

Effect of Potential and Aqueous Electrolyte In Different Anode Coating Steps on the Structure and Specific Capacitance of Titanium Dioxide Nanotubes

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Abstract:

We report the fabrication and electrochemical properties of anodic TiO₂ nanotube arrays (TNA) formed on Ti-alloy substrate as supercapacitor electrode. Physical or chemical cleaning method was applied for surface pretreatment of Ti-alloy sheet. The single-step and triple-step of anodization were carried out in ethylene glycol electrolyte containing 0.5wt % NH₄F under the applied potential of 40 and 50 V, and anodizing time for the last coating of 3 and 5 h. The influence of aqueous ethylene glycol electrolyte containing 0.5wt % NH₄F and 5wt% distilled water on the morphology of TNA was compared. Annealing the as-grown TNA at 500°C transformed an amorphous phase to crystalline phase. Morphologies, crystal structure and supercapacitor performances of samples were investigated by scanning electron microscopy, X-ray diffraction and electrochemical measurement, respectively. Cyclic voltammetry was measured in 1 M H₂SO₄ electrolyte at -0.7 V to -0.1 V with different scan rate from 5 to 60 mV/s. Electrochemical impedance spectroscopy was investigated with the frequency ranging of 0.01 Hz to 100 kHz in the same electrolyte. Results showed that triple-step anodization of chemical-cleaned Ti-alloy sheet with 5 h of the final coating in aqueous electrolyte under applied potential of 50 V flowed by air annealing gave the well-porous dense structured TNA. Moreover, its capacitance was up to 63.73 F/g at the scan rate of 5 mV/s corresponded to the electrochemical impedance behavior.

Keywords: Anodization method, Structure of titanium dioxide nanotube, Supercapacitor, Titanium dioxide nanotube

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I. INTRODUCTION

Supercapacitors (SCs) or electrochemical capacitors have received a lot of attentions worldwide in many research studies as energy storage devices in many fields. SCs have been developed to meet environmentally friendly properties with fast charge-discharge rates and higher capacitance value than other capacitors. Also SCs own high power density typically up to one hundred times with more energy per unit volume or mass than electrolytic capacitors. In addition, they have longer cycling lifetimes compared to most rechargeable batteries [1]. Hence, these benefits make SCs an affirmative power source candidate in

the field of flexible electronics. Different electrochemical properties of SCs are due to the internal interaction of electrode material and electrolyte solutions. According to the type of electrode material and the unique charge-storage mechanism within internal structure, superconductors are classified into electrochemical double-layer capacitors (EDLCs) and pseudocapacitors [2]. EDLCs is achieved by non-faradaic mechanism involving physically charge separation in a Helmholtz double layer at the interface between a conductive electrode and an electrolyte. On the other hand, the electron charge-transfer between electrode and electrolyte in pseudocapacitors is caused by the faradaic

mechanism that involving with redox reactions, intercalation or electrosorption. Therefore, pseudocapacitors have enhanced the capable of charging and discharging from tens of seconds to several minutes. So that they can store as much charge as some batteries, while operating much faster. In general, carbon based-materials are widely used for EDLCs while conducting polymer or metal oxides such as ruthenium oxide (RuO_2), nickel oxide (NiO), zinc oxide (ZnO), titanium dioxide (TiO_2) and manganese dioxide (MnO_2) are used as electrodes for pseudocapacitors [3], [4]. Because of the semiconducting properties and long-term chemical stability, TiO_2 is an interesting electrode material for electrochemical energy storage systems. The ideal capacitive response of TiO_2 was observed as the faradaic behavior as the rectangular cyclic voltammetry curves indicating that the storage mechanism in TiO_2 comprises conventional electric double-layer storage [3], [4]. TiO_2 nanoporous structured particles were synthesized by three different methods, namely sol gel, ultrasonic, coprecipitation, hydrothermal and anodization route [1]. Among all these methods, electrochemical anodization of the metal substrate has caught the most attention because of its controllable, ease of handling, reproducible results, simple in preparation, cost-effective method and giving TiO_2 nanotube arrays (TNA) with good adherent strength. Anodic oxidation of Ti using various fluoride-containing electrolytes like HF, NaF, NH_4F , $(\text{NH}_4)_2\text{H}_2\text{PO}_4$, $\text{NH}_4\text{F}/\text{CH}_3\text{COOH}$, $\text{H}_2\text{SO}_4/\text{HF}$, $\text{Na}_2\text{HPO}_4/\text{NaF}$, etc. [5]. Investigations of capacitive properties of anodic TiO_2 as supercapacitor were reported in the term of electrical capacitance. The TiO_2 nanotubes from single-step of anodization had the capacitance up to $1.84 \text{ mF}/\text{cm}^2$ [2], $853.3 \text{ F}/\text{g}$ at a current density of $1.0 \text{ A}/\text{g}$ [6] and $25.9 \text{ mF}/\text{cm}^2$ [7]. Synthesize TiO_2 nanotubes by triple-step anodization gave the hexagonal shaped-porous structure of the TiO_2 after the first anodic coating, well arrangement of porous structure was presented after the second anodic coating [8]. Moreover, the growth rate of TiO_2 nanotubes at the third anodic coating was faster giving the TiO_2 nanotubes with a

longer tube length and more consistent arrangement of the structure [9]. Influence on the specific capacitance of the electrode depends on the structure and morphology of TiO_2 nanotubes. These are related to various factors used in the preparation of the material such as the type of substrate, pretreatment, the curing of the crystal structure, electrolyte solution, the process of anode coating, the electric potential and the time used for anode coating etc. Most researchers used pure titanium sheets and pure titanium foil as the Ti-substrate in anodization, mostly the one-step of anodization has been reported. In the present paper, Ti-alloy was used as the substrate for anodization. The effects of substrate pretreatment, aqueous electrolyte, potential voltage, time and anodization step on surface morphology and electrochemical properties of TNA film as effective electrode for supercapacitor were carried out.

II. Experimental

a. Materials and Chemicals

Ti-alloy sheet was purchased to be used as the substrate. The reagents and electrolytes such as ethylene glycol (EG), ammonium fluoride (NH_4F), potassium hydroxide (KOH), hydrofluoric acid (HF) and ethanol ($\text{C}_2\text{H}_5\text{OH}$) were obtained from RCI Labscan Limited. All solutions were of analytical grade. Deionized water was used in all the experiment.

b. Pretreatment of Ti-Substrate

Ti-alloy sheet was cut in the small pieces of $2 \text{ cm} \times 2 \text{ cm}$. The methods of surface pretreatment of these substrates were used in order to compare the morphology of anodic TiO_2 nanotube arrays (TNA). Herein, Ti-substrate was pretreated either physical or chemical cleaning (PC and CC respectively). For the first method, it was mechanically polished using abrasive paper of No.2000 followed by washing with deionized water before drying in the ambient air. In contrast, the Ti substrate was chemical cleaned by the mixture of HF (49wt.%) and nitric acid (HNO_3 , 70%) at the ratio of 25 to 75 by volume.

c. Preparation of TiO₂ Nanotube Arrays

TiO₂ nanotube arrays (TNA) were synthesized by electrochemical anodization in a 2-electrode cell equipped with a direct current DC power supply as our previous study [10]. Non-aqueous electrolyte (NE) was ethylene glycol containing 0.5wt% NH₄F while an aqueous electrolyte (AE) was used ethylene glycol containing 0.5wt% NH₄F and 5wt% H₂O. The anodization was carried out at the applied potential of 40 and 50 V, for 3 and 5 h using the single- and triple-step anodization method. For the triple-step anodization, the constant potential was applied instantly at the first oxidation for 1 h, then the as-anodized TNA sample was removed by sonicating in deionized water, subsequently; this Ti-substrate was used as anode again for 1 h at the second-step of anodization. After that, the TNA layer was ultrasonically removed again. The exposed Ti-substrate was then treated in the same environment at the third anodization for 3 and 5 h. All anodization steps were conducted in fresh electrolyte at room temperature. After anodization completed, the samples were thoroughly cleaned with deionized water and dried in the ambient air. Then the as-prepared amorphous TNA on Ti-substrate was annealed in air at 500C for 3 h under the heating rate and cooling rate of 5C/min to convert the amorphous phases to crystalline phases.

d. Characterization

The morphology and microstructure of samples was examined by a scanning electron microscopy (SEM: Hitachi S-3000N) and field emission scanning electron microscopy (FESEM: FEI Helios, NanoLab G3 CX). The crystalline phase was analyzed by an X-ray Diffractometer (XRD: PANalytica, EMPYREAN) with Cu K source in the range of 2 from 10 to 90 at the scan rate of 4/min.

e. Electrochemical Measurement

The electrochemical properties were carried out using Reference 600™ Potentiostat/Galvanostat/ZRA using a 3-electrode configuration with a graphite and a saturated calomel electrode (SCE, Hg/Hg₂Cl₂) served as a counter and a reference electrode. The as-prepared electrode was used as a

working electrode directly. The measurements were carried out in 1 M H₂SO₄ aqueous solution by CV technique within the potential window of -0.7-0.1 V (vs. SCE) at a scan rate of 5, 10, 20, 30, 40, 50, and 60 mV/s. Electrochemical impedance spectroscopy (EIS) determinations were carried out in the frequency range from 0.01 Hz to 100 kHz at the constant potential of 5 mV in 1 M H₂SO₄ aqueous solution at room temperature. Equation (1) was used for the calculation of specific capacitance, where C represents the specific capacitance (F/g), I and V are the current density (A) and potential (V) illustrated in CV curves, μ is the scan rate (mV/s), m and ΔV are the mass of anodic TNA on Ti-electrode (g) and potential tested period (V), respectively.

$$C = \left(A \int IdV \right) / (\mu m \Delta V) \quad (1)$$

III. Results and discussion

a. Structure and Morphology

The prepared Ti-specimens for anodization were initially either physical or chemical cleaned; named PC-Ti and CC-Ti respectively, in order to remove the surface impurities. Well organized-anodic TNA with improved adhesion force between the film and the Ti-substrate was expected. As presented in Fig. 1(a), a rough, irregular and corrugated surface was revealed for the as-received Ti-alloy specimen because it was covered with native oxide layer. It can be seen in Fig. 1(b) that the surface of Ti-substrate after mechanically polishing using abrasive paper of No.2000; PC-Ti, showed a cleaner surface but still uneven surfaces. Chemical cleaning with the mixture solution of hydrofluoric acid and nitric acid gave the free-oxide substrate with obviously boundary grains; CC-Ti, suitably for the growth of anodic TNA as seen in Fig. 1(c) and 1(d).

Ti-alloy specimen had been cleaned by physical methods prior to oxidation using single-step of anodization under the applied potential of 40 V for 3 and 5 h in a water-free electrolyte solution (NE). The as-formed anodic TNA on Ti-substrate was annealed at 500C in air atmosphere for 3 hours to

present the morphology as shown in Fig.2. From 3 h of anodization, the typical SEM images show the irregular titania porous structured-layer on the top surface covering with the ion particles as seen in Fig. 2(a). Totally different distribution in nano-structure was revealed after 5 h of anodization (Fig. 2(b)), the structured-nanotube with a dense cluster of tubes and poor uniformity in tube length was obtained resulted from the partially etching of TNA after prolonged the anodization process. When using a aqueous electrolyte (AE) for anodization at 40 V, porous structure has been obviously noticed after oxidation for 3 h (Fig. 2(c)) with less particle covering on the top surface. The uniform dense nanotubes were distributed throughout the area after 5 h as seen in Fig. 2(d).

At the anodization equilibrium between the formation and the chemical dissolution of TiO_2 by the presence of fluoride-containing electrolyte, also the availability of oxygen donor in the electrolyte strongly influenced on the formation rate of TiO_2 at the metal-oxide interface. The donation of oxygen

with hydrous organic electrolytes was proceeding easier than of anhydrous electrolyte resulted to the stable TiO_2 formation and a compact thin oxide layer. However, an electrolyte that has excessive content of water resulted to the nanotubes with rough wall due to severe erosion of oxide array. By comparing the oxide surfaces formed after the anodic coating with one-step anodization in electrolyte containing water at 40 V, it had been found that the cluster of oxide film scattered over the PC-Ti substrate (Fig. 3(a) and 3(b)). While the CC-Ti substrate supported the denser oxide layer distributed all entire surface (Fig. 3(c) and 3(d)), since the grain boundaries had more clarify depth making more roughness surface which suitable for adhesion to the film. More growth of TiO_2 was presented with the prolonged anodizing time corresponded to the other reports [12]—that well arrangement of stable nanotube TiO_2 was developed due to the chemical dissolution of as formed-oxide layer. The dissolution was increased with longer anodic oxidation, resulting in the decrease of nanotube length and the bigger of nanotube diameter.

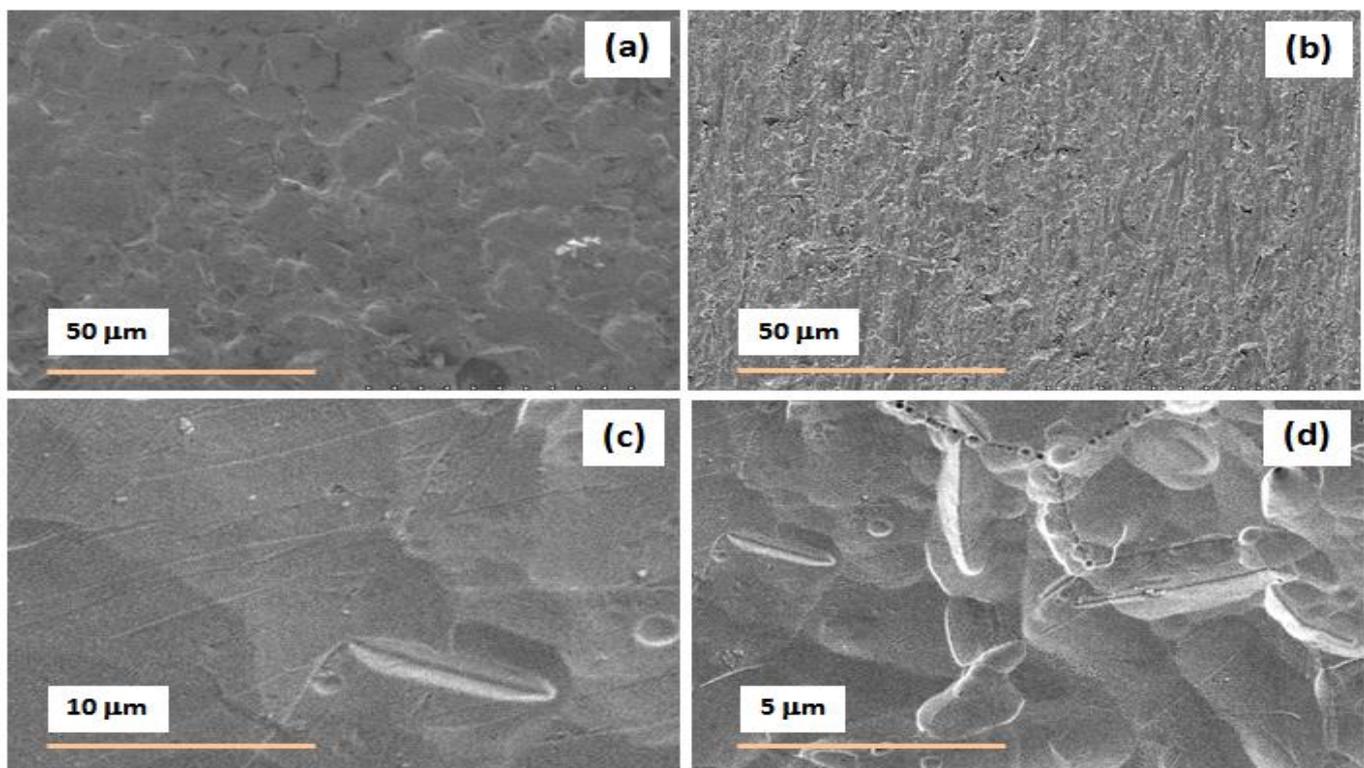


Figure 1 SEM top-surface images of: (a) as received-Ti substrate, (b) PC Ti-substrate and (c) CC- Ti substrate

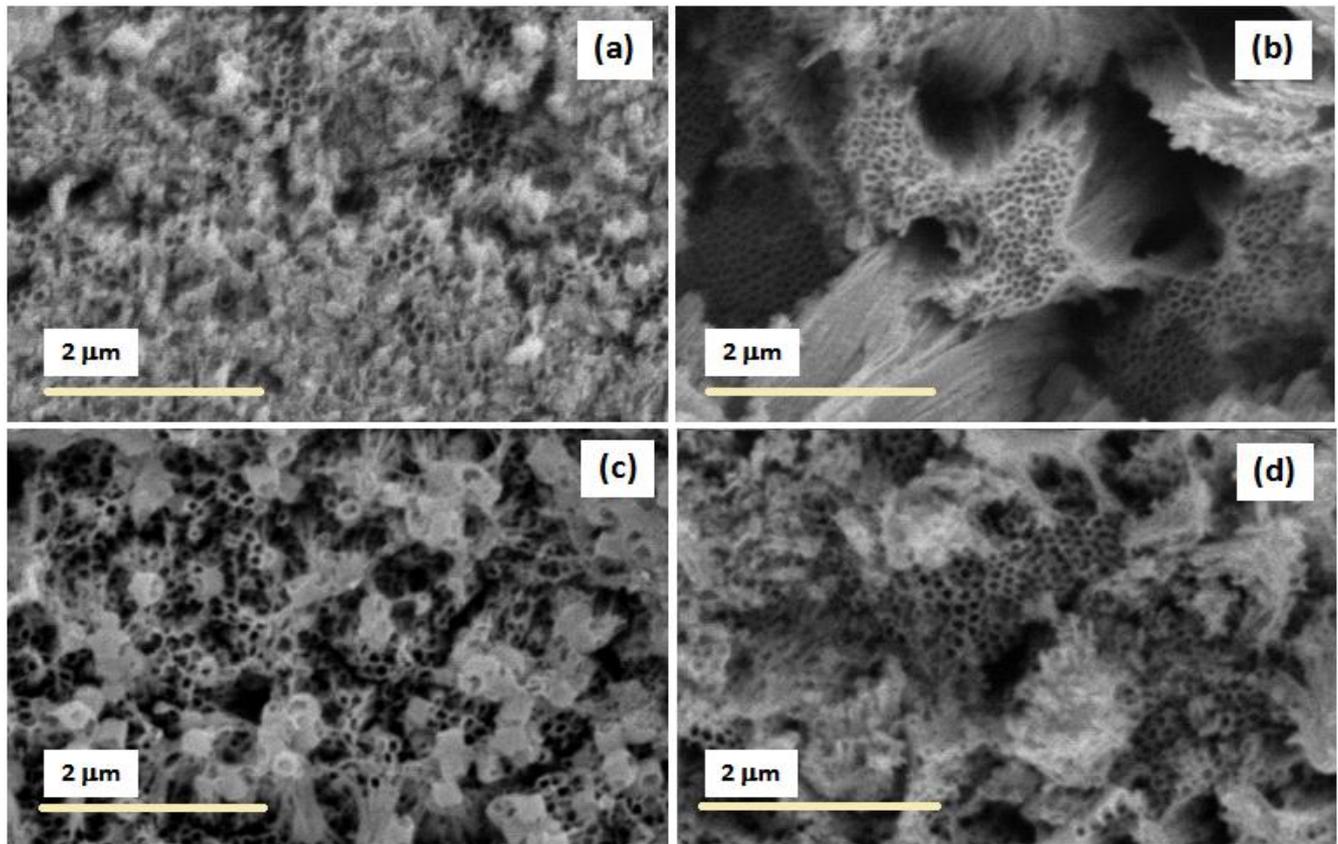


Figure 2 SEM top-surface images of annealed TNA arrays growth on PC-Ti substrate from single-step of anodization in NE at (a) 40V3 h, (b) 40V5 h, in AE at (c) 40V3 h and (d) 40V5 h

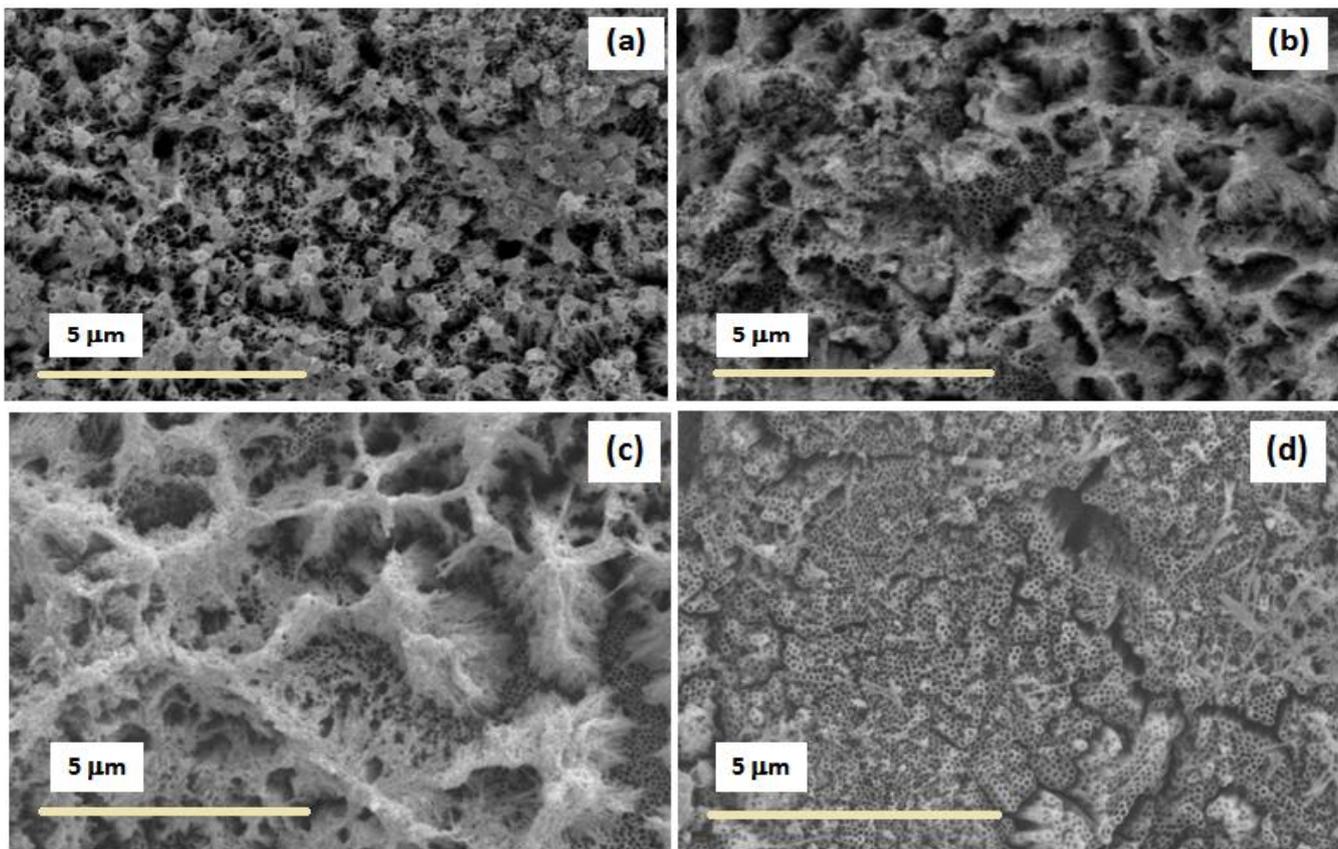


Figure 3 SEM top-surface images of as formed-TNA arrays from single-step of anodization in AE, on PC-Ti substrate at (a) 40V3 h and (b) 40V5 h, CC-Ti substrate at (c) 40V3 h and (d) 40V5 h

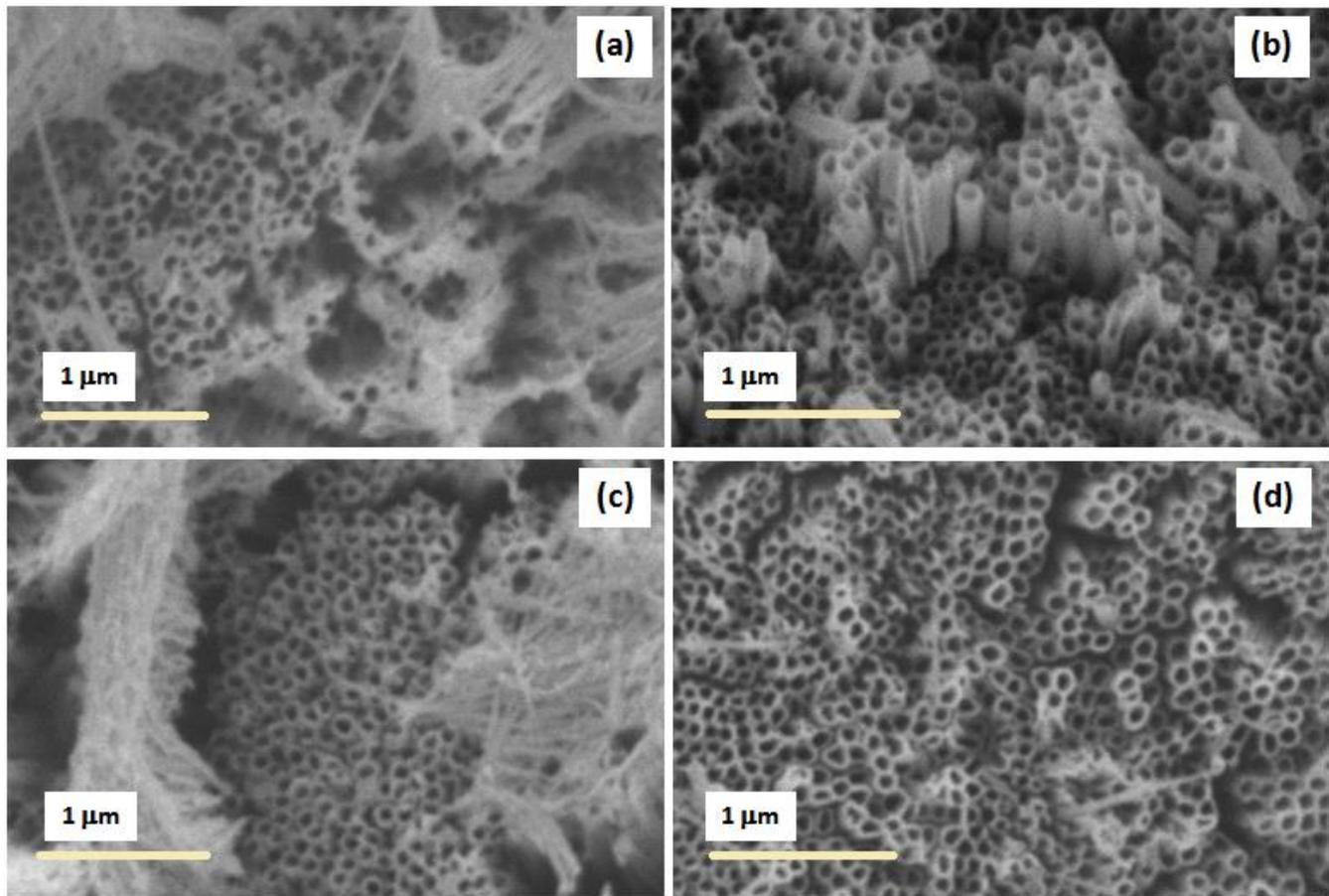


Figure 4 SEM top-surface images of TNA arrays growth on CC-Ti substrate from single-step of anodization in AE at
(a) 40V3 h (as-formed), (b) 40V3 h (annealed), (c) 40V5 h (as-formed) and (d) 40V5 h (annealed)

Fig. 4 shows the top-surface of TNA on CC-Ti substrate after the first anodization in EG electrolyte containing NH_4F and water at 40 V, for 3 and 5 h. The as-grown samples depict a flaky and uneven nanotube layer on the top surface covered by a passive oxide film on the top. Some fish pipe nano-structured with open-ended nanotubular structure appeared on these as-formed surface (Fig. 4(a) and 4(c)). Some precipitation and debris formed irregular nanotubes on the surface probably due to the erosion of initially as-grown nanotubes. Also, some grass-like bundles of nanotubes were distributed over the surface caused by the capillary force and the over etching. The surface of nanotube structures with 5 h of anodic coating was more pronounced with uniformly dense structure because of the fast dissolution of the precipitates. After annealing the as-anodized samples at 500C with the heating rate of 5C/min for 3 hr in air, the nano-structured surface was obviously presented without the grass-bundles as shown in Fig. 4(b) and

4(d). The annealing process has significantly alters the morphology of TNA on Ti-substrate [11], the nanotube structure were not destroyed at the low annealing temperature (200C to 500C). The electric current decreased more quickly when using a voltage greater than 40 V and longer anodic coating period. Consequently, the oxide layer was growing rapidly resulting in an increase of its thickness. Also, the electric current density at the steady state proportional increased with the applied potential used in the anodic oxidation, including the tube length, internal pore diameter and outer pore diameter [12].

Fig. 5 shows the top surface of annealed TNA arrays growth on CC-Ti substrate from single-step anodization in AE electrolyte at 40 V and 50 V, for 3 and 5 h. After anodization for 5 h at the constant applied potential, more amounts of nanotubes were developed on the oxide surface as seen in Fig. 5, obviously noticed in the insets. To achieve nanoporous structured TiO_2 layer, multi-steps of

anodization has been applied neither constant potential nor ramping voltage. At the initial anodization from each step, the surface of Ti-substrate was transformed to a rough surface which gradually changed to porous like structure and eventually converted to nanotubular morphology. As-formed anodic film was removed from the substrate surface to get an appropriate convex area on the metal surface for the new formation at the next anodization. In this study, triple-step

anodization at 50 V gave the well-arranged structure of anneal nanotube TiO_2 on CC-Ti substrate as shown in Fig. 6. Prolonging the anodization at the third step resulted to the growing of nanotubes from the former seeding sites (Fig. 6(b)), this grown nanotubes have more regularity with no nanograss appearance on the oxide surface in comparison to the previous samples. TiO_2 nanotubes had the average internal pore-diameter and thickness of 145 nm and 71 nm respectively.

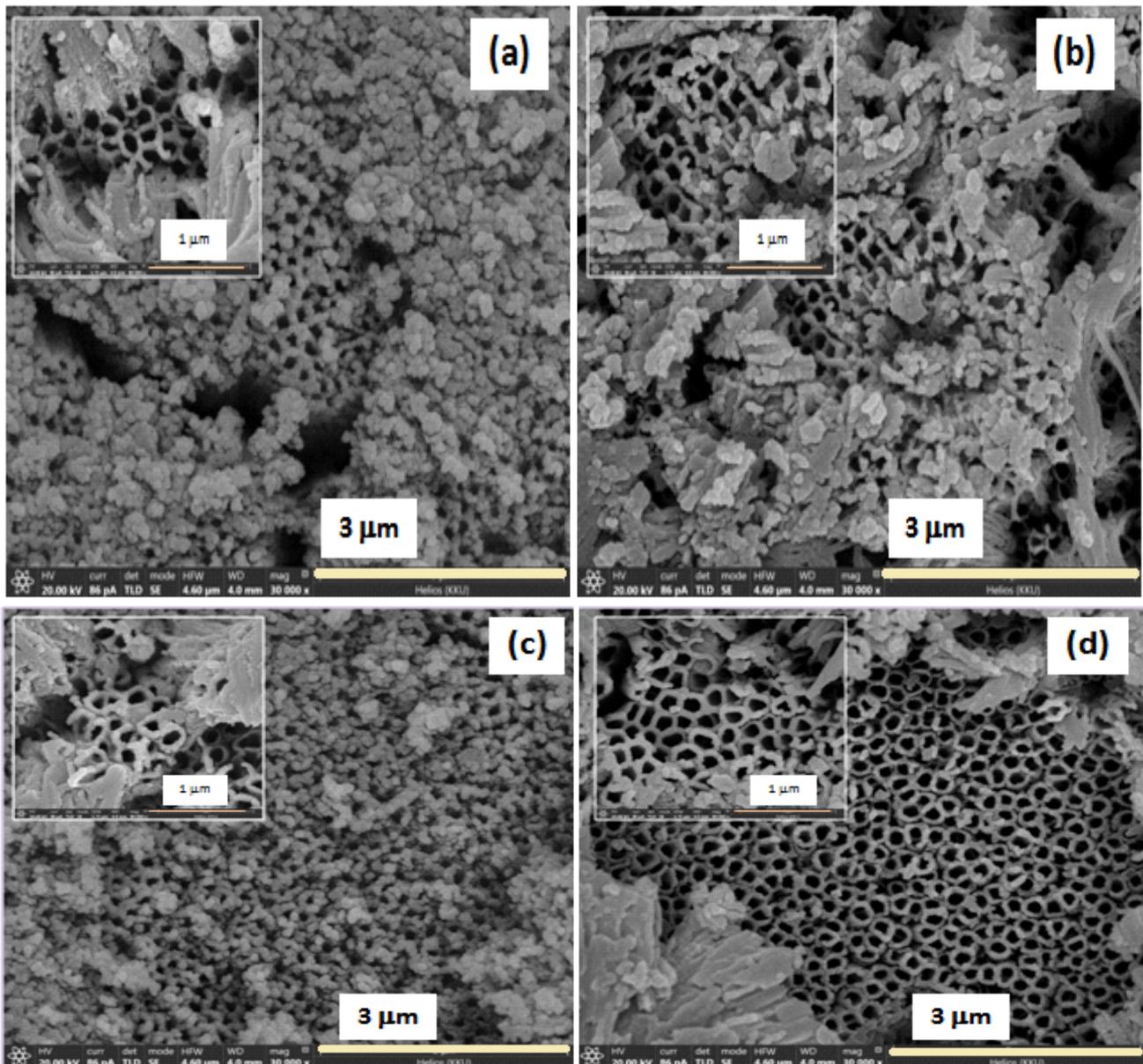


Figure 5 FESEM top-surface images of annealed TNA arrays growth on CC-Ti substrate from single-step of anodization in AE at (a) 40V3h, (b) 40V5 h, (c) 50V3 h and (d) 50V5 h

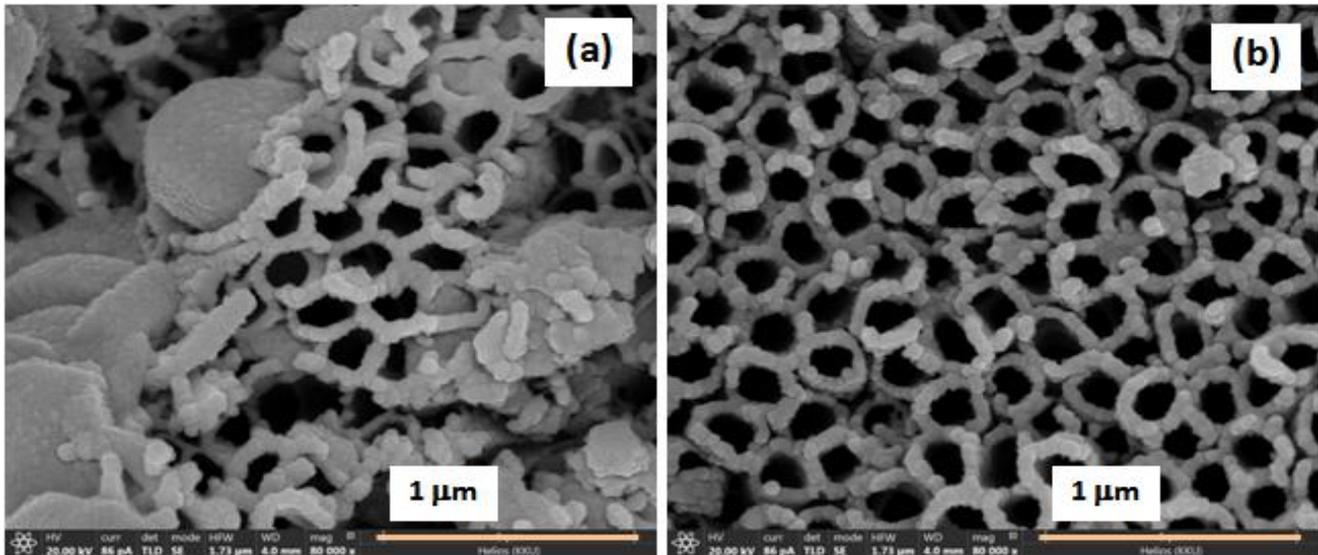


Figure 6 FESEM top-surface images of annealed TNA arrays growth on CC-Ti substrate from triple-step anodization in AE electrolyte at 50 V for (a) 3 h and (b) 5 h at the last step

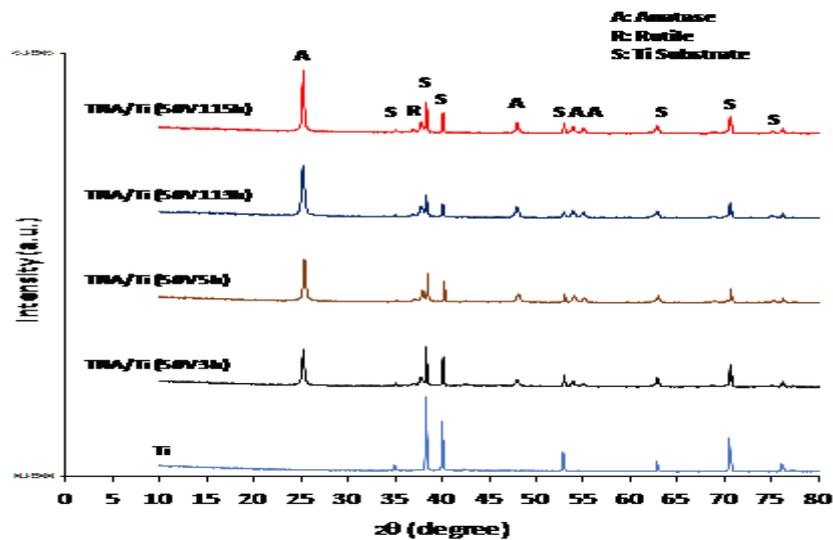


Figure 7 XRD patterns of the 1-step annealed TNA/Ti samples and 3-steps annealed TNA/Ti

Fig. 7 shows the XRD patterns of the annealed nanotube sample grown over CC-Ti substrate at 50 V in EG electrolyte containing 0.5wt% NH_4F and 5wt% distilled water using the single-step and triple-steps anodization, compared to the bared Ti sheet. Characteristic anatase TiO_2 peaks (JCPDS, No.001-0562), characteristic rutile TiO_2 peaks (JCPDS, No.87-0710) and peaks of Ti (JCPDS, No.001-1197) were observed. Only peaks assigned to Ti crystal phase were found in the pattern of bared-Ti sheet and of as-formed anodic TiO_2 nanotubes. After annealing at 500C in air atmosphere for 3 h, the structure of TNA changed from amorphous or weak crystalline to a mixture of

anatase and rutile phases. Also the peaks corresponding to Ti are also observed in XRD patterns of annealed TNA nanotubes due to the presence of Ti metal sheet.

b. Electrochemical Characterization

Cyclic voltammetry (CV) tests were carried out to characterize the capacitive behavior of the TNA/Ti electrodes. The electrochemical measurement was carried out in 1 M H_2SO_4 aqueous solution using 3-electrode configuration for an electrochemical window from -0.7 to +0.1 V (vs. SCE). Fig. 8 depicts the CV curves of TNA/Ti electrodes; 40V3h, 40V5h, 50V3h and 50V5h,

fabricating from single-step anodization using the scanning rate of 5, 10, 20, 30, 40, 50 and 60 mV/s. Different geometry TiO₂ nanotube electrodes prepared using single-step anodization gave quasi rectangular shaped CV curves. The capacitance behavior of TiO₂ nanotubes supercapacitor was strongly the dissolution was increased due to the non-faradiac behavior mechanism that ion adsorption onto the TiO₂ nanotubes. Generally, current density is directly proportional to the potential scan rate that agrees well with non-faradaic behavior. The CV shape becomes less distorted with increased potential voltage sweep rate indicating the excellent capacitive behavior as strongly adhesion between TNA layer and Ti-surface. At the higher potential scan rate, more ions from the electrolyte move towards TNA nanotube surface and get adsorbed onto it, so the higher rate capability and the faster charge discharge kinetics are enhanced to the organized and oriented nanotube architecture [13].

Fig. 9 shows the CV curves of different geometry TiO₂ nanotube electrodes prepared using triple-step of anodization; 40V113h, 40V115h, 50V113h and

50V115h using the scan rate of 5, 10, 20, 30, 40, 50 and 60 mV/s. The quasi rectangular shaped CV curves of were still obtained for the TNA/Ti electrode prepared at 40 V. In particular, the CV for TNA/Ti electrode prepared at 50 V shows a symmetric rectangular for all scan rates. Therefore, the capacitive behavior of this nanotube electrode is based on the electrical double layer principle. The ions have enough time to diffuse into the TNA surface for small potential scanning rate, thus the CV curves at 5 mV/s of TNT/Ti prepared from the single- and triple-steps anodization are compared in Fig. 10. As seen in Fig. 10(a), the quasi rectangular shaped CV of 50V115h electrode exhibits the higher range of current density than the others indicates that it would have better specific capacitance. Using the triple-steps of anodization resulted to the nearly rectangular shaped CV with higher capacitive behavior as shown in Fig. 10(b). It was found that the area and current density of 50V115h electrode is more than that of others owing to its larger geometrical parameter of TiO₂ nanotubes which reveals its superior capacitance properties.

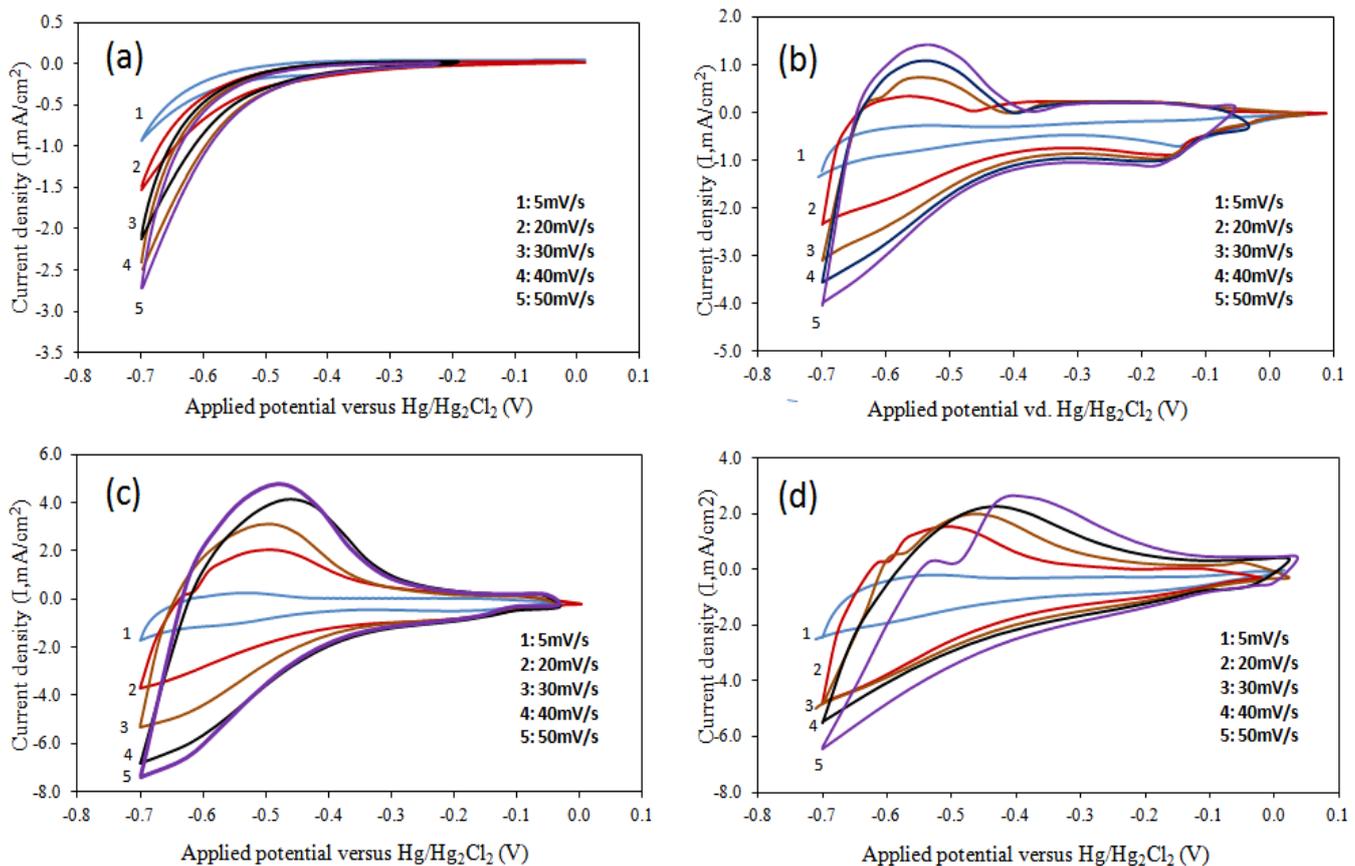


Figure 8 CV curves at different scanning rates of TNA/Ti electrodes fabricating from single-step anodization at (a) 40V3h, (b) 40V5h, (c) 50V3h and (d) 50V5h

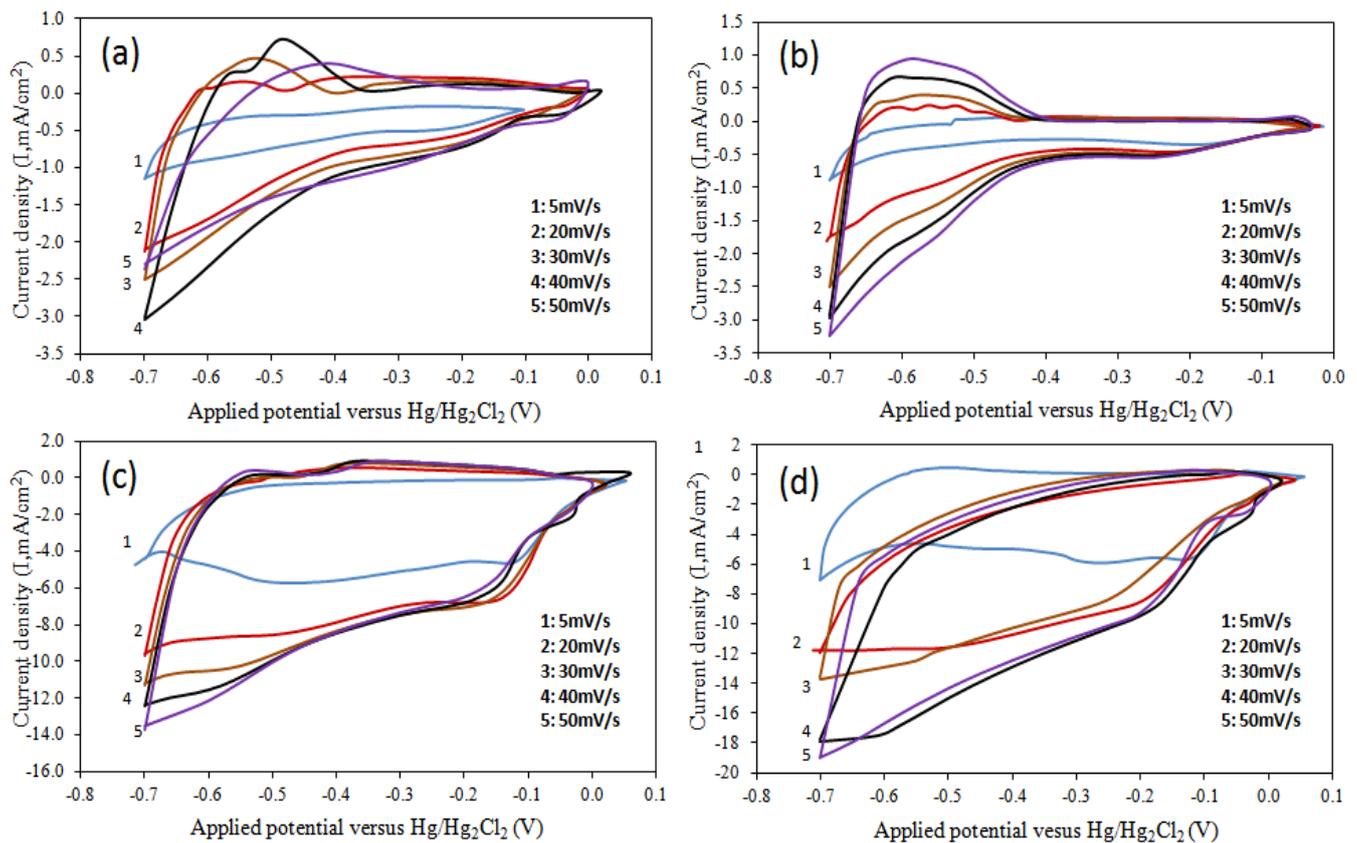


Figure 9 CV curves at different scanning rates of TNA/Ti electrodes fabricating from triple-steps anodization using (a) 40V113h, (b) 40V115h, (c) 50V113h and (d) 50V115h

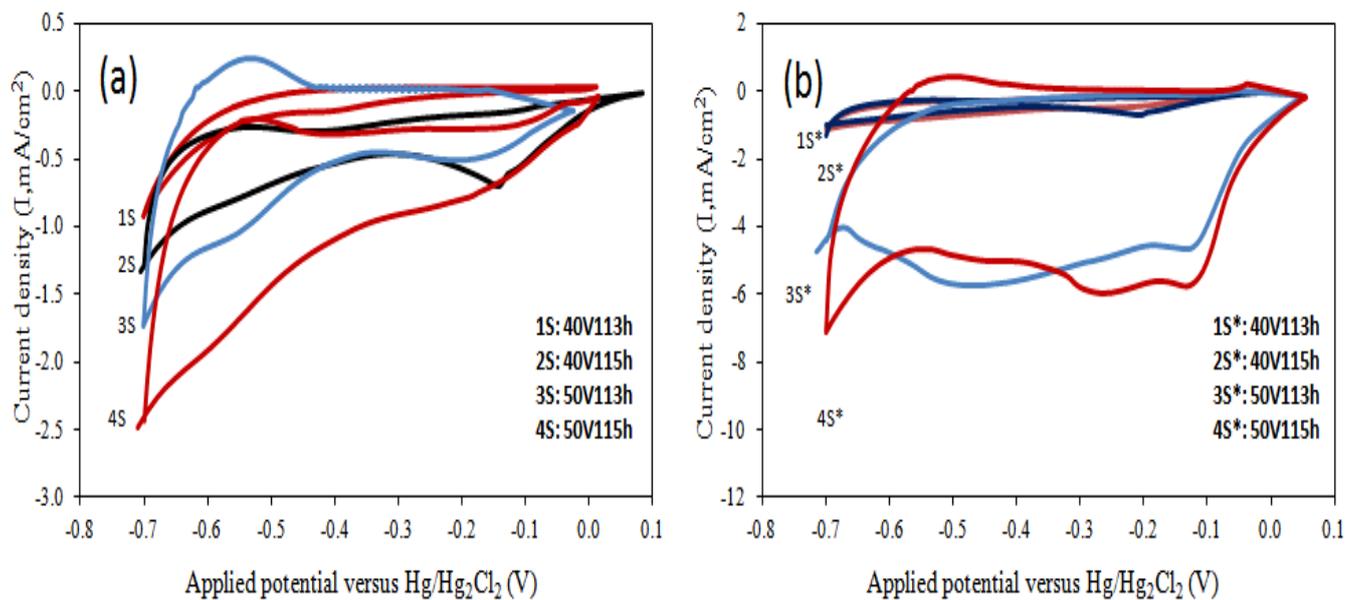


Figure 10 CV curves at 5mV/s of TNA/Ti electrodes fabricating using (a) single-step anodization and (b) triple-step anodization

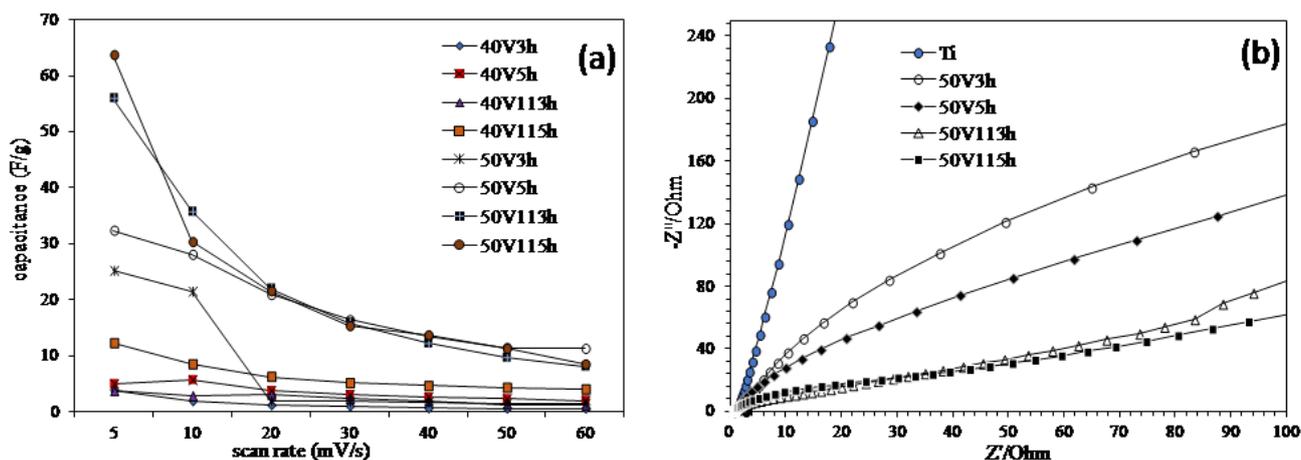


Figure 11 (a) The capacitances as a function of scan rates and (b) comparative Nyquist plots for prepared electrodes

Fig. 11(a) shows the specific capacitances of the anodic TNA/Ti electrodes calculated using CV tests versus scanning rates. In contrast to the current density behavior for all prepared electrode, the specific capacitances decreased with scanning rate due to the diffusion limitations in the nanotube channels. The highest specific capacitance of 63.73 F/g is obtained for 50V115h electrode at a scan rate of 5 mV/s. At low scan rate, a sharp decrease in specific capacitance is observed. Good power capability of the electrode was obtained at high potential scanning rate which the appearance of approximate stable capacitance. Fig. 11(b) compares the Nyquist plots of five working electrodes at the frequency range from 0.01 Hz to 100 kHz at the constant potential of 5 mV in 1 M H₂SO₄ aqueous solution at room temperature. The impedance spectra was divided into the region of high-frequency, mid-frequency and low-frequency identified the electrolyte properties, the effect of electrode/electrolyte interface and the property of capacitance, respectively. The impedance spectrum composes of semicircle at the high frequency region and a straight line in the low frequency region. A higher slope reveals a higher capacitance. Bare CC-Ti substrate shows high electric resistance while a slight semi-circle arc was observed in TNA/Ti electrode fabricated by single-step of anodization, indicating a charge transfer limiting process. However, the samples 50V113h and 50V115h anodized from three-step oxidation had none such semi-circle arc which corresponds to good charge transfer with none electrical resistance. Therefore, triple-steps of anodization was suggested for fabrication of anodic TiO₂ in the purpose of supercapacitor application.

IV. Conclusions

In summary, we have synthesized TiO₂ nanotube arrays on Ti-alloy sheet using the electrochemical anodization. Well-aligned TNA on Ti-substrate was achieved from the chemical pretreatment of Ti substrate for triple-steps of anodization in EG electrolyte containing containing 0.5wt% NH₄F and 5wt% H₂O under the applied potential of 50 V for 5 h at the third anodization. The annealed 50V115h TiO₂ nanotubes which composed of mainly anatase phase gave the better capacitive behavior than the others. The maximum capacitance was reached to 63.73 F/g at the potential scanning rate of 5 mV/s. EIS results confirmed the good charge transfer of the 50V115h electrode with no electrical resistance.

REFERENCES

- [1] M. Salari, "Functionalization of nanostructured titania (TiO₂) as electrode materials for supercapacitors." (2013).
- [2] H. Zhou, X. Zou, and Y. Zhang. "Fabrication of TiO₂@MnO₂ nanotube arrays by pulsed electrodeposition and their application for high-performance supercapacitors." *Electrochimica Acta*, vol. 192, pp. 259-267, 2016.
- [3] R. Kötz, and M.J.E.A. Carlen. "Principles and applications of electrochemical capacitors." *Electrochimica acta*, vol. 45, no. 15-16, pp 2483-2498, 2000.
- [4] H. Zhou, and Y. Zhang. "Electrochemically self-doped TiO₂ nanotube arrays for supercapacitors." *The Journal of Physical Chemistry C*, vol. 118, no. 11, pp. 5626-5636, 2014.
- [5] H.T. Fang, M. Liu, D.W. Wang, T. Sun, D.S. Guan, F. Li, J. Zhou, T.K. Sham, and H.M. Cheng. "Comparison of the rate capability of

- nanostructured amorphous and anatase TiO₂ for lithium insertion using anodic TiO₂ nanotube arrays." *Nanotechnology*, vol. 20, no. 22, pp. 225701, 2009.
- [6] Y. Xie, and X. Fang. "Electrochemical flexible supercapacitor based on manganese dioxide-titanium nitride nanotube hybrid." *Electrochimica Acta*, vol. 120, pp.273-283, 2014.
- [7] Y.G. Huang, X.H. Zhang, X.B. Chen, H.Q. Wang, J.R. Chen, X.X. Zhong, and Q.Y. Li. "Electrochemical properties of MnO₂-deposited TiO₂ nanotube arrays 3D composite electrode for supercapacitors." *international journal of hydrogen energy*, vil. 40, no. 41, pp. 14331-14337, 2015.
- [8] G. Zhang, H. Huang, Y. Zhang, H.LW Chan, and L. Zhou. "Highly ordered nanoporous TiO₂ and its photocatalytic properties." *Electrochemistry Communications*, vol. 9, no. 12, pp. 2854-2858, 2007.
- [9] J. Gong, Y. Lai, and C. Lin. "Electrochemically multi-anodized TiO₂ nanotube arrays for enhancing hydrogen generation by photoelectrocatalytic water splitting." *Electrochimica Acta*, vol. 55, no. 16, pp. 4776-4782, 2010.
- [10] M. Thabuot, and C. Kruehong. "Structural comparison of anodic nanoporous-titania fabricated from single-step and three-step of anodization using a two parallel electrode anodizing cell." *Engineering and Applied Science Research*, vol. 43, no. 1, pp. 13-20, 2016.
- [11] S. Sreekantan, R. Hazan, and Z. Lockman. "Photo-activity of anatase-rutile TiO₂ nanotubes formed by anodization method." *Thin solid films*, vol. 518, no. 1, pp 16-21, 2009.
- [12] G.D. Sulka, J. Kapusta-Kołodziej, A. Brzózka, and M. Jaskuła. "Fabrication of nanoporous TiO₂ by electrochemical anodization." *Electrochimica Acta*, vol. 55, no. 14, pp. 4359-4367, 2010.
- [13] M. Salari, S.H. Aboutalebi, K. Konstantinov, and H.K. Liu. "A highly ordered titania nanotube array as a supercapacitor electrode." *Physical Chemistry Chemical Physics*, vol. 13, no. 11, pp 5038-5041, 2011.

V. AUTHORS PROFILE

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