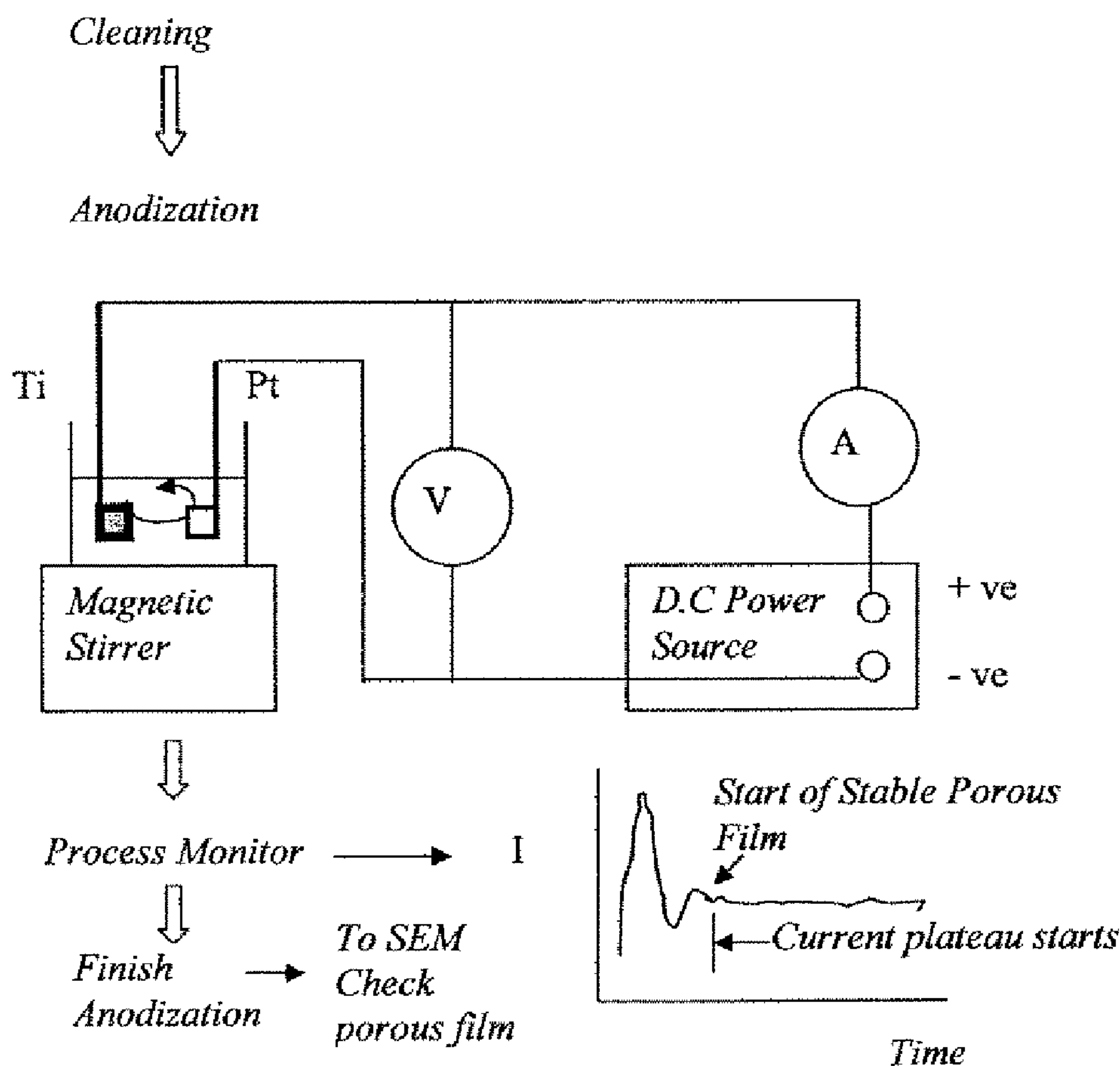




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(19) **United States**(12) **Patent Application Publication**
Misra et al.(10) **Pub. No.: US 2010/0320089 A1**(43) **Pub. Date: Dec. 23, 2010**(54) **SELF-ORDERED NANOTUBES OF TITANIUM
OXIDES AND TITANIUM ALLOY OXIDES
FOR ENERGY STORAGE AND BATTERY
APPLICATIONS**(86) PCT No.: **PCT/US07/87232**§ 371 (c)(1),
(2), (4) Date: **Jul. 14, 2009****Related U.S. Application Data**(76) Inventors: **Manoranjan Misra**, Reno, NV
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12, 2006.**Publication Classification**(51) **Int. Cl.**
C23C 28/00 (2006.01)
C25D 15/00 (2006.01)(52) **U.S. Cl. 205/109; 205/191**(57) **ABSTRACT**

The present disclosure provides oxide nanotubes formed by anodizing and oxidatively-annealing a titanium or titanium alloy substrate with or without ultrasonication. If desired, carbon nanotubes may be grown in the oxide nanotubes. The substrates show improved specific capacity and charge-discharge rates for use as an electrode in lithium-ion batteries.

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Reno, NV 89557 (US)(21) Appl. No.: **12/518,053**(22) PCT Filed: **Dec. 12, 2007***Schematic of Anodization Process Flow*

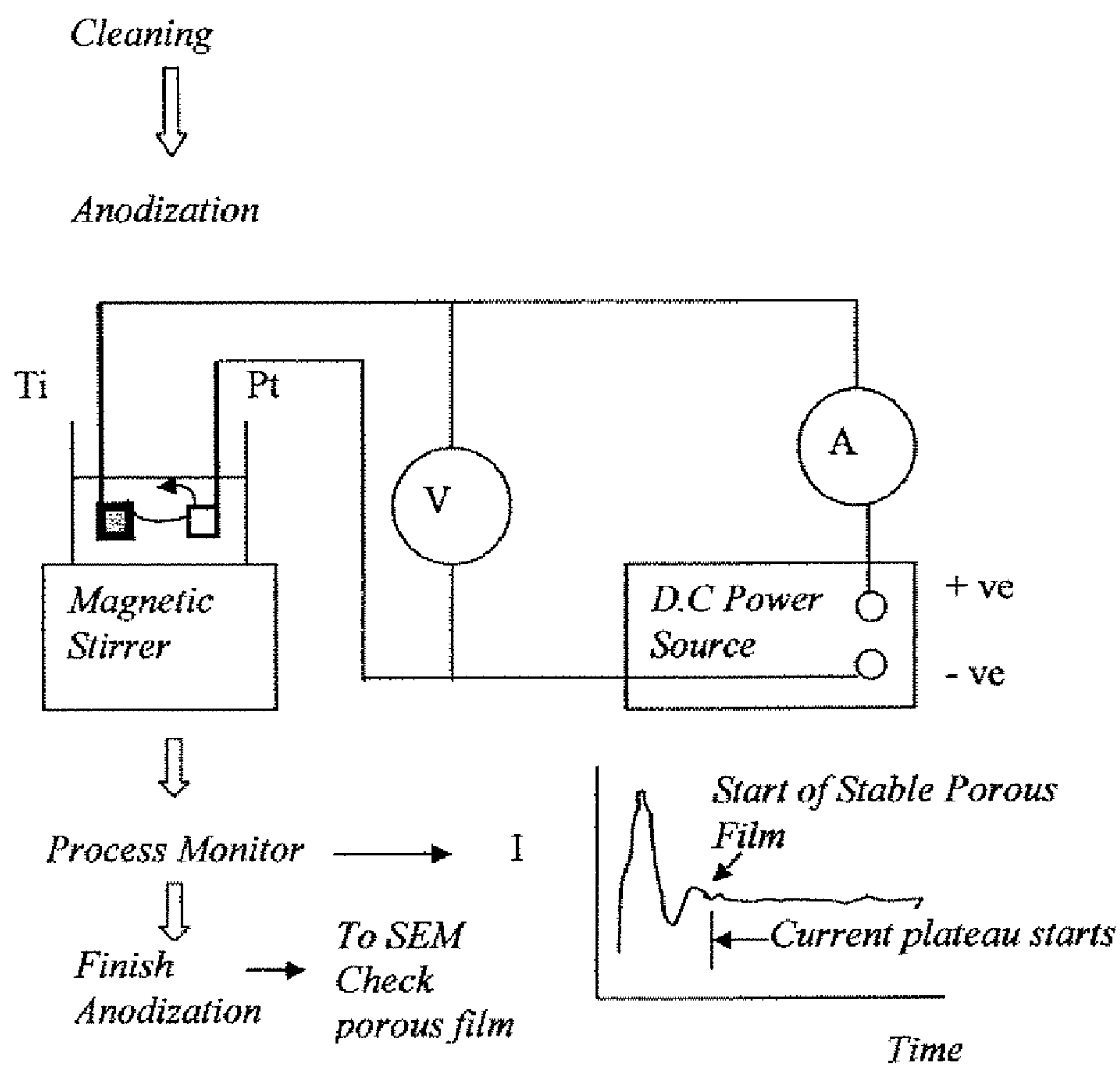


Figure 1: Schematic of Anodization Process Flow

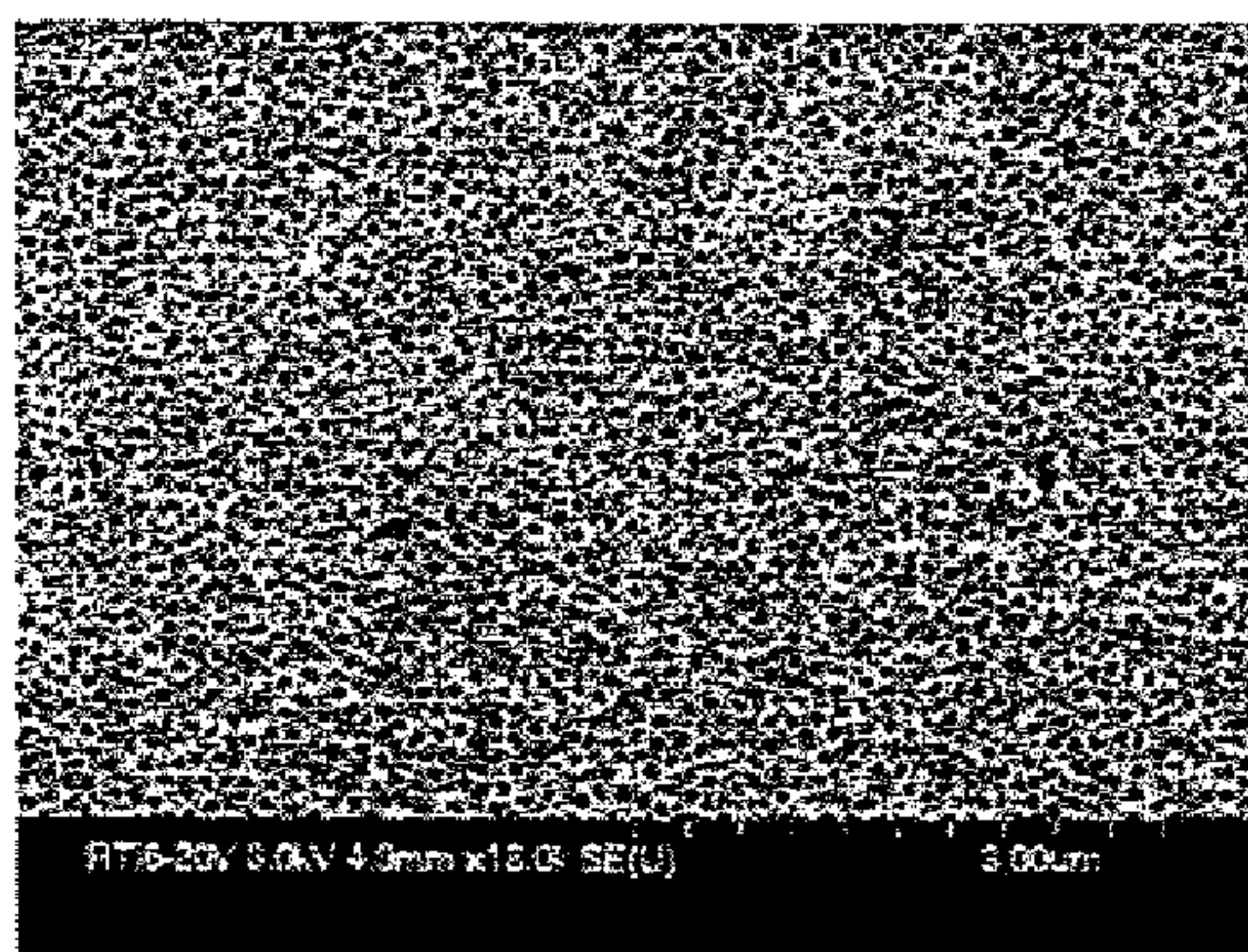


Fig 2 (a) Top view of the as anodized (in 0.5 M H_3PO_4 + 0.14 M NaF) Ti surface.

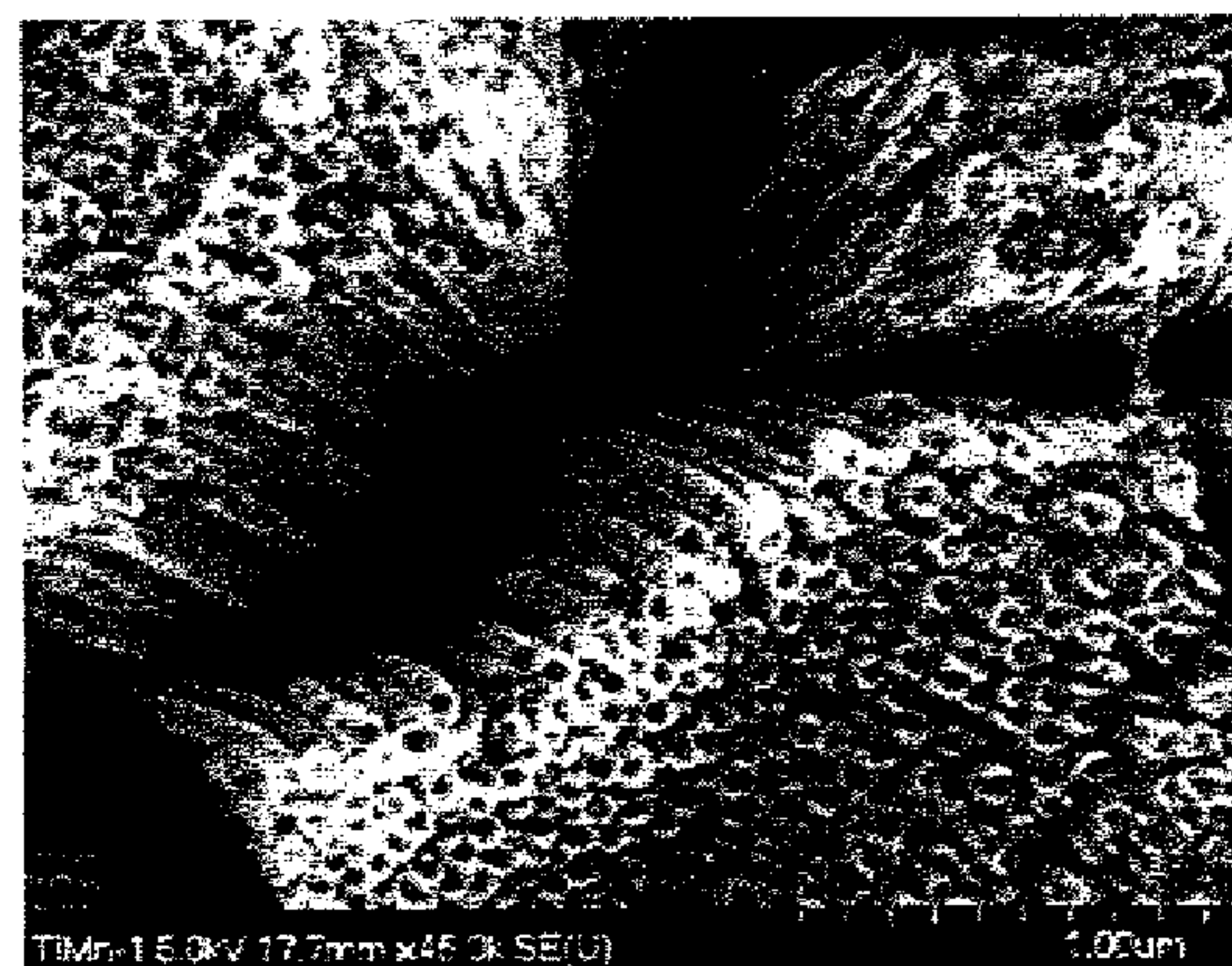


Fig. 2 (b) Anodized TiMn using 5% EG in water, Ultrasonication, 20V, ramped 1V/min, 90 min.

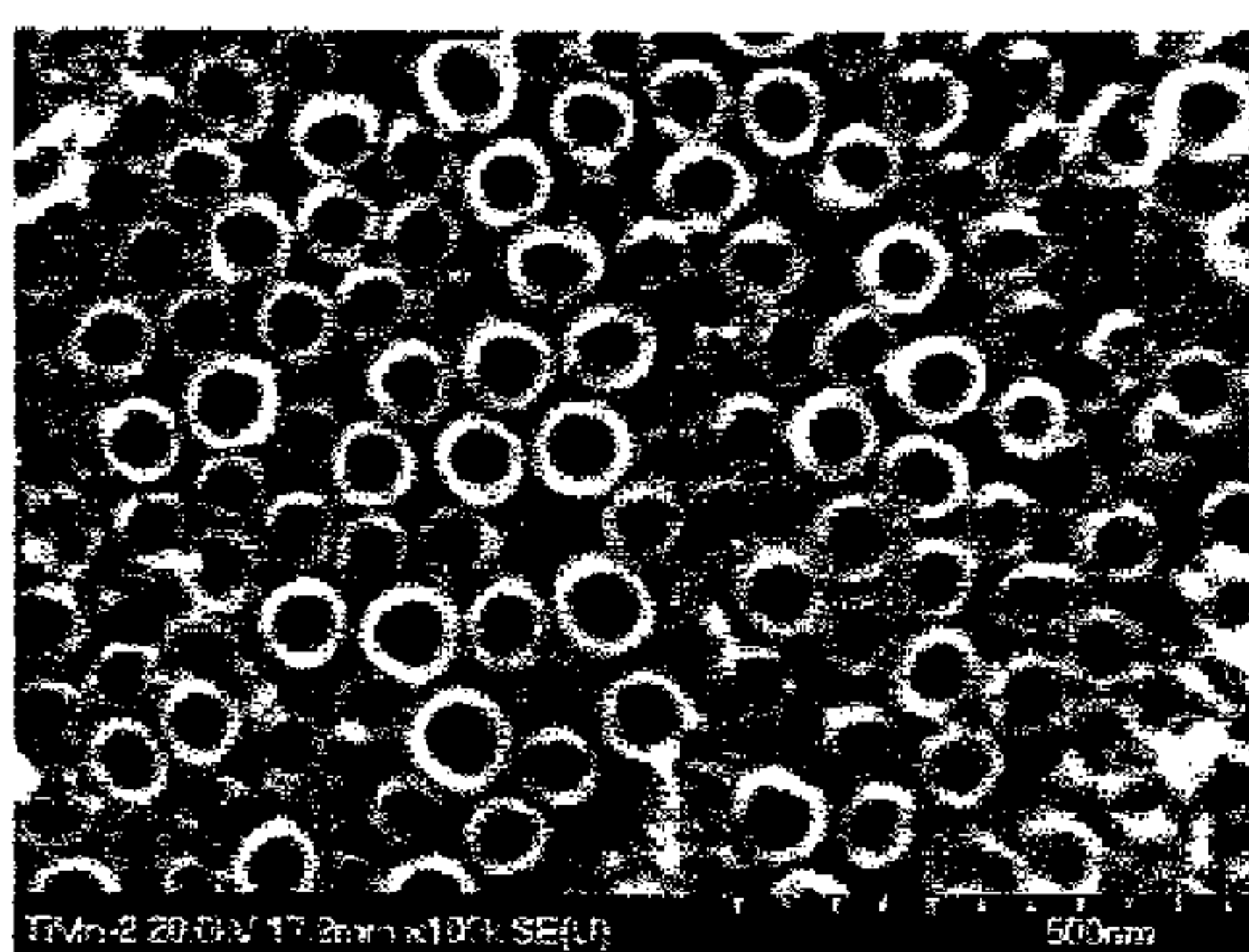


Fig. 2 (c) Anodized Ti-Mn using 10% EG in water, Ultrasonication, 20V, ramped 1V/min, 150 min

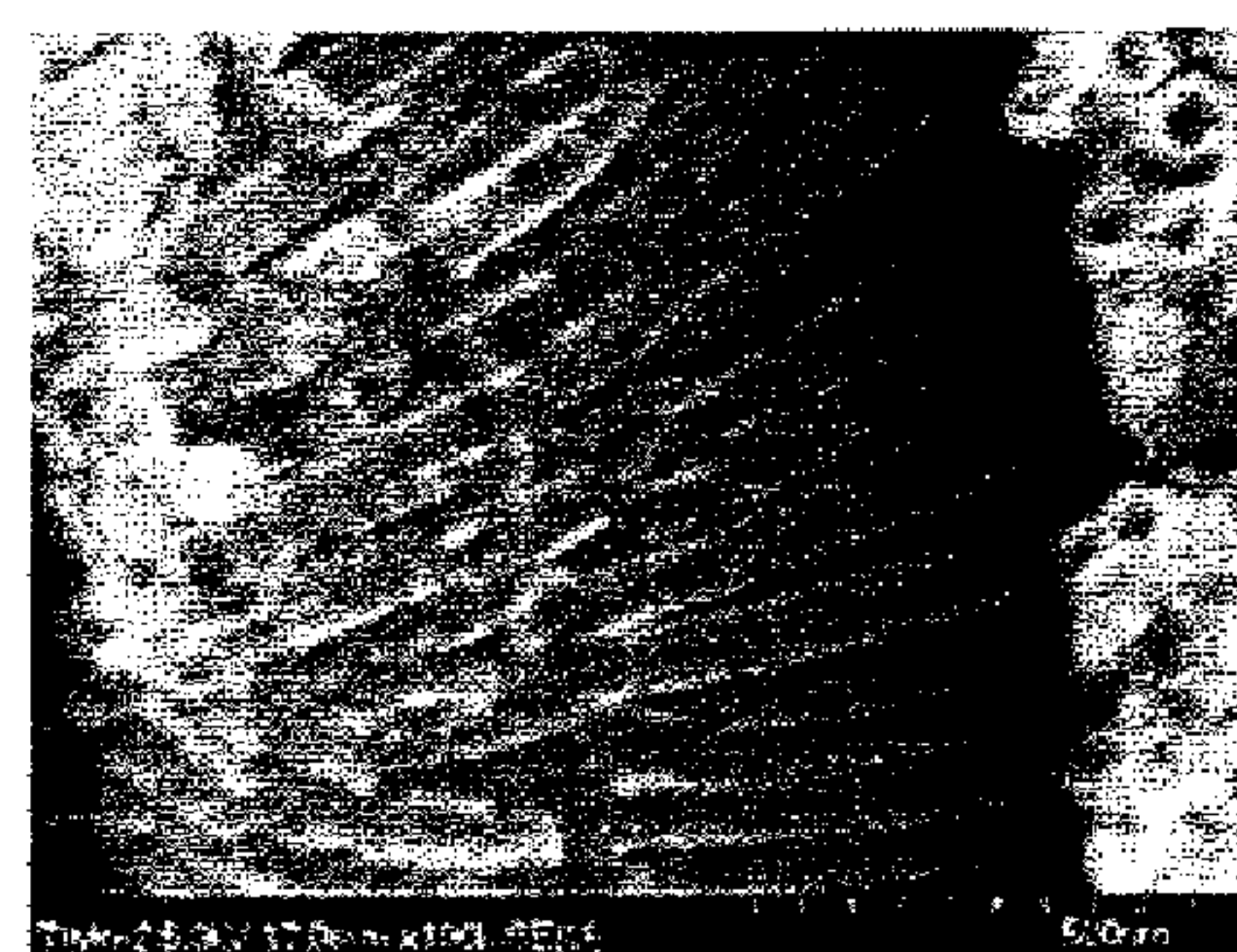


Fig. 2 (d) Side view of Fig. 2 (c).

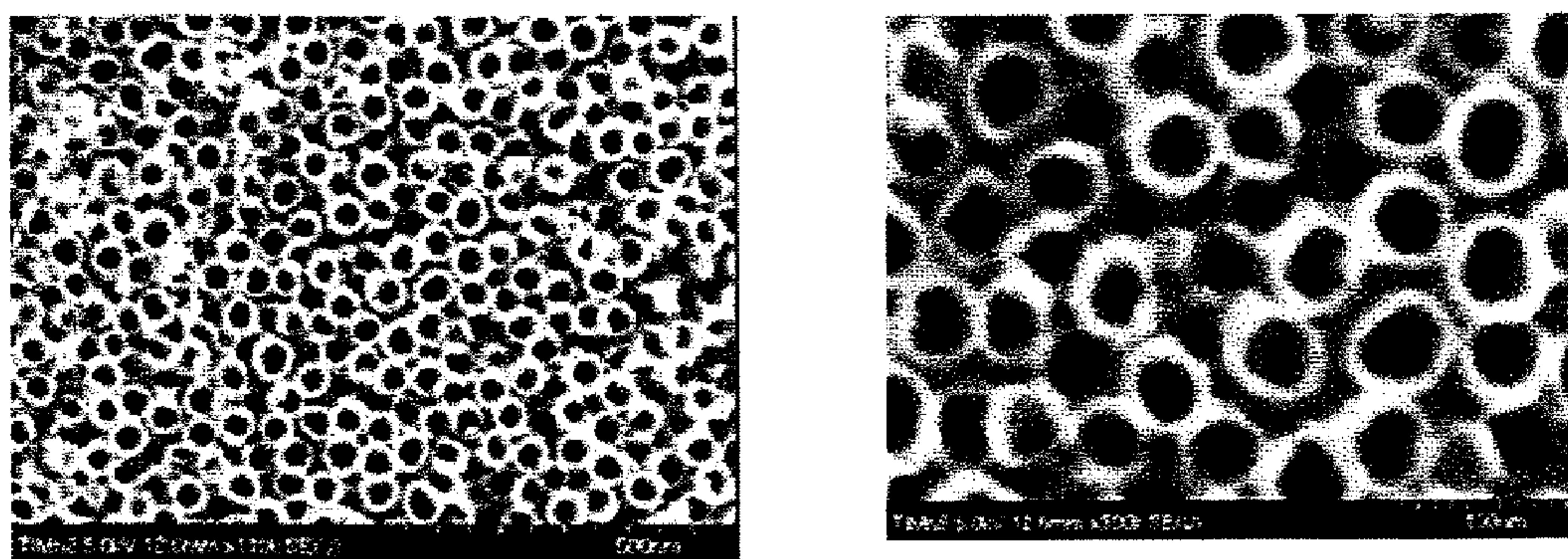


Fig. 3 Top view of the anodized Ti-Mn surface at two different magnifications.

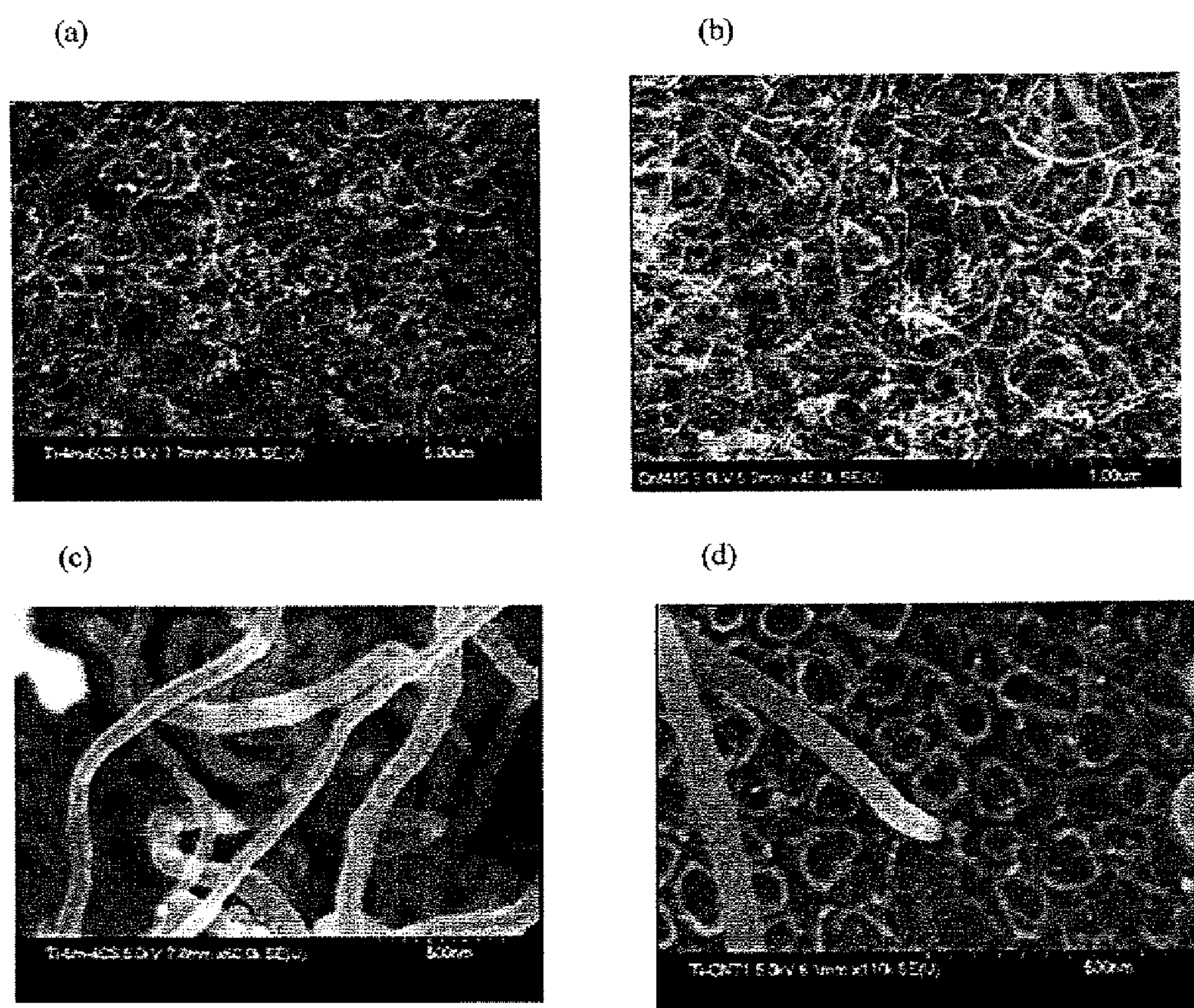


Fig 4 SEM images of the nanocomposite structure of carbon nanotubes grown onto TiO_2 nanotubular template at different magnifications

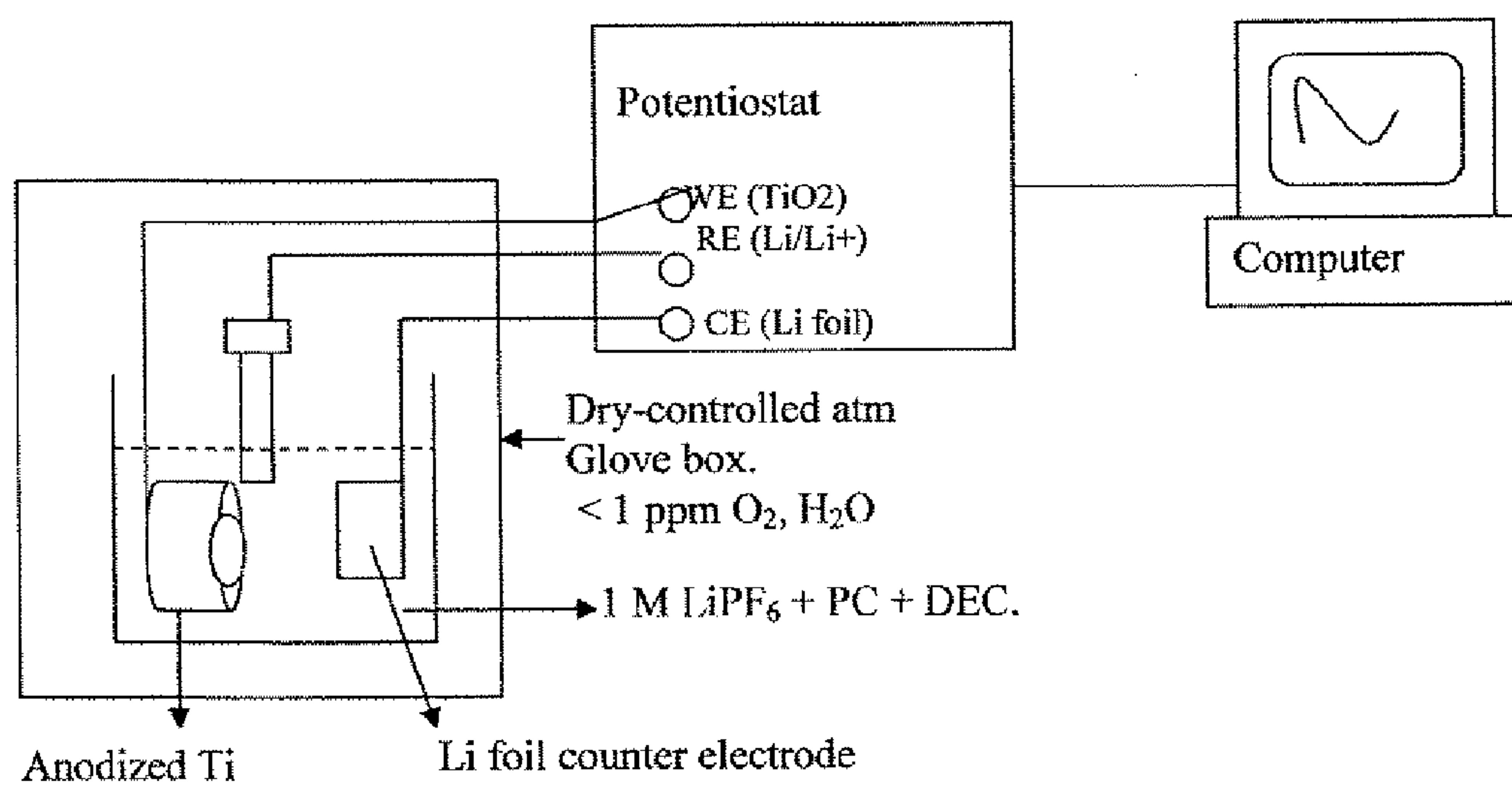


Fig.5: Schematic arrangement of Li-ion charge – discharge experiments

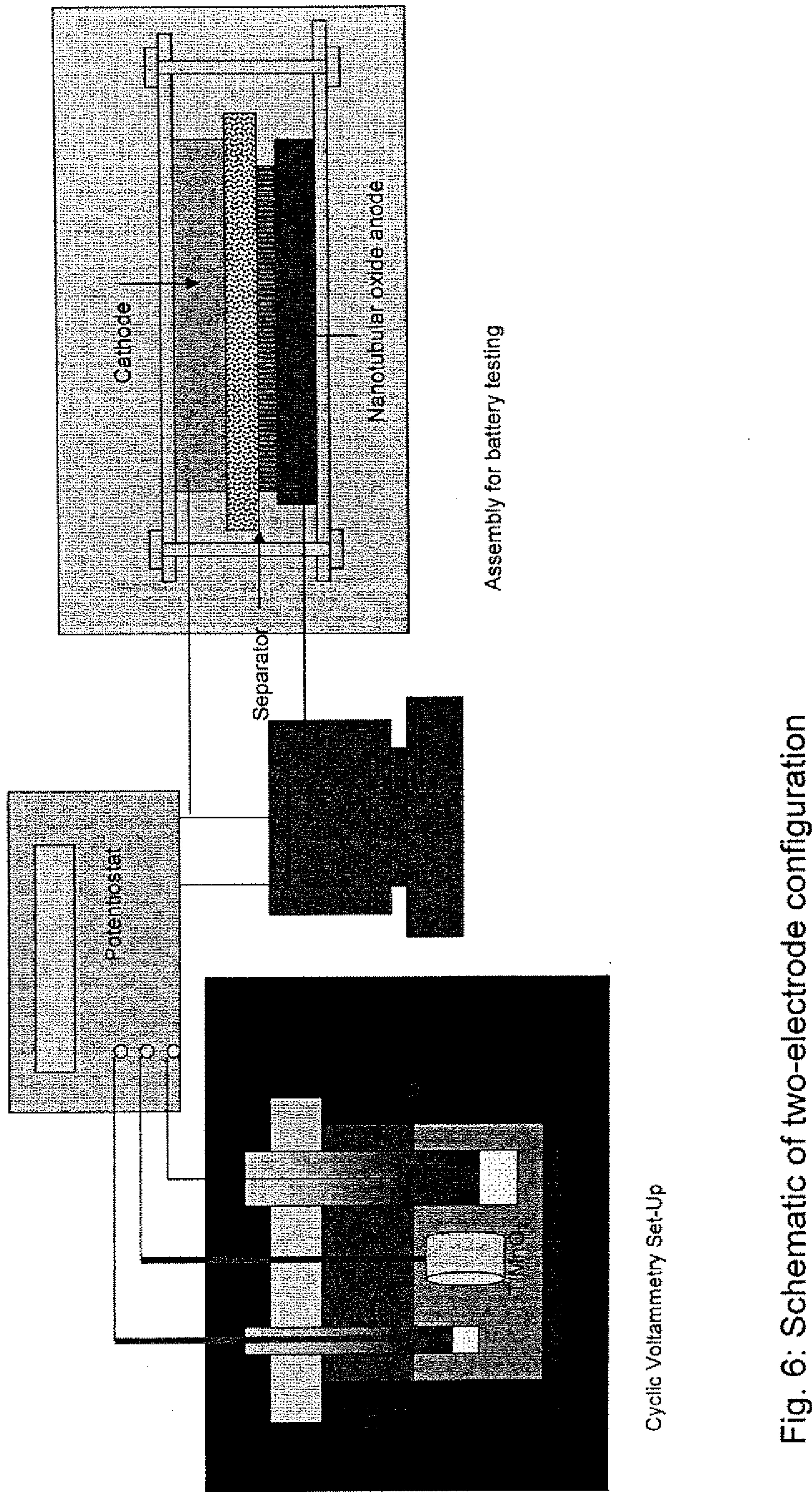


Fig. 6: Schematic of two-electrode configuration

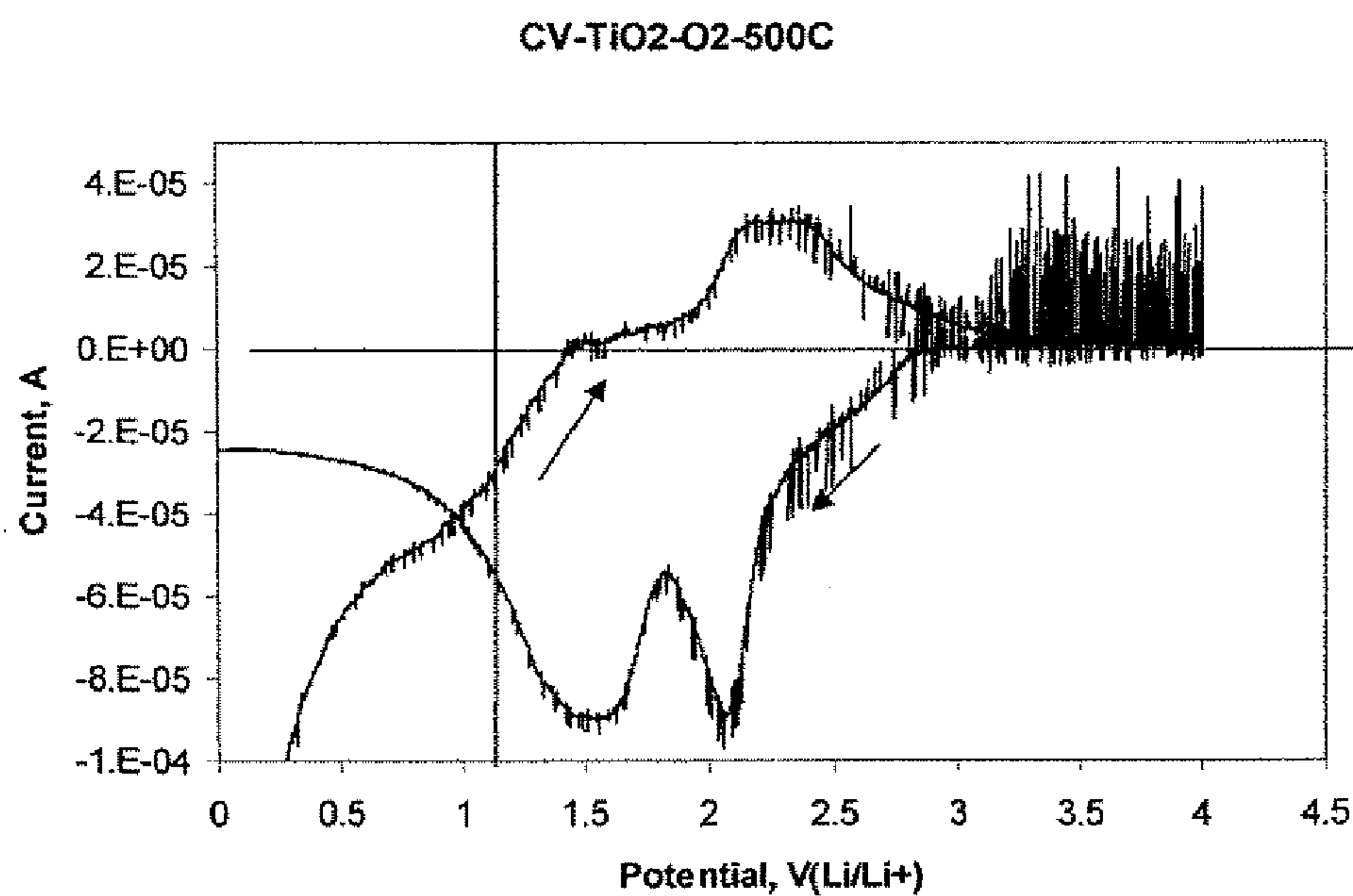


Fig. 7: Cyclic voltammogram of TiO₂ nanotubes oxidatively annealed at 500 °C for 6 h in oxygen.

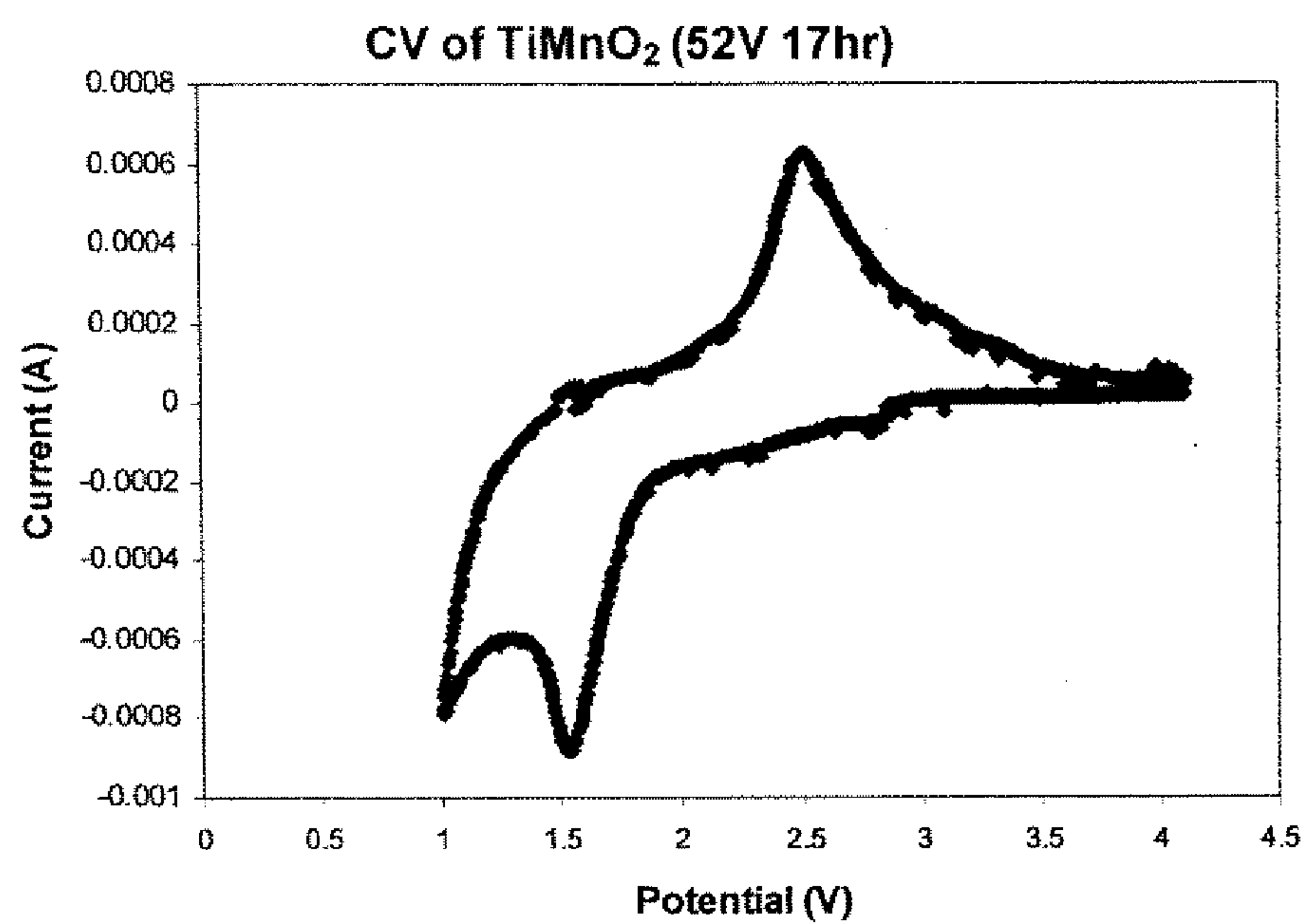


Fig. 8: Cyclic Voltammetry diagram depicting the capacity of $(\text{TiMn})\text{O}_2$ associated with Li-ion insertion and de-insertion

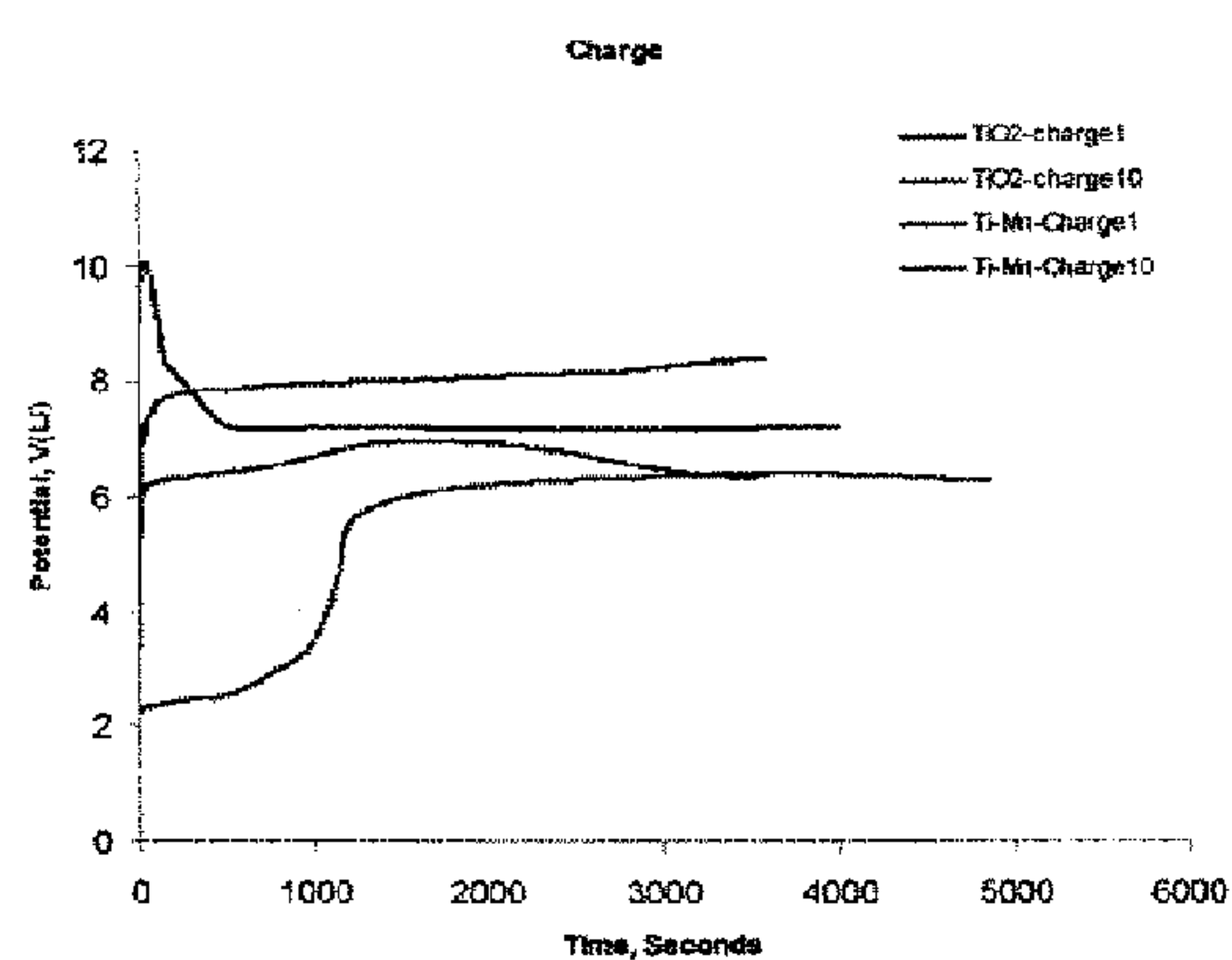


Fig. 9(a) Potential variation during charging of lithium ions at a current density of 0.1 mA/cm^2 .

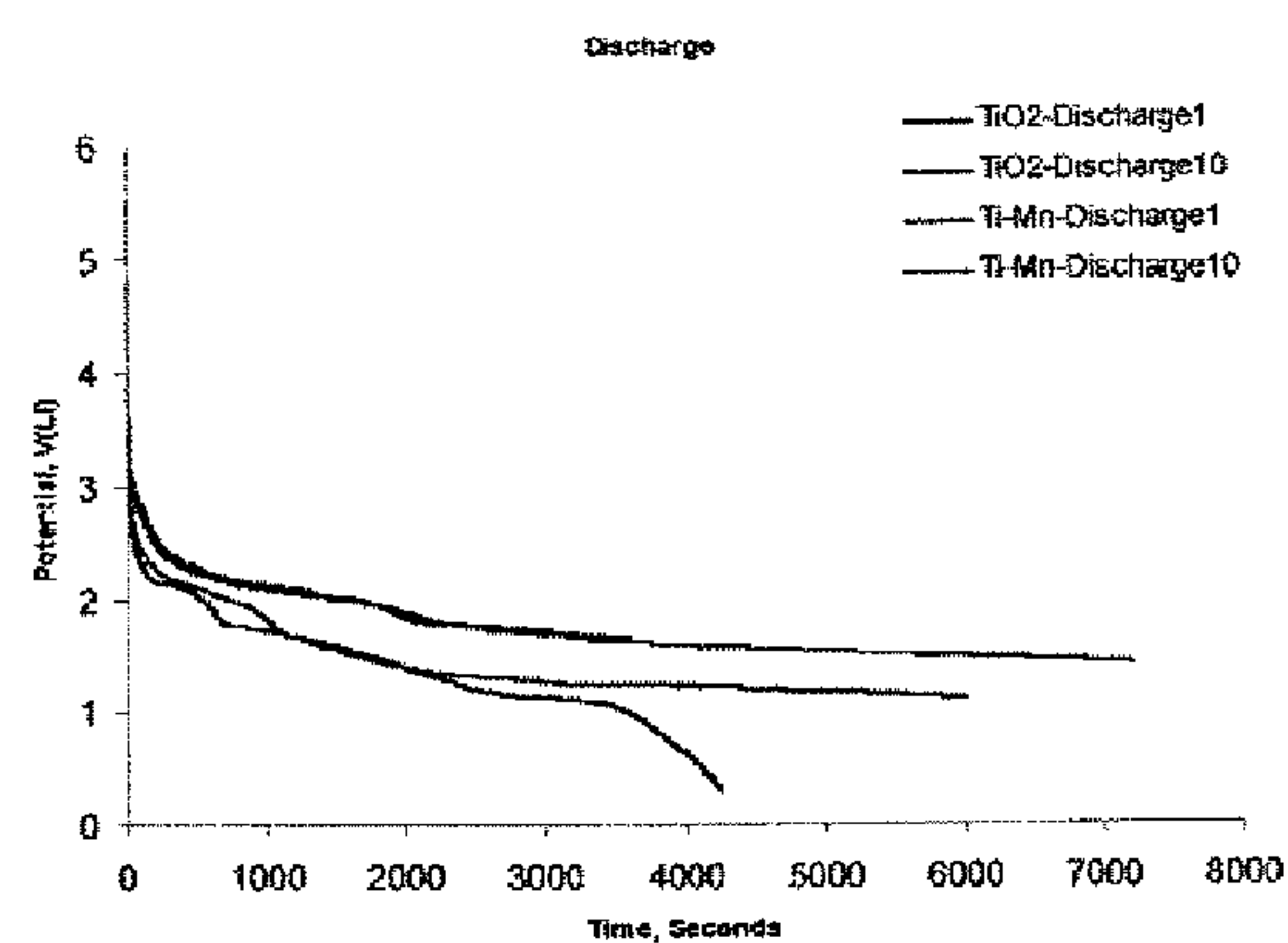


Fig. 9(b) Potential variation during discharging of lithium ions at a current density of -0.1 mA/cm^2 .

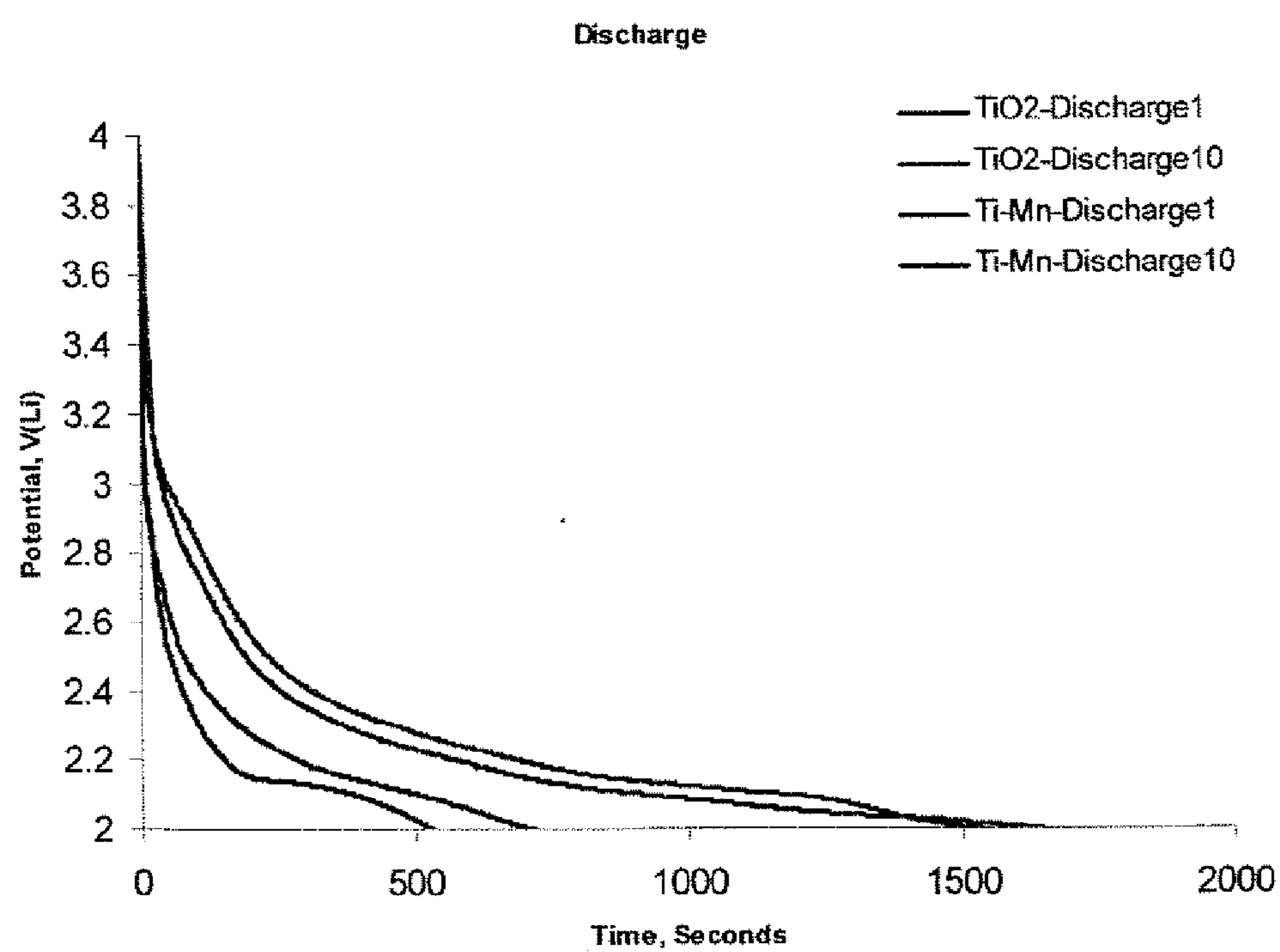


Fig. 10 Potential variation during discharge cycles with a cut off potential of 2 V.

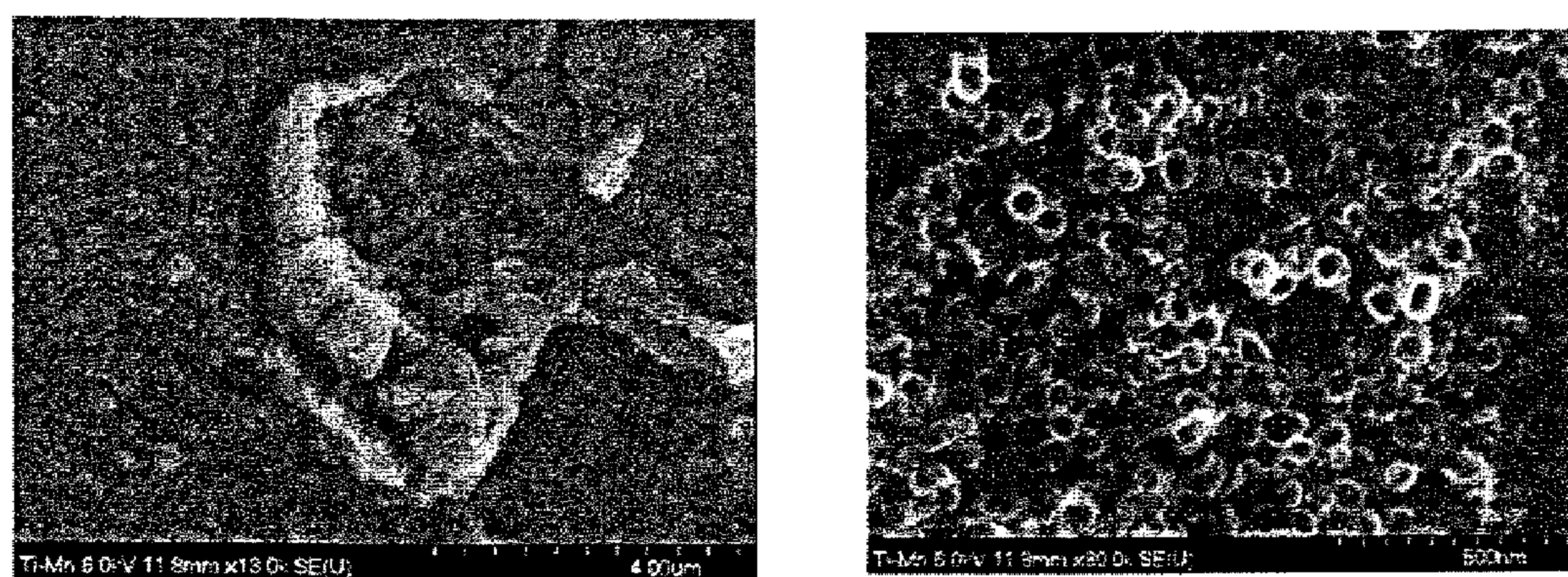


Fig. 11 SEM images of nanotubular oxide of Ti-Mn after Li charge-discharge experiments.

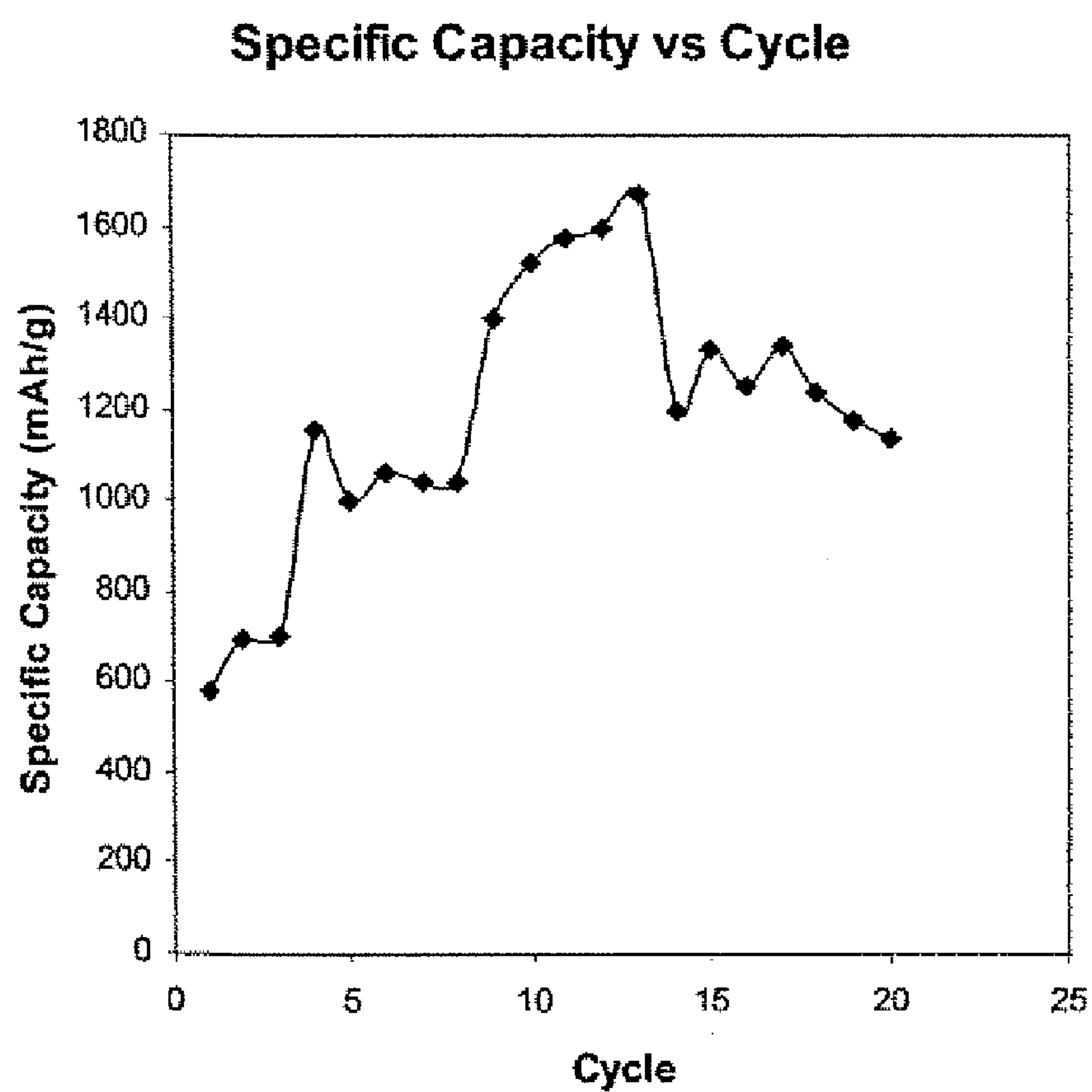


Fig. 12: Chart depicting the specific capacity of Example 2(b)

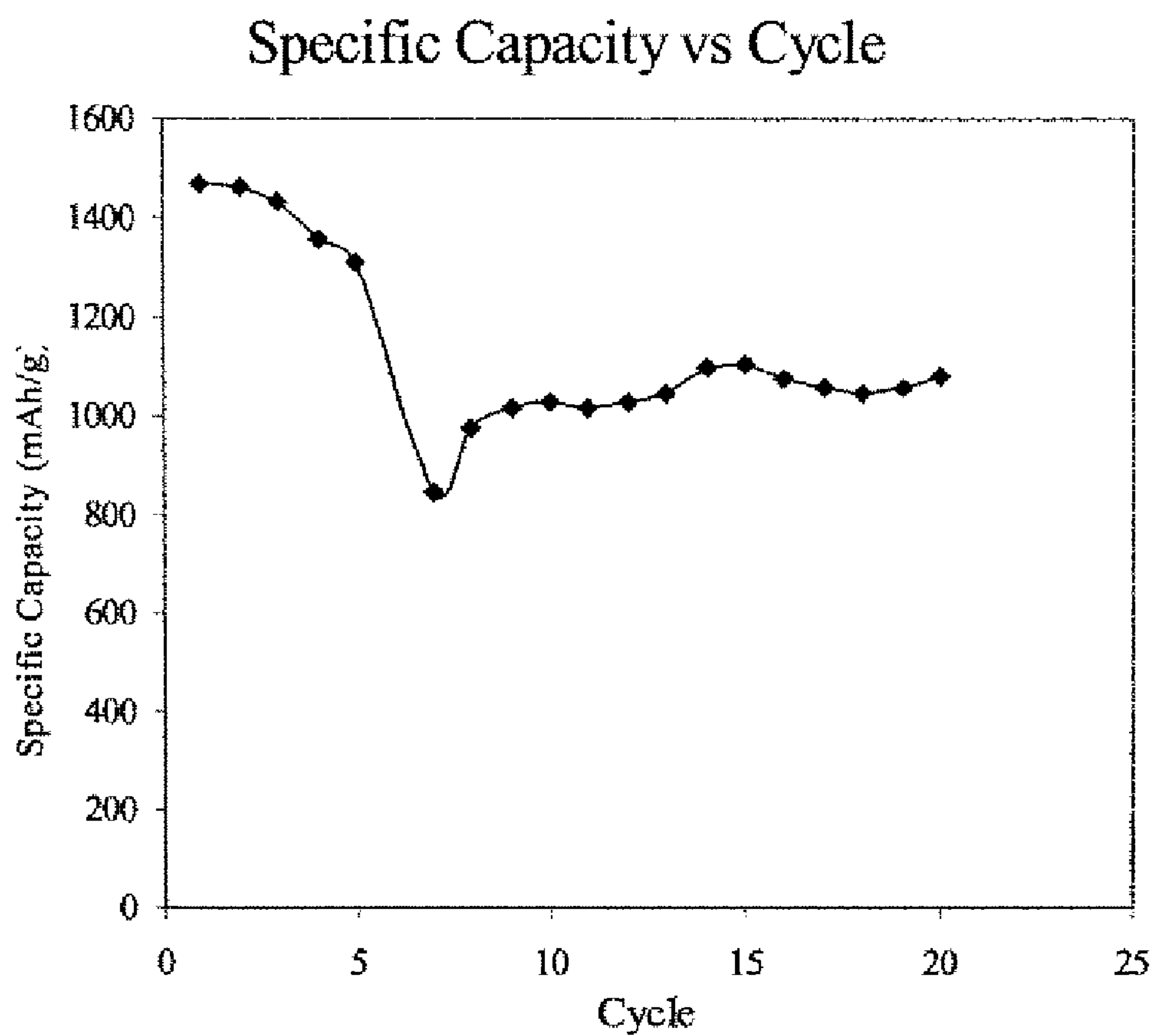


Fig. 13: Chart depicting the specific capacity of Example 2(c)

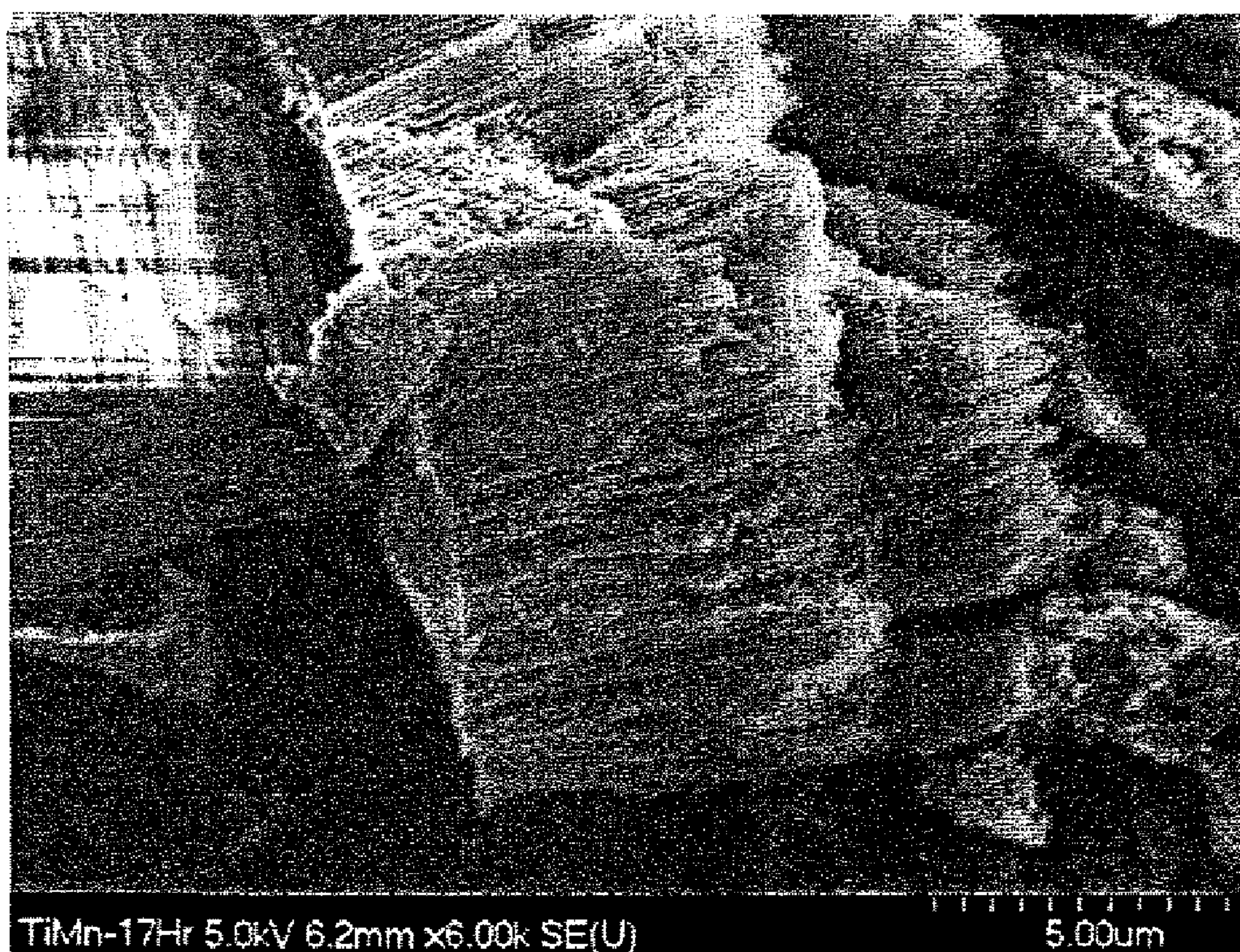


Fig. 14: Cross-section of $(\text{TiMn})\text{O}_2$ anodized for 17 hrs at 52V

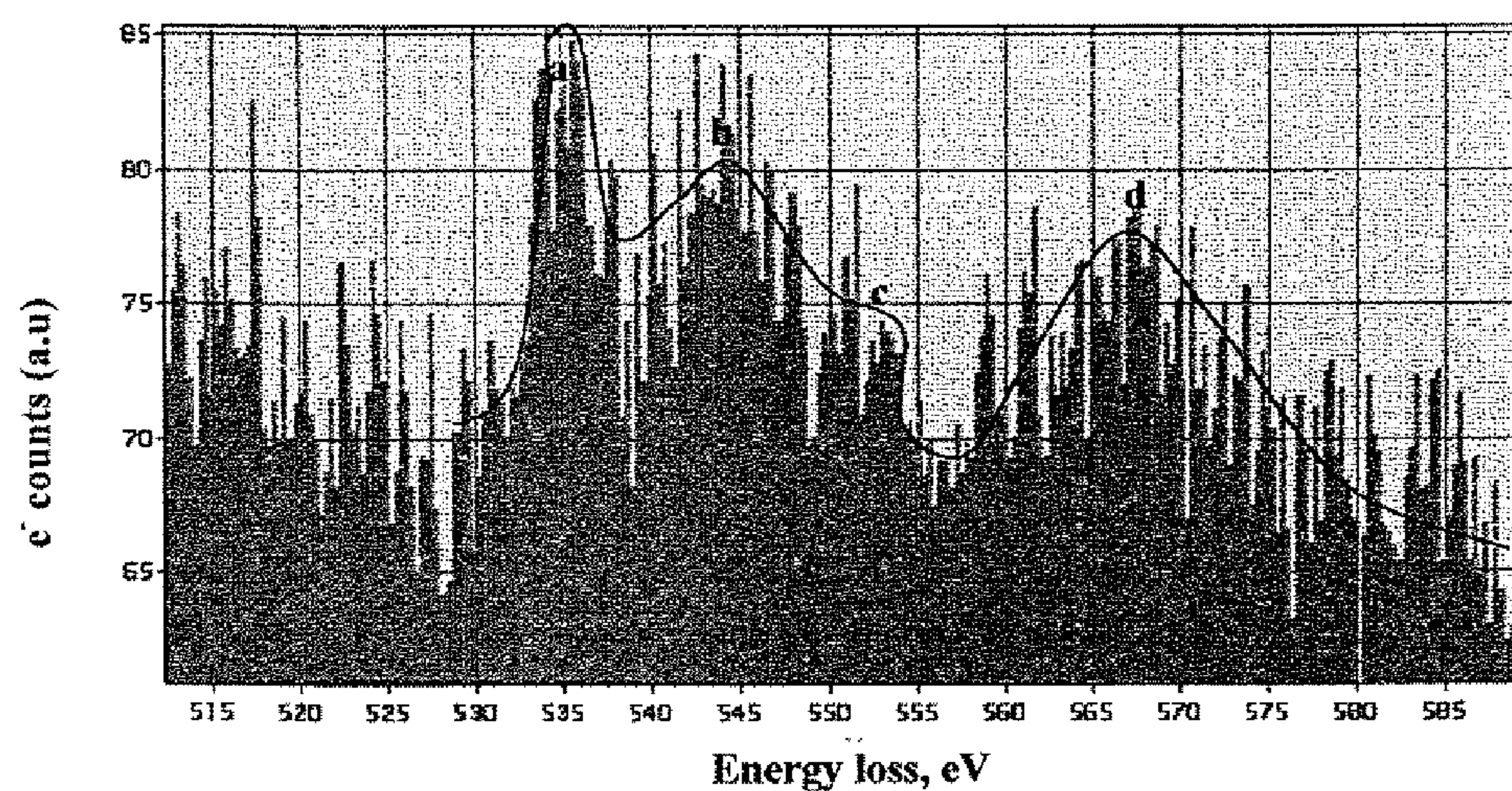


Fig. 15: Oxygen K-edge electron energy loss spectrum of an anodized single nanotube of Ti-Mn oxide.

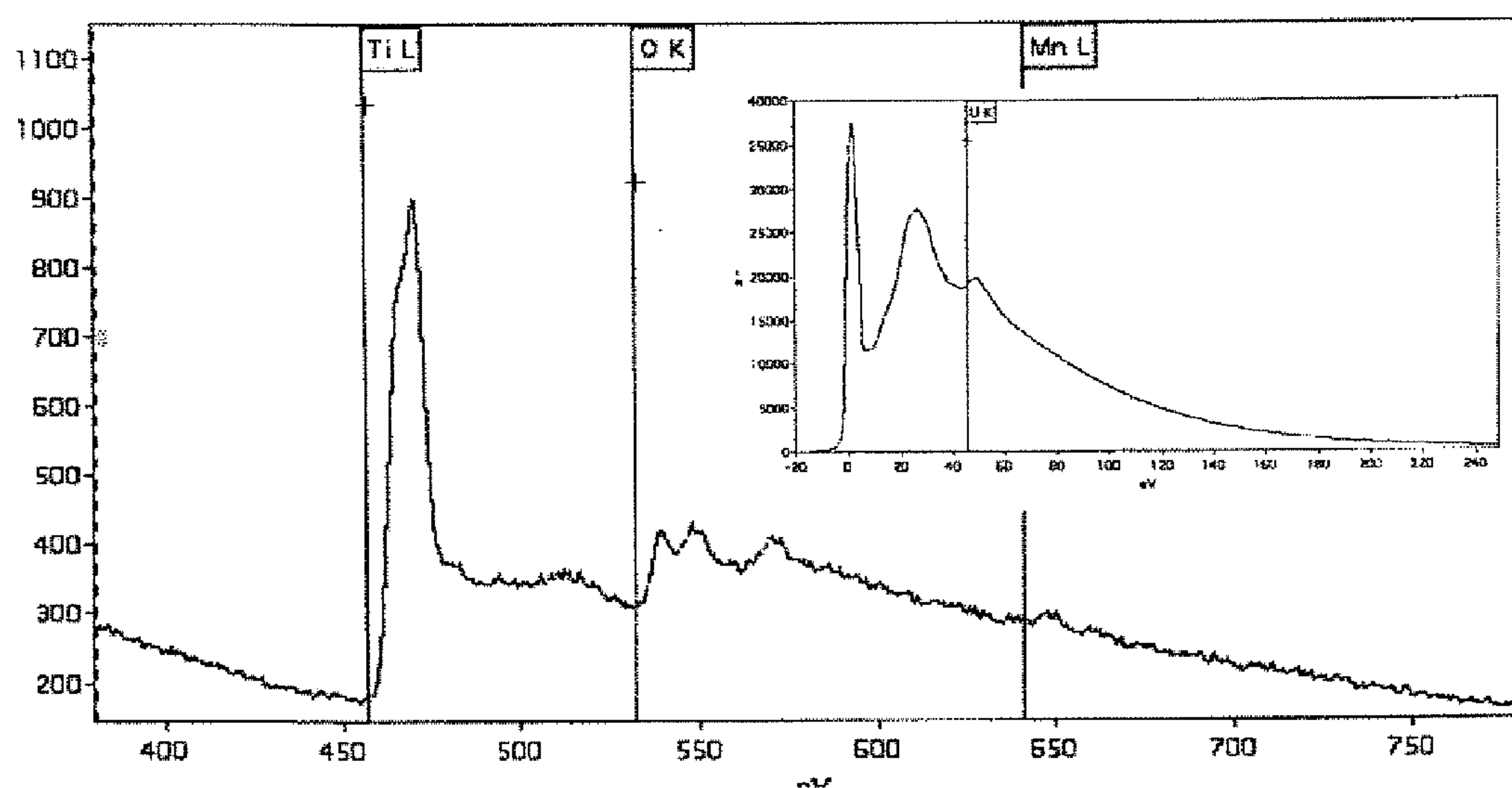


Fig. 16: Electron energy loss spectroscopy of the Ti-Mn oxide nanotubes after Li-ion insertion. The inset shows the Li- K edge.

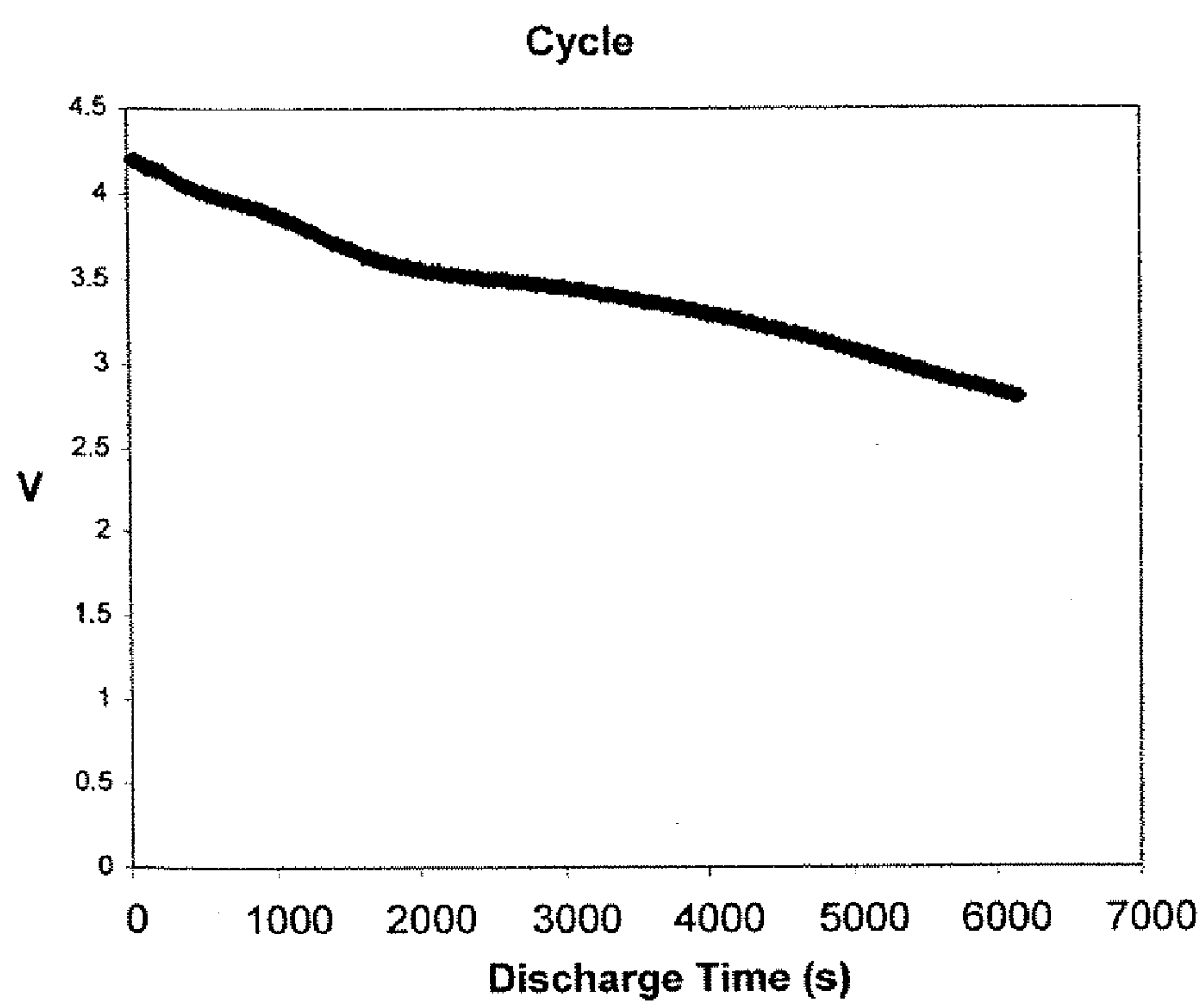


Fig. 17: Discharge potential profile of Ti-Mn oxide nanotubes using a two-electrode configuration.

SELF-ORDERED NANOTUBES OF TITANIUM OXIDES AND TITANIUM ALLOY OXIDES FOR ENERGY STORAGE AND BATTERY APPLICATIONS

PRIORITY STATEMENT

[0001] This application claims priority to U.S. Provisional Application No. 60/869,716, filed Dec. 12, 2006, which is herein incorporated by reference in its entirety.

FIELD OF THE INVENTION

[0002] This invention relates to synthesis and use of self-ordered arrays of nanotubular oxides of titanium and titanium alloys. The arrays can be used in energy storage applications, such as in Li-ion batteries.

BACKGROUND

[0003] In conventional lithium-ion batteries ~10 micron size graphite particles are used as host material (anode or negative electrode) for lithium-ion insertion. The specific capacity of such LiC_6 anode is about 372 mAh/g. Oxides of Co, Ni and Mn are used as cathodes (positive electrode) with a specific capacity ranging from 160-200 mAh/g. A significant problem with using a LiC_6 anode lies in the formation of a solid interface layer on the graphite from the reaction product with the aprotic electrolyte (typically propylene carbonate). This undesirably slows down the kinetics of lithium-ion transportation. The presence of such a solid interface layer has other detrimental effects on the effectiveness of the lithium battery, including decreasing in specific capacity, slowing its charge-discharge rate, and increasing the possibility of having the battery overheat.

[0004] Recently, alternate materials have been analyzed as anode materials that are inert to the electrolyte. Nanocrystalline titanium dioxides have been investigated as potential anode materials for Li-ion insertion. See, for example, V. Subramanian et al., *J. Power Sources*, 159 (2006) 186-192; S. W. Oh et al., *J. Power Sources*, 161 (2006) 1314-1318; A. R. Armstrong et al., *Advanced Materials* 17 (2005) 862-65; C. O. Avellanda et al., *Electrochimica Acta* 46 (2001) 1977-81; and Q.-H. Wu et al., *Surface Science* 578 (2005) 203-212, all of which are herein incorporated by reference in their entirety. In these systems, the nanostructured TiO_2 materials are prepared via the sol-gel or hydrothermal route. The use of nanophosphate particles as anode materials has also been disclosed in S. Chung et al., *Nature Materials*, 2 (2002) 123-128, herein incorporated by reference in its entirety.

[0005] A combination of TiO_2 and nanocarbon materials has also been investigated as a possible anode material by different research groups. See, for example, H. Huang et al., *Materials Letters*, 61 (2007) 296-299, and L. J. Fu et al., *J. Power Sources*, 159 (2006) 219-222, both of which have herein been incorporated by reference in their entirety. In these systems, the nanocomposite TiO_2 -carbon materials are prepared using doctor-blade or pelletization techniques.

[0006] While these systems have shown advantages over the graphite anodes, the methods used for preparing the materials often exhibit insufficient specific capacity and kinetics of charge-discharge cycles for certain lithium-ion batteries. The maximum reversible specific capacity reported for nanocrystalline TiO_2 anode was about 170 mAh/g by Subramanian et al., and Oh et al., and about 200 mAh/g by Armstrong et al. The composite of TiO_2 -nanocarbon disclosed by Huang et al.

reported a discharge capacity of about 168 mAh/g, with the TiO_2/C core-shell nanocomposite showing a charge capacity of 118 mAh/g.

[0007] Thus, what is needed in the art is an electrode that is inert to the electrolyte yet provides the desired specific capacity and charge-discharge cycles for improved use with lithium-ion batteries. This invention answers that need.

SUMMARY OF THE INVENTION

[0008] This invention relates to an electrode capable of storing energy. The electrode comprises an anodized and oxidatively-annealed titanium oxide or titanium alloy oxide substrate having a plurality of self-ordered oxide nanotubes. The electrode may be used in energy storage application, such as a component of a lithium-ion battery.

[0009] The invention also relates to a method of manufacturing an anodized and annealed titanium oxide or titanium alloy oxide substrate. The method involves (a) anodizing a titanium or titanium alloy substrate under conditions sufficient to form anodized titanium oxide or titanium alloy oxide having a plurality of self-ordered oxide nanotubes on the anodized surface, and (b) annealing the oxide nanotubes in a controlled gaseous atmosphere. When annealed in an oxidizing atmosphere, the anodized and oxidatively-annealed titanium oxide or titanium alloy oxide substrates produced through the process have a surface area sufficient to incorporate ions for energy storage.

[0010] The invention also relates to an anodized titanium alloy oxide substrate having a plurality of self-ordered oxide nanotubes. The substrate may be annealed in oxygen or another gaseous atmosphere. The substrate is suitable as an electrode or a component of a battery, as well as in other applications, such as the photo-electrolysis of water.

[0011] This invention also relates to a method of using an anodized and oxidatively-annealed titanium oxide or titanium alloy oxide substrate in an energy storage application. The method involves contacting an anodized and oxidatively-annealed titanium oxide or titanium alloy oxide substrate having a plurality of self-ordered oxide nanotubes with an energy source and an electric current, and receiving ions from the energy source in the oxide nanotubes.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] FIG. 1 depicts a schematic of an anodization process flow.

[0013] FIG. 2 depicts a top view of an anodized titanium surface (2(a)), and various views of anodized TiMn (2(b-d)).

[0014] FIG. 3 depicts top views of an anodized Ti—Mn surface at different magnifications.

[0015] FIG. 4 depicts SEM images of nanocomposite structures of carbon nanotubes grown on a titanium oxide nanotubular template at different magnitudes.

[0016] FIG. 5 depicts a schematic arrangement of a Li-ion charge-discharge experiment.

[0017] FIG. 6 depicts a schematic arrangement of a Li-ion multiple charge-discharge experiment using a two-electrode configuration.

[0018] FIG. 7 depicts a cyclic voltamogram of oxidatively annealed titanium oxide nanotubes.

[0019] FIG. 8 depicts a cyclic voltamogram showing the capacity of $(\text{TiMn})\text{O}_2$ associated with Li-ion insertion and de-insertion.

[0020] FIG. 9 depicts the potential variation during charging (8(a)) and discharging (8(b)) of lithium ions using TiO_2 and $(\text{TiMn})\text{O}_2$ substrates.

[0021] FIG. 10 depicts potential variation during discharge cycles using TiO_2 and $(\text{TiMn})\text{O}_2$ substrates.

[0022] FIG. 11 depicts SEM images of nanotubular oxide of Ti—Mn after Li charge-discharge experiments.

[0023] FIGS. 12 and 13 depict the specific capacity shown in exemplified Ti—Mn substrates.

[0024] FIG. 14 depicts a cross-section of anodized $(\text{TiMn})\text{O}_2$.

[0025] FIG. 15 depicts the oxygen K-edge electron loss spectrum of an anodized single nanotube of Ti—Mn oxide.

[0026] FIG. 16 shows the electron energy loss spectroscopy results of the Ti—Mn oxide nanotubes after Li-insertion.

[0027] FIG. 17 shows a typical potential profile of Ti—Mn oxide discharge using a two-electrode configuration.

DETAILED DESCRIPTION

[0028] The invention relates to a method of manufacturing an anodized and annealed titanium oxide or titanium alloy oxide substrate. The method involves (a) anodizing a titanium or titanium alloy substrate under conditions sufficient to form anodized titanium oxide or titanium alloy oxide having a plurality of self-ordered oxide nanotubes on the anodized substrate, and (b) annealing the oxide nanotubes in a controlled gaseous atmosphere, for example, when the substrate is annealed in an oxygen or other oxidizing atmosphere. The anodized and oxidatively-annealed titanium oxide or titanium alloy oxide substrates of the invention have a surface area sufficient to incorporate ions for energy storage.

[0029] The anodization may take place using electrochemical techniques known in the art. For example, the titanium or titanium alloy material may be electrochemically anodized in an aqueous or non-aqueous acidified electrolyte solution containing a fluoride salt. The anodization process can be set up in a system similar to the schematic shown in FIG. 1.

[0030] Any type of titanium metal may be used as the titanium substrate. The only limitation on the titanium metal is the ability to anodize to form the titanium oxide nanotubes on the surface of the substrate. The titanium substrate may be titanium foil, a titanium sponge or a titanium metal layer on an other substrate, such as, for example, a semiconductor substrate, plastic substrate, and the like, as known in the art. Titanium metal may be deposited on a substrate using conventional film deposition techniques known in the art, including but not limited to, sputtering, evaporation using thermal energy, E-beam evaporation, ion assisted deposition, ion plating, electrodeposition (also known as electroplating), screen printing, chemical vapor deposition, molecular beam epitaxy (MBE), laser ablation, and the like. The titanium substrate and/or its surface may be formed into any type of geometry or shape known in the art. For example, the titanium substrate may be planar, curved, tubular, non-linear, bent, circular, square, rectangular, triangular, smooth, rough, indented, etc. There is no limitation on the size of the titanium substrate. The substrate size depends only upon the size of the anodization tank. For example, sizes ranging from less than a square centimeter to up to square meters are contemplated. Similarly, there is no limit on thickness. For example, the titanium substrate may be as thin as a few nanometers.

[0031] Likewise, any type of titanium alloy may be used as the titanium alloy substrate, provided the titanium alloy has the ability to anodize to form the titanium alloy oxide nano-

tubes on the surface of the substrate. Preferred titanium alloys include Ti—Mn, Ti—Nb, Ti—Zr, Ti—Si, and Ti—Al—V, however other titanium alloys known in the art may also be used. Titanium alloys may be purchased from commercial suppliers, such as Titanium Metals Corporation (TIMET), based in the U.S., or KOBELCO, based in Japan.

[0032] The content of the elements in the alloy vary as known in the art. Generally, the titanium alloy contains from about 0.1-50 wt % of elements other than titanium, with the balance of the alloy being titanium. For instance, a Ti—Mn alloy will typically contain 3-8 wt % manganese, with the balance titanium; a Ti—Al—V alloy will typically contain 3-8 wt % aluminum, 2-4 wt % vanadium, with the balance titanium (a Ti-6Al-4V contains 6 wt % Al, 4 wt % V, with the balance Ti).

[0033] Depending on the composition of the titanium alloy, the titanium—either by itself or with the other metal(s) in the alloy—will become oxidized during the anodization process. For instance, in a titanium-manganese alloy, both the titanium and manganese typically oxidize, thus forming oxide nanotubes having both titanium oxide and manganese oxide. This type of reaction where all the metals in the alloy become oxidized and form part of the oxide nanotubes represent the majority of known titanium alloys. However, there may be instances where the non-titanium metals do not oxide easily.

[0034] The oxide stoichiometry of the nanotubes can change depending on how easily the non-titanium metals in the alloy form a solid solution with the titanium upon anodization. In titanium-manganese alloys, both the titanium and manganese form a solid solution together, and the resulting nanotubes have a composition where the manganese oxide is distributed throughout the nanotubular structure. In other instances when the other elements in the alloy do not form solid solution with titanium oxide easily, the self-ordered oxide nanotubes will contain two or more regions of varying oxide stoichiometries. For example, when anodizing Ti—Si alloy with Si content varying from 2-28%, the oxide nanotubes have two distinct chemistries, where the top layer is predominately TiO_2 and bottom layer is predominantly SiO_2 . This dual oxide layer is mainly attributed to the large difference in transference numbers of Ti^{4+} and Si^{4+} ions in the oxide layer.

[0035] Prior to anodization, the titanium or titanium alloy substrate may be cleaned and polished using standard metallographic cleaning and polishing techniques known in the art. For instance, the material surface may be cleaned using soap and distilled water. Preferably, the titanium or titanium alloy metal substrate is chemically and/or mechanically cleaned and polished prior to anodization. Mechanical cleaning is preferably done by sonication. As an example, a titanium metal surface may be incrementally polished by utilizing 120 grit emery paper down to 1200 grit emery paper followed by wet polishing in a 15 micron alumina slurry. After polishing, the metal substrate may be thoroughly washed with distilled water and sonicated for about 10 minutes in isopropyl alcohol, as known in the art. Performing such optional cleaning and polishing aids in consistency of the titanium and titanium alloy metal substrates used in the invention and better ensures that the substrates have uniform starting points (e.g., planar surfaces when desired). While it is preferred to use clean or polished surfaces, there may be instances when the material is clean prior to use or using a clean material is otherwise undesirable or unnecessary.

[0036] An acidified fluoride electrolyte may be used in the anodization step. The electrolyte may be an aqueous electrolyte, an organic electrolyte solution, or a mixture thereof. Fluoride compounds which may be used in the electrolytes are those known in the art and include, but are not limited to, hydrogen fluoride, HF; lithium fluoride, LiF; sodium fluoride, NaF; potassium fluoride, KF, ammonium fluoride, NH_4F ; and the like.

[0037] It is preferred that the fluoride electrolytes have a pH below 5, with a pH range of 4-5 being most preferred. Adjusting the pH may be done by adding acid, as is known in the art. Inorganic acids such as sulfuric, phosphoric, or nitric acid, are generally preferred when adjusting the pH is needed or desired. Suitable acidified fluoride electrolytes include, for example, a 0.5 M H_3PO_4 +0.14 M NaF solution, a 0.5-2.0 M $\text{Na}(\text{NO}_3)$ +0.14 M NaF solution, a 0.5-2.0 M NH_4NO_3 +0.14 M NH_4F , or a combination of 0.5 M H_3PO_4 +0.14 M NaF+0.05-1.0 M $\text{Na}(\text{NO}_3)$.

[0038] Any organic solvent, or mixture of organic solvents, which is capable of solvating fluoride ions and is stable under the anodization conditions may be used as an organic electrolyte. The organic electrolyte may also be a miscible mixture of water and an organic solvent. It is preferred that about 0.16 wt % to about 95% wt % water be present in an organic electrolyte because water participates in the initiation and/or formation of the nanotubes. Preferably, the organic solvent is a polyhydric alcohol such as glycerol, ethylene glycol (EG) or diethylene glycol (DEG). One advantage of using an organic electrolyte is that during the annealing step, the organic solvent is volatilized and decomposes under the annealing conditions but also results in carbon doping of the titanium dioxide or titanium alloy nanotubes. The incorporation of carbon in the TiO_2 lattices increases the conductivity of the nanotubes and improves the charge-discharge performance as an anode material in Li-ion batteries. Preferred electrolyte solutions containing a non-aqueous solution include ethylene glycol+0.2-0.5 wt % NH_4F , and glycerol+0.2-0.5 wt % NH_4F .

[0039] Various elements in the electrolyte solution may be doped into the oxide nanotubes, such as carbon, nitrogen, phosphorus, sulfur, or fluorine. If desired, doping may be accomplished through the interaction with the electrolyte, as discussed above, or by conventional means known in the art, such as solid source diffusion, gas diffusion, or via a thermal treatment, such as in the annealing step. Incorporation of fluorine in the titanium and titanium alloy oxides is believed to expand the lattice structure, in some cases significantly. This expanded lattice, in turn, is believed to lead to increase in the concentration of ions that can be stored in the oxide lattice. Thus, incorporating or doping the oxide nanotubes with fluorine is a preferred embodiment of this invention.

[0040] Various combinations of solutions can be employed in order to tailor the morphology of the nanotubes, such as surface with ridges or without ridges (straight nanotubes). Different electrolyte solutions can be used depending on the compatibility with the materials being anodized, as appreciated by one of skill in the art. For example 0.5 M H_3PO_4 +0.14 M NaF solution can be used for creating titanium oxide nanotubes with ridges. Such a solution appears to work adequately for all titanium and titanium alloy materials, such as Ti-6Al-4V. For instance, using a Ti or a Ti-6Al-4V alloy material, anodization in 0.5 M H_3PO_4 +0.14 M NaF results in nanotubes with ridges; using a Ti-Mn alloy, anodization in 0.5 M H_3PO_4 +0.14 M NaF results in nanoparticle morphology. The electrolyte solution can also be varied depending on the

length of the nanotube that is desired. For instance, a 2.0 M $\text{Na}(\text{NO}_3)_2$ +0.14 M NaF solution with a pH of 3.8-6.0 can be used for growing relatively long nanotubes. The combination of 0.5 M H_3PO_4 +0.14 M NaF+0.05-1.0 M $\text{Na}(\text{NO}_3)_2$ is also preferred.

[0041] The electrolyte solution may also contain a complexing agent, e.g. EDTA, tri-sodium citrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7\cdot 2\text{H}_2\text{O}$), citric acid, sodium pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7\cdot 10\text{H}_2\text{O}$), gluconate, gluconic acid, tartarate, malate, glycine, and other complexing agents known in the art. The complexing agent, which is preferably added in the amount of 0.1-5.0 wt %, with 0.5-1.0 wt % being most preferred, allows for the formation of improved nanopores at a faster rate. It is believed that the addition of EDTA in aqueous electrolyte solutions increases the kinetics of nanotubular formation.

[0042] The formation of the nanotubes may be improved by mixing or stirring the electrolyte during anodization. Conventional techniques for mixing or stirring the electrolyte may be used, e.g. mechanical stirring, magnetic stirring, etc. The electrolyte solution should preferably be stirred continuously during the entire anodization process, or at least until a steady state is reached.

[0043] In a preferred embodiment, the mixing is achieved by ultra-sonicating the electrolyte solution during anodization. Sonication may be done using commercially available devices. Ultra-sonicating the electrolyte during anodization aids in nanotube formation giving more uniform and smooth nanotubes than achieved with other mixing techniques. Ultra-sonication also provides more uniform concentration of radicals and pH preventing or at least minimizing the existence of concentration and pH gradients which may occur during anodization. Various ultra-sonication techniques may be found in PCT Application No. PCT/US06/35252, filed Sep. 11, 2006 and PCT Application No. PCT/US06/47349, filed Dec. 13, 2006, both of which are herein incorporated by reference in their entirety.

[0044] When employing ultrasonication, the container of the electrolyte may be placed inside an ultrasonication bath. Alternatively, an ultrasonic field may be introduced near the anode surface by immersing an ultrasonicator horn/probe in the solution. The ultrasonication frequency typically ranges from 16-50 kHz and the power intensity typically varies from 0.1-10 W/cm².

[0045] Self-ordered oxide nanotubes can typically be obtained more quickly with ultrasonic mixing than conventional mixing techniques (i.e. 20 minutes), for example, when under an applied external potential of 20 V in phosphoric acid and sodium fluoride electrolytes. The effect of different synthesis parameters viz., synthesis medium (inorganic, organic and neutral), fluoride source, applied voltage and synthesis time are discussed below. The pore diameters can generally be tuned from 30-120 nm by changing the anodization process parameters such as anodization potential and temperature. The pore diameter generally increases with anodization potential and fluoride concentration, and the diameter generally decreases with the electrolyte temperature. A 300-1000 nm thick self-ordered porous titanium dioxide or titanium alloy layer can be prepared by this procedure relatively quickly.

[0046] Anodization by ultrasonic mixing is also more efficient than the conventional magnetic stirring. The anodizing approach discussed above is able to build a porous titanium oxide film of controllable pore size, good uniformity, and

conformability over large areas at low cost. Generally, the anodization step occurs over period of 1-30 hours. However, by using ultrasonic mixing techniques, the anodization time can be reduced by more than 50%. It also leads to better ordered and more uniform titanium oxide and titanium alloy oxide nanotubes compared to nanotubes prepared using conventional magnetic stirring.

[0047] The growth of nanotubes can be improved as anodization time increases. For example, after about 120 seconds of anodization, small pits start to form on the surface of titanium and titanium alloy. These pits increase in size after about 600 seconds, though still retaining the inter-pore areas. After about 900 seconds, most of the surface is covered with an oxide layer, however the pores are not well distinct. After about 1200 seconds, the surface is completely or almost completely filled with self-ordered nanotubes. Anodizing from about 1200 to about 7200 seconds will increase the size of the nanotubes and increase the pore diameter. Further increase in time past 7200 seconds generally does not affect the pore diameters or the length of the nanotubes. However, these times will vary depending the material being anodized, the voltage, the electrolyte, the agitation methods, and other factors appreciated by one of skill in the art.

[0048] The applied potential can affect nanotubes formation and pore size. Generally, 10 V is sufficient to prepare the titanium oxide or titanium alloy oxide nanotubes, with typical voltages ranging from 5-60 V. However, pore uniformity and order have been found to increase upon an application of increased applied potentials, such as 15 V to 20 V, to the system. Preferably, the power source in the anodization reaction is a direct current power source that can supply 40 V of potential and support 20 mA/cm² current density. The anodization voltage may be applied in steps (0.5 V/min) or the voltage may be continuously ramped at a rate of 1-10 V/min from open circuit potential to higher values. It is believed that this process results in pre-conditioning of the surface to form nanoporous surface layer. After reaching the final desired anodization potential, the voltage is generally maintained at constant value. The anodization process is continued for approximately 20 minutes or more after the current has reached a plateau value.

[0049] Pore size also increases with the application of the higher applied potentials. Thus, the pore openings of the titanium oxide and titanium alloy oxide nanotubes can be tuned as desired by changing the synthesis parameters, including applied voltage and/or fluoride ion concentrations. Preferably, the surface of the material forms nanopores and nanotubes ranging from 10-150 nm diameter, more preferably 60-100 nm.

[0050] The anodization process produces oxide nanotubes that appear on the surface of the material being anodized. FIGS. 2 and 3 show titanium oxide nanotubes produced on a titanium surface after anodization, the anodization being carried out in ethylene glycol (2.5 wt % water) and 0.5 wt % NH₄F solution, 20V, 1 h. As can be seen from these figures, the diameter of the nanotube varies from 30-100 nanometers and the length varies from 400-800 nm.

[0051] Under different anodization conditions, the nanotubes can be increased up to 25 micron in length. For example, anodization of Ti—Mn alloys at 52 V in an ethylene glycol solution containing 2 wt % water and 3 wt % NH₄F for 17 hours produced nanotubes about 12 micron in length. Nanotubes more than 20 micron in length were obtained after anodization time was increased to 20 hours. In this regard,

anodization of Ti—Mn alloys at 30-60 V in an ethylene glycol solution containing 2 wt % water and 3 wt % NH₄F for 3-20 hours represents a preferred embodiment of the invention capable of producing nanotubes having preferred morphologies.

[0052] Longer nanotubes may be desired for certain purposes while shorter nanotubes may be desired for other purposes. In certain embodiments, nanotubes ranging from 10-20 micron in length is preferred, while in other embodiments, for instance the embodiments of the invention relating to CNT growth in the nanotubes, the nanotubes are preferably 3-4 micron in length.

[0053] After anodization, the samples may be cleaned by means known in the art. To sufficiently clean the samples, it is preferred that they are thoroughly washed with distilled water and ultrasonicated in acetone for at least 2 minutes. The cleaned samples may then be dried in air or nitrogen stream and stored in a desiccator.

[0054] After the anodization and optional cleaning step, the nanotubes are annealed in an gaseous atmosphere under conditions known by those of skill in the art. The gaseous atmosphere can be under oxidizing conditions or reducing conditions, as known in the art. If a titanium substrate was used, then the gaseous atmosphere should be an oxidizing atmosphere so that the substrate is oxidatively-annealed. If a titanium alloy substrate was used, the gaseous atmosphere may be include gases known in the art that can be used during annealing, such as oxygen, nitrogen, hydrogen, cracked ammonia, argon, helium, carbon monoxide, or mixture of these gases. Preferably, the titanium alloy is annealed in an oxidizing atmosphere such as oxygen.

[0055] Annealing in an oxidizing atmosphere is preferred when the substrate is used in an energy storage application. Unlike processes used to prepare nanotubes with oxygen vacancies, where annealing in an oxidizing atmosphere is avoided, it has been found that annealing in an oxidizing atmosphere leads to unexpected advantages in energy storage applications, such as increased capacity.

[0056] Any conventional annealing techniques and heating apparatus may be used. The annealing typically takes place at temperatures of approximately 300° C. or higher, preferably 350-650° C., and more preferably from about 450-550° C. As appreciated by those of skill in the art, certain temperature ranges will be preferred for certain substrates. For instance, for Ti—Mn alloy substrates, the preferred temperature range is 300-500° C.

[0057] The reaction may take place for a time period of approximately 1-10 hours. The annealing process is preferably conducted at a heating and cooling rate of about 1-50° C./min, preferably about 1-10° C./min.

[0058] An embodiment of this invention relates to growing carbon nanotubes (CNT) in the titanium oxide and titanium alloy oxide nanotubes. In this embodiment, the nanotubular oxide samples may be used as templates to grow the CNT. To grow CNT, a plurality of catalyst particles should first be deposited in the oxide nanotubes to provide nucleation sites for carbon nanotube growth. Any catalyst particle suitable for CNT growth via chemical vapor deposition may be used. Preferably, the catalyst is cobalt, nickel, iron, or combinations thereof. Cobalt sulfate is a particularly preferred catalyst. The electrolyte composition containing the catalyst is preferably maintained at a pH ranging from 3-7, and is preferably maintained at temperatures ranging from 20-50° C.

[0059] The catalyst particles may be deposited through any technique known in the art. Preferably, the catalyst is electrochemically deposited in the nanotubes via a computer-controlled pulse-reverse electrochemical deposition process, using equipment such as a pulse reverse DC rectifier. See U.S. patent application Ser. No. 11/033,839, filed Jan. 13, 2005, herein incorporated by reference in its entirety, for suitable pulse-reverse electrodeposition techniques.

[0060] For instance, a short cathodic pulse can be given for the potential drop across the semi-conducting barrier layer, while maintaining the current density at a high density. The cathodic pulse assists in making the cathode work piece (for instance, the nanoporous titania) and the high current density assists in depositing the catalyst into the pores in a high-aspect ratio and depositing the catalyst in areas that have high chemical potential. Next, a short anodic pulse is applied. The pulse has a three fold objective: It discharges the capacitance developed in the barrier layer, stops the catalyst deposition immediately, and removes or depletes any extra catalyst deposited other than at bottom of the nanopores. Lastly, a delay time is introduced when no pulse is applied. During this time, it is believed that the metal ions migrate from the outer solution to inside of the pores, thereby replenishing the depleted regions with the catalyst. The entire process is repeated several times. For instance, the process may be repeated for at least 500 cycles or at least 5 minutes, thus providing a minimum of 4 cathodic seconds of deposition time. This process preferentially deposits the catalyst at the bottom of the pores to support CNT growth.

[0061] Conventional chemical vapor deposition (CVD) techniques known in the art may be used to grow the CNT at the catalyst nucleation sites. Under typical CVD conditions, the nanoporous template having the catalyst at the bottom of the pores may be loaded into the chamber of a suitable CVD furnace (typically a quartz chamber) and heated in an inert atmosphere. For example, CNT growth may be accomplished by introducing a carbon source, hydrogen gas, and an inert gas onto the titanium oxide or titanium alloy oxide substrate under typical CVD process conditions. More particularly, the carbon-containing gas that acts as the carbon source is introduced into the CVD chamber with hydrogen and the inert gas.

[0062] The carbon source is preferably acetylene, methane, or carbon monoxide. The inert gas is preferably argon. Preferred chemical vapor deposition conditions include temperatures ranging from 500-700° C., more preferably from 600-650° C.; reaction times starting at about one minute or longer; and flow rates ranging from about 10-200 sccm for the carbon source, about 5-50 sccm for the hydrogen, and about 100-300 sccm of the inert gas.

[0063] This invention also relates to an electrode capable of storing energy. The electrode comprises an anodized and oxidatively-annealed titanium oxide or titanium alloy oxide substrate having a plurality of self-ordered oxide nanotubes. The electrode may be used in an energy storage application, such as a component of a lithium-ion battery.

[0064] None of the available techniques known in the art employ a self-ordered nanotubular array structure or disclose electrodes having a plurality of self-ordered oxide nanotubes that can be used for energy storage applications. The ordered arrays of the nanotubes present in the electrodes provide a large surface area for enhanced incorporation of the lithium ions and an easy pathway for unhindered transportation of ions.

[0065] The anodized and oxidatively-annealed substrate is either a titanium oxide substrate or a titanium alloy oxide substrate. Any alloy that contains titanium may be used. Preferred titanium alloys include Ti—Mn, Ti—Nb, Ti—Zr, Ti—Si, and Ti—Al—V, as discussed above. Nanotubular oxide of alloys such as Ti—Mn, where oxides of Ti and Mn are present, have been shown to produce a multifold increase in discharge capacity.

[0066] The electrode may contain a plurality of catalyst particles deposited at the bottom of the oxide nanotubes to provide nucleation sites for carbon nanotube growth. Preferred catalyst particles include Co, Ni, Fe, and combinations thereof. The catalyst particles may be used to grow carbon nanotubes in the oxide nanotubes.

[0067] This invention also relates to an anodized titanium alloy oxide substrate having a plurality of self-ordered oxide nanotubes. The substrate may be annealed in a gaseous atmosphere, preferably oxygen, as discussed above. The substrate may be used in an energy storage application, or it may be used in other applications, such as in the photo-electrolysis of water and other applications known in the art.

[0068] This invention also relates to a method of using the electrode in an energy storage application. Suitable energy storage applications include as an anode or cathode for batteries. The method involves contacting an anodized and oxidatively-annealed titanium oxide or titanium alloy oxide substrate having a plurality of self-ordered oxide nanotubes with a cell and an electric current, and receiving ions from the energy source in the oxide nanotubes.

[0069] The cell may be a fuel cell or a battery, for instance, a lithium-ion battery or other hydride batteries. The substrate may be contacted to or connected with the cell by any means known in the art, such as that of a conventional battery arrangement where the substrate acts as an electrode, preferably the anode, when the electric current is passed through the cell. The substrate can receive ions, store them, and take on the customary functions of an electrode, as appreciated by those of skill in the art.

[0070] To prepare the electrode in conventional energy storage devices, the electrode components are typically prepared in an initial step and then assembled onto a current collector as a second step. However, in this invention, the oxide nanotubes and substrate are formed as a single component. This allows the titanium or titanium alloy substrate to act as both the current collector and a container that houses the battery. Anodizing the inner surface of the container forms oxide nanotubes on this surface, which can then act as the electrode to the battery in the container. Therefore, one embodiment of this invention is directed towards a battery housed in a container having at least one titanium oxide or titanium alloy oxide inner surface of the container; the surface of the container is anodized under sufficient conditions to grow oxide nanotubes on the surface that can act as the anode to the battery.

[0071] This invention also relates to a lithium-ion battery that contains an electrode that comprises an anodized and oxidatively-annealed titanium oxide or titanium alloy oxide substrate having a plurality of self-ordered oxide nanotubes.

[0072] Lithium-ion batteries having the above-referenced electrodes have been shown to exhibit improved storage capacities and ability to carry lithium load. When the electrode contains an anodized and oxidatively-annealed titanium oxide substrate, the battery has been shown to have a storage capacity of at least 555 mAh/g and a lithium load of at least

1.68 moles per mole of titanium oxide. When the electrode contains an anodized and oxidatively-annealed titanium oxide substrate containing carbon nanotubes grown in the oxide nanotubes, the battery has been shown to have a storage capacity of at least 1.7 Ah/g. When the electrode contains an anodized and oxidatively-annealed titanium alloy oxide, such as an oxide of a titanium-manganese alloy, the battery has been shown to have a storage capacity of at least 1.5 Ah/g. The lithium load for preferred batteries ranges from 3.6-4.3 moles per mole of oxide.

[0073] Accordingly, the electrode preferably has a storage capacity of at least 500 mAh/g, more preferably has a storage capacity of at least 1.0 Ah/g, and most preferably has a storage capacity of 1.5 Ah/g or higher. Additionally, the electrode preferably has a lithium load of at least 1.5 moles per mole of oxide, more preferably a lithium load of at least 3.6 moles per mole of oxide.

[0074] The following examples are intended to illustrate the invention. These examples should not be used to limit the scope of the invention, which is defined by the claims.

EXAMPLES

[0075] The following general procedure may be used to prepare arrays of ordered oxide nanotubes:

[0076] 1. Clean the titanium metal or titanium alloy surface.

[0077] 2. Immerse the material in anodizing solution at room temperature.

[0078] 3. Set up the anodization similar to the schematic shown in FIG. 1, where the material is Ti.

[0079] 4. Provide a direct current power source that can supply 40 V of potential and support 20 mA/cm² current density. Connect the material to be anodized to the positive terminal of the power source and connect a platinum foil (Pt rod/mesh) having an equal or larger area of the metal surface to the negative terminal of power source. An external volt meter and an ammeter may be connected to the circuit in parallel and series respectively for measuring the actual potential and current during anodization. The distance between material and the metal foil is maintained, typically at about 4 cm.

[0080] 5. Apply the anodization voltage in steps (0.5 V/min) or continuously ramp the voltage at a rate of 1-10 V/min from open circuit potential to higher values, typically 5-30 V. The electrolyte should be continuously stirred during the anodization process. This process results in pre-conditioning of the surface to form nanoporous surface layer. After reaching the final desired anodization potential, maintain the voltage at constant value, as described in the next step.

[0081] 6. Anodize the surface at 5-30 V to form nanopores/tubes (10-150 nm diameter) on the material. Monitor the current and allow typically 20 minutes or more after the current has reached a plateau value.

[0082] 7. Optionally, ultrasonication of the electrolyte can be carried out during anodization. When employing ultrasonication, the container of the electrolyte is placed inside an ultrasonication bath or an ultrasonic field is introduced near the anode surface by immersing an ultrasonic horn/probe. The ultrasonication frequency can be 16-50 kHz and the power intensity can vary from 0.1-10 W/cm².

[0083] 8. After anodization, the samples are thoroughly washed with plenty of distilled water and ultrasonicated

in acetone for 2 minutes. The cleaned samples are dried in air or nitrogen stream and stored in a desiccator for further annealing.

[0084] 9. Annealing of the anodized specimens is carried out in a controlled oxidizing atmosphere furnace with continuous gas purging. The annealing temperature varies from 350-650° C. and the annealing time varies from 1-10 h. The heating and cooling rates are controlled at 1-50° C./min.

Preparation of Catalyst in the Nanotubular Oxide Template

[0085] The following general process is used to deposit Co catalyst at the bottom of the nanotubes through which the CNTs then grow.

[0086] An electrolyte of 300 g/L of CoSO₄·7H₂O (Cobalt Sulphate)+45 g Boric acid was prepared. The electrolyte was maintained at a pH of 4.5 and at 35° C. A pulse reverse DC rectifier was used for electrodeposition. An 8 msec cathodic pulse (with current control) was given for the potential drop across the semi-conducting barrier layer. The current density was limited to -70 mA/cm². An anodic pulse was applied for 2 msec with the current density restricted to +70 mA/cm². A delay time of 600 msec is given when no pulse is applied.

[0087] The whole process described above is repeated for 500 cycles or 5 min to provide 4 cathodic seconds of deposition time.

Preparation of CNT on the Nanotubular Oxide

[0088] The CNTs were produced by chemical vapor deposition (CVD). The nanoporous titania template with Co at the bottom of the pores was loaded into the quartz chamber of a CVD furnace and heated in argon atmosphere at a flow rate of 200 standard cubic centimeters (sccm) for 5 min to reach a stable temperature of 635° C. After this, a mixture of acetylene, hydrogen, and argon was introduced into the chamber at flow rates of 40, 20 and 200 sccm, respectively, for 3 min at the same temperature. FIGS. 4(a)-(d) illustrate the SEM images of the nanocomposite structure of CNT and TiO₂ nanotubes.

Li-Ion Charge-Discharge Experiments

[0089] FIG. 5 schematically illustrates the experimental arrangement for Li-ion charging-discharging studies. Li foil (1 mm thick) and Li wire (3 mm diameter) were used as counter electrode and reference electrode respectively. As Li is very reactive with air and moisture, the experiments were carried out in a tightly sealed environment by controlling the oxygen and moisture level below 1 ppm. This was achieved by using a dry glove box and evacuating and purging with dried ultra high purity argon multiple times. Filling the glove box with dry Ar during experiments and maintaining low levels of oxygen and moisture was ensured by burning a pierced 25 W continuously. When the pierced bulb burned for more than two hours, the atmosphere was considered satisfactorily dry and oxygen free.

[0090] The preparatory work of the experiments such as mixing the electrolyte and electrical connections is generally carried out only after achieving the desired atmospheric condition. The electrolyte typically contains 1 M of lithium salt such as LiPF₆, LiClO₄, LiBF₄, LiAlCl₄, lithium perfluoromethylsulfonimide (Li(CF₃SO₂)₂N), lithium perfluoromethyl-

sulfomethanide ($\text{Li}(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}$), or lithium perfluoromethylsulfomethanide ($\text{Li}(\text{CF}_3\text{SO}_2)_3\text{C}$). In this case, LiPF_6 was used.

[0091] The solvent is typically a mixture of alkyl carbonates such as propylene carbonate (PC), ethylene carbonate (EC), dimethyl carbonate (DMC), or diethyl carbonate (DEC). PC+DEC, or EC+DMC. In this case, PC+DMC with 1:1 v/v ratio was used.

[0092] Charge-Discharge cycles were carried out on the nanotubular oxide samples using the similar set up described in FIG. 5. The samples investigated were (1) pure TiO_2 nanotubular arrays annealed at 500°C . in oxygen for 6 h, and (2) anodized Ti—Mn alloy annealed at 500°C . for 6 h in oxygen. Charging was carried out by supplying a constant positive current density of 0.1 mA/cm^2 and recording the potential.

[0093] Multiple Charge-Discharge cycles were carried out using a two-electrode configuration to simulate commercial battery testing. This set up is similar to that used in the charge-discharge cycles with the addition of an assembly for battery testing that includes a cathode and an anode. A representative schematic is shown in FIG. 6. In this configuration, the sample of oxide substrate containing the nanotubular arrays was connected to the negative terminal of the potentiostat and acted as anode. The cathode (positive terminal) used was a commercial LiCoO_2 electrode (a 70-micron thick LiCoO_2 coating on both sides of an 85-micron thick Al foil). A commercially available polymer-film separator was placed in between the anode and cathode, and a few drops of the electrolyte was placed inside the electrode assembly.

[0094] Using this set-up, charge-discharge experiments were run. Charging was carried out in two steps. In the first step, charged was performed at a constant current of 300 mA/g until the potential reached 4.3 V . In the second step, charging was performed at a constant potential of 4.3 V until the charging current reached 10% of its initial value. After this charging cycle, the discharge cycle was carried out at a constant current that varied from $0.3\text{--}0.9\text{ A/g}$ (typically 1 C-3 C of a commercial battery).

[0095] Cyclic voltammetry (CV) was carried out using nanotubular TiO_2 specimens annealed at 500°C . in oxygen for 6 h. The results of CV indicate the potentials associated with Li-ion insertion and de-insertion in addition to the oxidation-reduction conditions of the metal, for instance Ti^{4+} and Ti^{3+} . The separation of the oxidation-reduction peaks shows the reversibility of the system when different potential scan rates are employed.

[0096] FIG. 7 illustrates a cyclic voltammogram of TiO_2 nanotubes annealed at 500°C . for six hours in oxygen. The electrolyte is 1 M LiPF_6 with lithium as counter and reference electrode. Two anodic and cathodic peaks indicate presence of lower symmetry phase in the TiO_2 nanotubes. The peak at 1.5 V corresponds to Li—Ti—O spinel and peak at higher potential is associated with lower symmetry anatase.

[0097] A similar cyclic voltammogram for $(\text{TiMn})\text{O}_2$ is shown in FIG. 8. As shown in FIG. 8, the cathodic and anodic peaks occurred at similar potentials as that of TiO_2 shown in FIG. 7. This may indicate that the manganese is not directly involved in the electrochemical reaction. Under one theory, it is believed that the manganese instead acts to expand the lattice of the titanium oxide. This, it is believed, provides the ability for the titanium oxide nanotubular structure to take on additional ions and increase its capacity.

[0098] FIG. 9(a) illustrates the potential variation during the charging cycles. Discharging was carried out by applying

a negative current density of -0.1 mA/cm^2 . The potential of the nanotubular sample was recorded continuously during the discharge as shown in FIG. 9(b). The initial potential during discharge was about 4 V , which is closer to the open circuit potential of the nanotubular oxide in 1 M lithium solution. The potential decreased rapidly during first 200 seconds and the decay was almost steady. The capacity was calculated factoring in the amount of discharge that occurred above 2 V .

[0099] FIG. 10 shows the discharge behavior of titanium oxide and a titanium-manganese alloy oxide until 2 V . No fading of capacity was observed with number of cycles. After 200 seconds of discharge, a quasi plateau potential region was observed. In view of the plateau capacity (for $\sim 200\text{ s}$), the lithium insertion was calculated to be 1.68 mole per mole of TiO_2 .

[0100] From the figure, the discharge capacity of the titanium oxide nanotubes was calculated as 1.3 Ah/g . The discharge capacity of titanium-manganese oxide nanotubes was found to be about three times that of titanium oxide substrate based on the 2 V cut-off potential. For example, TiO_2 nanotubes took about 500 seconds to reach 2 V , whereas Ti—Mn oxide nanotubes took about 1500 seconds. In this calculation, the weight of the nanotubes present on the metal substrate was theoretically estimated based on the geometry. The estimated weight of the nanotubes was about 0.01 mg/cm^2 . Even considering only rapid discharge behavior for capacity determination that occurred within 200 seconds, the capacity of TiO_2 nanotubes would still be 555 mAh/g . As 1 M Li in TiO_2 would result in 330 mAh/g , this capacity corresponds to 1.68 M Li per mole of TiO_2 . It should be noted that the capacity did not fade with cycling. Experiments were carried out up to 10 cycles. The capacity remained almost constant in all the cycles.

[0101] The SEM images of the nanotubular structures after ten cycles of Li-ion insertion and de-insertion are shown in FIG. 11. As shown in the images, the cyclic lithium intercalation and removal did not alter the nanotubular structure.

[0102] The following examples were run based on the anodization conditions, charge-discharge cycles, and battery performance conditions described above:

Example 1

Titanium Oxide as a Negative Electrode

[0103] 1. Conditions:

[0104] a) Material: Ti.

[0105] b) Anodizing time: 17 hr at 51.6 V .

[0106] c) Anneal time: 350°C . 5 hr in O_2 .

[0107] d) Thickness of nanotube: $8.6\text{ }\mu\text{m}$, area of electrode: 0.28 cm^2 .

[0108] e) Weight calculation: density= 4 g/cm^3 , porous rate=50%, $\text{Wt}=4\times 50\%\times 1\times 0.00086=1.72\text{ mg/cm}^2$ or 0.47 mg .

[0109] 2. Discharge Storage capacity of TiO_2

| Cycle | 1 | 2 | 3 | 4 | 5 |
|---------------------------|------|------|------|-----|-----|
| Specific capacity (mAh/g) | 1310 | 1080 | 1020 | 844 | 756 |
| Cycle | 6 | 7 | 8 | 9 | 10 |

| -continued | | | | | |
|---------------------------|-----|-----|-----|-----|-----|
| Specific capacity (mAh/g) | 737 | 721 | 667 | 655 | 453 |

Example 2a
(TiMn)O₂ as a Negative Electrode

- [0110] 1: Conditions:
[0111] a) Material: Ti8Mn (titanium alloy having 8 wt % manganese).
[0112] b) Anodizing time: 1.0 hr at 20V.
[0113] c) Anneal time: 350° C. 1 hr in O₂.
[0114] d) Thickness of nanotube: 1 μm, area of electrode: 0.88 cm².
[0115] e) Weight calculation: density=4 g/cm³, porous rate=50%, Wt=4×50%×1×0.0001=0.20 mg/cm² or 0.18 mg.
[0116] 2: Charge/discharge:
[0117] Discharge current: 0.067 mA=370 mA/g, 20000 s cut off at 2.8V.
[0118] Charge current: Charge: 0.45 mA for 1000 s or maximum 4.3V, 9000 s at constant voltage cut off at 0.10 mA.
[0119] 3: Battery performance:

| | | | | | | | | |
|---------------------------|------|------|------|------|------|------|------|-----|
| Cycle | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| Specific capacity (mAh/g) | 730 | 1020 | 1670 | 1560 | 1670 | 1400 | 1172 | 912 |
| Cycle | 9 | 11 | 12 | 13 | 14 | 15 | 16 | 17 |
| Specific capacity (mAh/g) | 1070 | 1390 | 860 | 611 | 584 | 678 | 584 | 488 |

- [0120] 4: Capacity for Cycle 5: 0.28 mAh.
Charge rate=0.95 C; discharge rate=0.24 C.

Example 2b
(TiMn)O₂ as a Negative Electrode

- [0121] 1: Conditions:
[0122] a) Material: Ti8Mn.
[0123] b) Anodizing time: 3.0 hr at 20V.
[0124] c) Anneal time: 500° C. 5 hr in O₂.
[0125] d) Thickness of nanotube: 1.2 μm, area of electrode: 0.85 cm².
[0126] e) Weight calculation: density=4 g/cm³, porous rate=50%, Wt=4×50%×1×0.00012=0.24 mg/cm² or 0.20 mg.
[0127] 2: Charge/discharge:
[0128] Discharge current: 0.065 mA=325 mA/g, 20000 s cut off at 2.8V.
[0129] Charge current: Charge: 0.40 mA for 1000 s or maximum 4.3V, 9000 s at constant voltage cut off at 0.10 mA.

- [0130] 3: Battery performance:

| | | | | | | | |
|---------------------------|------|------|------|------|------|------|------|
| Cycle | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| Specific capacity (mAh/g) | 580 | 694 | 704 | 1160 | 1000 | 1060 | 1040 |
| Cycle | 8 | 9 | 10 | 11 | 12 | 13 | 14 |
| Specific capacity (mAh/g) | 1040 | 1400 | 1520 | 1580 | 1600 | 1670 | 1200 |
| Cycle | 15 | 16 | 17 | 18 | 19 | 20 | |
| Specific capacity (mAh/g) | 1330 | 1250 | 1340 | 1240 | 1180 | 1140 | |

- [0131] The specific capacity for this example is shown in FIG. 12.
[0132] 4: Capacity of cycle 10: 0.30 mAh.
Charge rate=0.87 C; discharge rate=0.22 C.

Example 2(c)
(TiMn)O₂ as a Negative Electrode

- [0133] 1: Conditions:
Anodizing Voltage: 51.6V.
[0134] a) Material: Ti8Mn.
[0135] b) Anodizing time: 17 hr at 51.6V.
[0136] c) Anneal time: 350° C. 5 hr in O₂.
[0137] d) Thickness of nanotube: 8.6 μm, area of electrode: 0.28 cm².
[0138] e) Weight calculation: density=4 g/cm³, porous rate=50%, Wt=4×50%×1×0.00086=1.72 mg/cm² or 0.47 mg.
[0139] 2: Charge/discharge:
[0140] Discharge current: 0.40 mA=850 mA/g, 20000 s cut off at 2.8V.
[0141] Charge current: Charge: 2.0 mA for 1000 s cut off at 4.3V, 9000 s at constant voltage cut off at 0.10 mA.
[0142] 3: Battery performance:

| | | | | | | | |
|---------------------------|------|------|------|------|------|------|------|
| Cycle | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| Specific capacity (mAh/g) | 1470 | 1464 | 1434 | 1361 | 1313 | 1200 | 846 |
| Cycle | 8 | 9 | 10 | 11 | 12 | 13 | 14 |
| Specific capacity (mAh/g) | 977 | 1019 | 1031 | 1019 | 1031 | 1050 | 1099 |
| Cycle | 15 | 16 | 17 | 18 | 19 | 20 | |
| Specific capacity (mAh/g) | 1106 | 1078 | 1057 | 1050 | 1057 | 1085 | |

- [0143] The specific capacity for this example is shown in FIG. 13.

[0144] 4: Capacity of cycle 5: 0.62 mAh.
Charge rate=0.63 C; discharge rate=0.65 C.

Example 3

Comparison of Battery Materials

[0145] Table 1 shows a comparison of the output current voltage, specific capacity, specific energy, and specific power of various battery materials using tests similar to those described above. The table compares the following cathodes: (a) a conventional graphite/LiCoO₂ electrode; (b) a nano-phosphate prepared in accordance with the disclosure set forth in Chung et al., *Nature Materials*, 2 (2002) 123-128, described above; (c) a titanium oxide nanoparticles electrode, prepared in accordance with the disclosure set forth in Subramanian et al., *J. Power Sources*, 159 (2006) 186-192, described above; (d) a titanium dioxide nanotubular array, prepared in accordance with this invention; and (e) titanium manganese nanotubular array, prepared in accordance with this invention.

TABLE 1

| Electrode | Output Current Voltage (V) | Specific capacity (mAh/g) | Specific Energy (kWh/kg) | Specific Power (kW/kg) |
|--------------------------------|----------------------------|---------------------------|--------------------------|------------------------|
| Graphite/LiCoO ₂ | 3.7 | 290 | 1.38 | 0.7 |
| Nano-phosphate | 3.5 | 140 | 0.11 | 1.7 |
| TiO ₂ nanoparticles | 2.0-2.5 | 120 | 0.2 | 0.5 |
| TiO ₂ nanotubes | 3-4 | 475-1300 | 1.3-4.0 | ~2.0 |
| (TiMn)O ₂ nanotubes | 3.5 | 1200-1500 | 3.8-4.8 | ~2.7 |

[0146] As can be seen in Table 1, the electrode prepared in accordance with the invention (TiO₂ nanotubes and (TiMn)O₂ nanotubes) demonstrated an improvement over the convention electrodes for specific capacity, specific energy, and specific power, while also demonstrating the same or about the same output current voltage.

[0147] In particular, the table confirms that the titanium oxide and titanium alloy oxide nanotubes of this invention outperform titanium oxide nanoparticles for important battery measurements. It is believed that the better current transport and easy diffusion pathways for Li-ions provided by the titanium oxide and titanium alloy oxide nanotubes enables this improvement. Additionally, the titanium oxide and titanium alloy oxide nanotubes exhibit a diffusion length of a half of wall thickness. In contrast, the titanium oxide nanoparticles are believed to exhibit higher contact electric resistance and longer diffusion lengths, which results in poorer properties as an energy storage device.

[0148] FIG. 14 shows a cross-section of anodized (TiMn)O₂ showing the length of the nanotubes. FIG. 15 depicts the oxygen K-edge electron energy loss spectrum of an anodized single nanotube of Ti—Mn oxide. The identified peaks, shown as (a), (b), (c), and (d) suggest (Ti, Mn)O₂ stoichiometry in the anodized conditions.

[0149] FIG. 16 shows the electron energy loss spectroscopy results of the Ti—Mn oxide nanotubes after Li-insertion. The inset figure indicates Li-insertion is present in the nanotubes. The ability of the nanotubes to receive and store a charge, as confirmed in this figure, indicates that the nanotubes are acting as an battery rather than as a super capacitor.

[0150] FIG. 17 depicts an electrode on an 8.3 micro 0.28 cm² cycle. The electrode is a TiMn substrate, anodized at 51.5 V for 17 hours at 350° C. The substrate was annealed for five hours producing nanotubes having a thickness of 8.3 micron

and weighing 0.47 mg. The charge cycle was 2.0 mA for 1000 s, cut off at 4.3 V, 9000 at constant V, cut off at 0.1 mA. The discharge cycle was 850 mA/g or 0.40 mA for 20,000 s, cut off at 2.8 V. The specific capacity of the electrode was calculated at 2.44 mAh/cm² or 1470 mAh/g.

[0151] The graph in FIG. 17 shows the potential profile of the Ti—Mn oxide discharge using a two-electrode configuration where the cathode was a commercial-grade LiCoO₂ electrode having an anode-to-cathode mass ratio of 1:50. The plateau potential of discharge is shown to be around 3.5 V.

1-20. (canceled)

21. A method of manufacturing an anodized and oxidatively-annealed titanium oxide or for energy storage, comprising: anodizing a titanium substrate under conditions sufficient to form an anodized titanium oxide having a plurality of self-ordered oxide nanotubes on the anodized surface; and annealing the oxide nanotubes in a controlled oxidizing atmosphere to produce an anodized and oxidatively-annealed titanium oxide substrate having a surface area sufficient to incorporate ions for energy storage.

22. The method of claim 21, wherein the anodizing step comprises electrochemically anodizing the titanium material in an aqueous or non-aqueous electrolyte solution containing a fluoride salt.

23. The method of claim 22, wherein the non-aqueous solution is a polyhydric alcohol selected from the group consisting of glycerol, ethylene glycol, diethylene glycol, and mixtures thereof.

24. The method of claim 22, wherein the electrolyte solution further comprises a complexing agent.

25. The method of claim 21, wherein the anodizing step further comprises ultrasonication the electrolyte solution during anodization.

26. The method of claim 21, further comprising the steps of:

electrodepositing a plurality of catalyst particles in the oxide nanotubes to provide nucleation sites for carbon nanotube growth, and growing carbon nanotubes at the nucleation sites by introducing a carbon source, hydrogen gas, and an inert gas onto the titanium oxide or titanium alloy oxide substrate under chemical vapor deposition process conditions.

27. A method of manufacturing an anodized titanium alloy oxide substrate, comprising: anodizing a titanium alloy substrate under conditions sufficient to form anodized titanium alloy oxide having a plurality of self-ordered oxide nanotubes on the anodized surface; and annealing the oxide nanotubes in a controlled gaseous atmosphere to produce an anodized titanium alloy oxide substrate.

28. The method of claim 27, wherein the anodizing step comprises electrochemically anodizing the titanium alloy material in an aqueous or non-aqueous electrolyte solution containing a fluoride salt.

29. The method of claim 28, wherein the non-aqueous solution is a polyhydric alcohol is selected from the group consisting of glycerol, ethylene glycol, diethylene glycol, and mixtures thereof.

30. The method of claim 27, wherein the electrolyte solution further comprises a complexing agent.

31. The method of claim 27, wherein the anodizing step further comprises ultrasonication the electrolyte solution during anodization.