UNIVERSITI PUTRA MALAYSIA

PREPARATION OF NICKEL COBALT OXIDE ON TITANIA NANOTUBES VIA WET IMPREGNATION FOR SUPERCAPACITOR

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FS 2018 64

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By

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Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master of Science

July 2018

Abstract of thesis presented to the Senate of Universiti Putra Malaysia
in fulfilment of the requirement for the degree of Master of Science

PREPARATION OF NICKEL COBALT OXIDE ON TITANIA NANOTUBES VIA WET IMPREGNATION FOR SUPERCAPACITOR

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Chair: Professor Zulkarnain bin Zainal, PhD
Faculty: Science

Titania nanotubes array and nickel cobaltite are both widely studied metal oxide materials for applications in the field of energy storage and delivery. However, the electrochemical capacitive charge storage of titania nanotubes is generally poor because of their inferior electrical conductivity. A number of attempts at chemical modifications by doping and making composites have been performed but the effect of decorating the surface of titania nanotubes with ternary metal oxide has not been adequately addressed. This study aims to evaluate the electrochemical performance of combining titania nanotubes array with nickel cobaltite for the purpose of fabricating composite electrochemical capacitors. Further, this study also aims to evaluate the possibility of using wet impregnation method to introduce metal oxides onto titania nanotubes array.

The techniques that were used in the characterisation of the samples were X-ray diffraction (XRD), cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), electrochemical impedance spectroscopy (EIS), field-emission–scanning electron microscopy (FESEM), and energy dispersive X-ray microanalyses (EDX). Parameters that were studied included anodisation duration, anodisation potential, initial molar concentration of nickel(II) nitrate solution and cobalt(II) nitrate solution, thermal treatment temperature of the precursor solution, impregnation duration, and types of electrolytes.

The optimum synthesis conditions for the unmodified titania nanotubes were 60 minutes anodisation duration and 17 V anodisation potential, whereas the optimum synthesis conditions for the nickel cobaltite – titania nanotubes composite were 1.0 M initial molar concentration of nickel (II) nitrate solution and cobalt(II) nitrate solution, thermal treatment temperature of the precursor solution was 375 °C, and an impregnation duration of 60 minutes. The nickel cobaltite – titania nanotubes composite performed optimally in 1.0 M KOH.

By the use of optimised synthesis conditions, it was found that the composite possessed the best electrochemical behaviour in 1.0 M KOH. CV tests demonstrated that the composite exhibited a small degree of electrocatalytic behaviour due to a sharp increase in current density in the 0.6 V region. The areal capacitance was 214.76 $\mu F/cm^2$ at 350 $\mu A/cm^2$, which decreased to 210.02 $\mu F/cm^2$ when the current density increased to 400 $\mu A/cm^2$. Further, it was found that the composites relied largely of electric double layer charge storage mechanism. Cycle stability study shows the composite deteriorated to 62.38% in 250 cycles of charge-discharge. Micrographs of the composite has shown that the nickel cobaltite nanoclusters preferred to deposit on the surface of the nanotubes rather than on the inside of the nanotube pores. EDX microanalyses indicated that the deposition of nickel and cobalt was very small, which were ~0.06 mol.% and ~0.13 mol.%, respectively.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
sebagai memenuhi keperluan ijazah Master Sains

PENYEDIAAN NIKEL KOBALT OKSIDA PADA TIUB NANO TITANIA MELALUI KAEDAH IMPREGNASI BASAH UNTUK SUPERKAPASITOR

Oleh

CHUA CHI WING

Julai 2018

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Tiub nano titania tersusun serta nikel kobalt oksida merupakan bahan logam oksida yang lazim dikaji untuk kegunaan dalam bidang penyimpanan dan pembekalan tenaga. Walaubagaimanapun, penyimpanan cas kapasitif elektrokimia tiub nano titania secara amnya adalah kurang memuaskan kerana kekondusian elektriknya yang rendah. Pelbagai percubaan pengubahsuaian kimia melalui pendopanan dan pembuatan komposit telah dilakukan tetapi kesan daripada penghiasan permukaan tiub nano titania dengan logam pertigaan tidak dijelaskan dengan secukupnya. Kajian ini bertujuan membuat penilaian pada ciri-ciri elektrokimia tiub nano titania–nikel kobalt oksida, dengan tujuan membentuk kapasitor elektrokimia komposit. Selain itu, kesesuaian kaedah impregnasi basah untuk memperkenalkan logam oksida kepada tiub nano titania tersusun juga dinilai.

Teknik-teknik pencirian bahan yang digunakan dalam kajian ini termasuklah pembelauan sinar-X (XRD), voltametri berkitar (CV), cas-nyahcas galvanostatik (GCD), spektroskopi impedans elektrokimia (EIS), mikroskopi elektron imbasan pancaran medan (FESEM), dan analisis mikro sinar-X tenaga tersebar (EDX). Parameter-parameter yang dikaji termasuklah tempoh penganodan, potensi penganodan, kepekatan asal larutan nikel(II) nitrat dan kobalt(II), suhu rawatan haba larutan impregnasi, tempoh impregnasi, dan jenis elektrolit.

Kaedah sintesis optimum bagi tiub nano titania adalah tempoh penganodan selama 60 minit dan potensi penganodan 17 V manakala kaedah sintesis optimum bagi komposit nikel kobalt oksida – tiub nano titania adalah kepekatan molar permulaan larutan nikel(II) nitrat dan larutan kobalt(II) nitrat sebanyak 1.0 M, suhu rawatan haba bagi larutan pelopor pada 375 °C, dan tempoh impregnasi selama 60 minit. Komposit nikel kobalt oksida – tiub nano titania berfungsi secara optimum dalam 1.0 M KOH.

Melalui penggunaan kaedah sintesis optimum, komposit tersebut mempunyai ciri-ciri yang terbaik dalam elektrolit 1.0 M KOH. Ujian CV menunjukkan bahawa komposit tersebut juga mempunyai serba sedikit sifat elektropemangkin kerana berlakunya peningkatan ketumpatan arus mendadak pada sekitar potensi 0.6 V. Kapasitans spesifik permukaan pula mencatat nilai sebanyak 214.76 $\mu F/cm^2$ pada ketumpatan arus 350 $\mu A/cm^2$, manakala nilai tersebut menurun ke 210.02 $\mu F/cm^2$ pada ketumpatan arus 400 $\mu A/cm^2$. Tambahan pula, mekanisme pengecasan dwilapis elektrik merupakan kaedah utama yang digunakan oleh komposit tersebut untuk menyimpan cas. Ujian kitaran cas-nyahcas menentukan bahawa komposit tersebut mengalami penurunan kapasitans spesifik permukaan kepada 62.38% selepas 250 kitaran cas-nyahcas, berbanding dengan nilai pada kitaran cah-nyahcas pertama. Gambar mikro-gambar mikro komposit tersebut menunjukkan kluster mikro nikel kobalt oksida lebih cenderung termendap pada permukaan tiub nano dan bukannya dalam liang-liang tiub nano. Menurut ujian EDX, nikel(II) dan kobalt(II) masing-masing termendap pada nilai ~0.06 *mol.*% dan ~0.13 *mol.*%, dan nilai ini adalah amat kecil.

ACKNOWLEDGEMENTS

First and foremost, all praise to the Almighty for His providence throughout my studies. My heartfelt appreciation also goes out to my supervisor, Professor Zulkarnain bin Zainal, for his guidance and mentorship. I would also like to extend my appreciation to Associate Professor Janet Lim Hong Ngee, for her constructive suggestions and also providing certain chemicals needed for this study.

I would also like to thank Madam Zaidina Mohd. Daud, from the Department of Chemistry Faculty of Science, UPM, for her guidance on how to use the X-ray diffractometer (Shimadzu XRD 6000) and Mister Azmi Mohd. Amban, from the Microscopy Unit, Bioscience Institute, UPM, for his assistance in obtaining FESEM micrographs and microanalyses of the samples.

I would also like to express my gratitude to all my supportive labmates and seniors, Dr. Chang Sook Keng, Dr. Nurul Asma Samsudin, Madam Mahanim Sarif @ Mohd Ali, Mister Laimy bin Mohd Fudzi, and Madam Siti Nor binti Ab Hamid, who were instrumental in helping me succeed in completing my studies. The same also goes out to my course mates from my undergraduate days until my postgraduate days; Gan Yen Li, Khoo Wai Chat, Tee Keng Hong, and Chiam Sin Ling.

Last but not least, I would want to appreciate both my parents, who were very supportive of my decision to further my studies, as well as providing material and emotional support whenever I felt inadequate. Not forgetting both my siblings, Lynn Yen and Ivan, for providing comic relief and endless laughter when I am under stress. Without them, it would be difficult journey to complete my studies.

I certify that a Thesis Examination Committee has met on 26 July 2018 to conduct the final examination of Chua Chi Wing on his thesis entitled “Preparation of Nickel Cobalt Oxide on Titania Nanotubes via Wet Impregnation for Supercapacitor” in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science.

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LIST OF ABBREVIATIONS

CPE	Constant phase element
CV	Cyclic voltammetry analysis
EDX	Energy dispersive X-ray spectroscopy
EIS	Electrochemical impedance spectroscopy
FESEM	Field emission scanning electron microscopy
GCD	Galvanostatic charge – discharge analysis
NCO/TNT/Ti	$NiCo_2O_4$/Titania nanotubes/Titanium foil
R_p	Equivalent parallel resistance
R_s	Equivalent series resistance
SEM	Scanning electron microscopy
TNT/Ti	Titania nanotubes/Titanium foil
vol.%	Volume percentage
wt.%	Weight percentage
Z_w	Warburg impedance

CHAPTER 1

INTRODUCTION

1.1 Research Background

Different classes of materials have been researched for creating supercapacitors. An extremely broad class of these materials consist of carbon-based materials and its derivatives such as activated carbon, carbon nanotubes, and graphene (Lokhande *et al.*, 2016). Carbon-based materials store charge predominantly via electric double layer charging mechanism. On the other hand some metal oxides and conducting polymers store charge through redox reactions apart from electric double layer charging mechanism, in which the active materials can gain or release electrons to and from ionic species in the electrolyte to enable charge storing and delivery. This kind of charge-storing mechanism is called pseudocapacitance (Lokhande *et al.*, 2016). The formation of composites or mixing of materials for the fabrication of supercapacitors is common due to a few reasons. Firstly, pure materials such as carbon, that store charge solely through electric double layer charging mechanism generally possess very low capacitance, that is, it is not able to store a lot of charge, measured in Farads. Secondly, materials as metal oxide powders usually possess low porosity and may impede electrolyte diffusion. Thus, composites are usually fabricated and their electrochemical charge storage performance usually outperforms their original constituents, or novel synthesis methods to generate unique microscale or nanoscale architecture are often performed to improve the charge storage properties of the materials. To date, various composites have been reported in literature such as metal oxides on carbon nanotubes (Wu *et al.*, 2015), metal oxides on carbon microfibre (Chiam *et al.*, 2017), metal oxides on graphene (Bai *et al.*, 2016; Naveen & Selladurai, 2015; Xu *et al.*, 2015), metal oxides on metal oxides (Bo *et al.*, 2006), conducting polymer on graphene (Alvi *et al.*, 2011; Gómez *et al.*, 2011), and conducting polymer on metal oxide (Xie *et al.*, 2011; Xie *et al.*, 2014), to list a few. Titania nanotubes store charge using electric double layer mechanism and does not possess very apparent pseudocapacitance properties. It is highly resistive and possesses low capacitance values, but the ease of tailoring its nanostructure is one of the main attractive features that can be exploited for the fabrication of nanotubes. To date, many titania nanotubes composite supercapacitors have been reported, such as conducting polymer-graphene-titania nanotubes composite (Huang *et al.*, 2015), metal oxide-titania nanotubes composite (Zhou & Zhang, 2014b), and conducting polymer-titania nanotubes composite (Shao *et al.*, 2015), to name a few. The number of literature continues to grow with more new methods of composite preparation being discovered frequently.

1.2 Problem Statement

Supercapacitors are useful charge-storing electronic components that deliver huge bursts of energy in a short time and are used in video recorders, car electronic devices such as radios and taxi meters, cameras, mobile phones, toys, and much larger applications such as electric buses running on supercapacitors, to providing electric pulse burst to start diesel locomotive engines (Kötz & Carlen, 2000). Ideally, supercapacitors should possess high power and energy density, long life expectancy, long storage life, robust operating conditions, use environmentally-friendly materials, economically feasible to be produced, and safe for consumer consumption. However, current supercapacitors are plagued with problems such as relatively low from desired energy density, high materials and fabrication costs, rapid self-discharging rates, and also the lack of industrial standards pertaining to the commercialisation of supercapacitors. (Wang *et al.*, 2012). Regarding titania nanotubes, the largest obstacle that prevents it from being commercialised as it is is due to its very large resistivity and small capacitance values, owing to its semiconducting nature. To improve its capacitance values, self-doping and/or adding dopants such as metal oxides or conducting polymers can be performed. However, the methods to introduce self-doping and/or adding dopants often involves the use of equipments such as potentiostat and special vessels for hydrothermal growth, as well as complex automation, which could lead to increased cost, increased chemical usage, and may sometimes be an obstacle for research facilities that can only afford low-cost approach to introduce these chemical modifications to titania nanotubes.

Through our study, we aim to improve the the low capacitance values of titania nanotubes through doping of the nanotubes using wet impregnation method. This method has been widely used to prepare titania nanotubes for photocatalysis applications but is not sufficiently understood for the application in the preparation of titania nanotubes for supercapacitors application. The rationale of using this technique is two-fold; it requires no complex equipments and automation as it can be done by simply immersing the unmodified titania nanotubes into metal ion precursors followed by thermal treatment and the usage of chemicals for doping is largely minimised to only the use of precursor solutions. This study is also aimed at exploring the feasibility of this technique to form mixed metal oxides on titania nanotubes, which was found to be possible using hydrothermal growth (Yang *et al.*, 2013) and electrodeposition (Yuan *et al.*, 2012) on various substrates, but not documented for this technique, particularly on titania nanotubes. Nickel and cobalt were selected as the metal species due to their high theoretical capacitance values, as high as 3750 F/g for nickel(II) oxide (Wang *et al.*, 2012) and 3560 F/g for cobalt(II,III) oxide (Lokhande *et al.*, 2016), and relatively cheaper cost compared many other metal oxides with charge-storage properties.

1.3 Objectives

1. To synthesise and optimise synthesis parameters for TiO_2 nanotubes/Ti (TNT/Ti).
2. To synthesise and optimise synthesis parameters for $NiCo_2O_4/TiO_2$ nanotubes/Ti composites (NCO/TNT/Ti).
3. To characterise the prepared TNT/Ti and NCO/TNT/Ti composites using cyclic voltammetry analysis (CV), galvanostatic charge – discharge analysis (GCD), electrochemical impedance spectroscopy (EIS), X-ray diffractometry analysis (XRD), field emission scanning electron microscopy – energy dispersive X-ray spectroscopy (FESEM-EDX), and cycle stability analysis using GCD for the sample obtained from optimised synthesis parameters.

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