₂ nanotube arrays on the Ti mesh are as long as 50.5 μm, the TiO₂/Ti mesh cell always maintains its high area capacity, stable cycling performance, and high rate capability. The cycling stability and rate performance of the TiO₂/Ti-600min mesh electrode could be attributed to the particular geometry, in which the TiO₂ nanotubes extend radially in a 3D array on a grid of Ti wires, allowing e⁻ and Li⁺ to more easily access the TiO₂ surface.

To further understand the kinetic processes of the electrode reactions, electrochemical impedance spectroscopy (EIS) measurements were performed on the TiO₂/Ti-60min and TiO₂/Ti-600min mesh electrodes. Fig. 6(a) shows the Nyquist plots of the electrodes at a discharge potential of 1.7 V vs. Li/Li⁺ at 25 °C after cycling over 10 cycles. All the impedance curves show two partly overlapping semicircles in the high to medium frequency region, which could be assigned to the film resistance (R_f) of the solid electrolyte interphase (SEI) and the charge transfer resistance (R_{ct}), respectively. A line inclined at approximately 45° reflects the Warburg impedance (W), which is associated with the lithium-ion diffusion in the TiO₂ nanotubes. The high-frequency intercept of the semicircle reflects the uncompensated resistance (R_l), which includes the particle-particle contact resistance, the electrolyte resistance, and the resistance between the TiO₂ nanotube arrays and the Ti wire [29, 30]. The R_f , R_{ct} , and R_l for the TiO₂/Ti-60min and TiO₂/Ti-600min mesh electrodes were obtained using the equivalent circuit shown in the inset of Fig. 6(a) (calculated by Zview). The R_l of the TiO₂/Ti-60min mesh electrode (7.8 Ω) is similar to that of the TiO₂/Ti-600min mesh electrode (8.3 Ω), indicating that the interface between the nanotube arrays and the Ti wire is stable and adhesive. On comparing the diameters of the semicircles, the R_f of the

TiO₂/Ti-60min mesh electrode is similar to that of the TiO₂/Ti-600min mesh electrode (15.7 Ω and 24.2 Ω, respectively), due to the particular geometry, which hinders SEI formation. The thickness of the TiO₂ nanotubes is about 20 nm, so the R_{ct} values of the TiO₂/Ti-60min mesh and the TiO₂/Ti-600min mesh electrodes are very small (3.1 Ω and 6.8 Ω, respectively). The EIS can also be used to calculate the lithium diffusion coefficient using the following equation [31-33]

$$D = R^2 T^2 / 2 A^2 n^4 F^4 C^2 \sigma^2 \quad (7)$$

where R is the gas constant, T is the absolute temperature, A is the surface area of the cathode (1 cm²), n is the number of electrons transferred in the half-reaction for the redox couple, which is equal to 0.5, F is the Faraday constant, C is the concentration of Li ions in the solid material (1.39×10^{-3} mol cm⁻³), D is the diffusion coefficient (cm² s⁻¹), and σ is the Warburg factor, which is relative to Z_{re} [34]. σ can be obtained from the slope of the lines in Fig. 6(b).

$$Z_{re} = R_l + R_{ct} + \sigma \omega^{-1/2} \quad (8)$$

The lithium diffusion coefficients are calculated to be 6.0×10^{-9} cm² s⁻¹ and 3.3×10^{-9} cm² s⁻¹ for the TiO₂/Ti-60min mesh and the TiO₂/Ti-600min mesh, respectively, at 25 °C. This indicates that the TiO₂/Ti-600min mesh electrode can maintain good electrochemical kinetics.

A morphological study of the electrodes before cycling and after 100 cycles was also conducted. The TiO₂/Ti-60min mesh electrode before cycling shows a smooth surface [Fig. 2(b) and Fig. 4(a)], while the TiO₂/Ti-600min mesh electrode shows some TiO₂ nanotube arrays interspaced with fissures at irregular intervals on the Ti wire surface [Fig. 2(e) and Fig. 4(b)]. Compared with before cycling, the electrodes after cycling show similar morphology. Fig. 7(a) is a FESEM image showing the surface of the TiO₂/Ti-60min mesh after 100 cycles.

No changes can be observed on the surface of the electrode. The high magnification image of the cross-section shows that some electrolyte particles have not been washed off, and the surface of the TiO₂ nanotube is very smooth due to the particular geometry [Fig. 7(b, c)]. The TiO₂/Ti-600min mesh electrode surface shows the same morphology as before cycling, and the SEI layer can be seen on the inside and outside of the TiO₂ nanotubes [Fig. 7(e, f)] [35, 36]. This excellent stability of the electrode should be attributed to the particular architecture. Traditional nanostructured electrodes are easy to damage after long cycling, however, for the TiO₂/Ti mesh electrodes used here, the Ti wires act as the current collector and as a frame to protect the TiO₂ nanotube arrays from being damaged and detached [37, 38]. As can be seen from the cross-section of the TiO₂/Ti-600min mesh electrode, the 3D TiO₂ nanotube arrays efficiently prevent the SEI layer from increasing, even though the length of the TiO₂ nanotube is 50.5 μm [Fig. 7(e)].

4. Conclusions

In summary, a new type of electrode consisting of long 3D TiO₂ nanotube arrays on Ti mesh was manufactured using the electrochemical anodization method. The TiO₂ nanotubes extend radially in a 3D array on a grid of Ti wires. The Ti wires acted as the current collector during LIB testing. The Ti conversion rate was increased to around 22wt%. This electrode, which does not need a current collector or binder, has flat potential plateaus, high specific area capacity, and high rate capability, on the same level as reported for nanostructured TiO₂ anode. Therefore, this novel 3D structured TiO₂/Ti mesh is a very promising anode material for LIBs.

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Figure captions

Figure 1. XRD patterns of TiO₂/Ti-*t* mesh (*t* = 0, 60, 180, 420, 600, 720 min) annealed at 500 °C.

Figure 2. FESEM images of TiO₂/Ti mesh prepared by anodization in EG electrolyte containing 0.25 wt% NH₄F with different anodization processing times: a) 0 min; b) 60 min; c) 180 min; d) 420 min; e) 600 min; f) 720 min. The corresponding cross-sections of TiO₂ nanotubes on Ti mesh are shown in the insets.

Figure 3. (a) Geometric parameters of Ti mesh and TiO₂/Ti mesh obtained with anodization in EG electrolyte containing 0.25 wt% NH₄F. (b) Length and diameter parameters of TiO₂/Ti mesh versus anodization processing time. (c) FESEM image of single wire of mesh from TiO₂/Ti-600min (cross-section); high magnification images of (d) TiO₂ nanotube and (e) Ti wire for selected areas in (c).

Figure 4. High magnification FESEM images of TiO₂/Ti mesh prepared by anodization in EG electrolyte containing 0.25 wt% NH₄F: a) cross-sectional image of TiO₂ nanotubes from TiO₂/Ti-60min mesh; b) cross-sectional image of TiO₂ nanotubes from TiO₂/Ti-600min mesh.

Figure 5. Electrochemical behaviour of the TiO₂/Ti-60min mesh and TiO₂/Ti-600min mesh electrodes: (a, b) cyclic voltammograms for the first 5 cycles at a scan rate of 0.1 mV s⁻¹; (c, d) 5th cycle discharge and charge curves at different current densities from 50 μA cm⁻² to 1000 μA cm⁻²; (e) cycling performance at 50 μA cm⁻²; (f) rate capability at different current densities.

Figure 6. (a) Impedance plots of the TiO₂/Ti-60min mesh and TiO₂/Ti-600min mesh anodes after cycling over 10 cycles at a discharge potential of 1.7 V vs. Li/Li⁺ at 25 °C at frequencies from 100 kHz to 10 mHz. The equivalent circuit is shown in the inset. (b) Real part of the complex impedance versus $\omega^{-1/2}$ at 25 °C at a discharge potential of 1.7 V vs. Li/Li⁺.

Figure 7. FESEM images of TiO₂/Ti mesh after 100 cycles: (a) top view of the TiO₂/Ti-60min mesh; (b) cross-sectional image of the TiO₂/Ti-60min mesh; (c) high magnification image of the TiO₂ nanotubes from (b); (d) top view of the TiO₂/Ti-600min mesh; (e) cross-sectional image of the TiO₂/Ti-600min mesh; (f) high magnification image of TiO₂ nanotubes from (e).