NICKEL-COBALT HYDROXIDE/rGO TERNARY ELECTRODE MATERIALS FOR ASYMMETRIC SUPERCAPACITOR

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To my parents

ABSTRACT

Supercapacitor is an interesting electrochemical device in energy storage application. Its prominent properties such as low cost, excellent cycling stability, high power density, and fast energy charging have drawn great attention over the last few decades. It mainly can be classified into three types; double layer capacitor; which is carbon-based and stores charge electrostatically, pseudocapacitor; which is mostly conducting polymer and metal oxide-based and stores charge electrochemically, and hybrid capacitor; which is combining both materials and charge storage mechanism of double layer capacitance and pseudo capacitance. Transition metal hydroxides are the most sought-after materials in hybrid supercapacitor but single component hydroxides have poor conductivity and low mass diffusion thus low capacitance. One approach to increase the capacitance is to use binary or ternary hydroxides. Recent studies have also showed that incorporating electronic conductive materials into binary or ternary hydroxides can enhance their conductivity and subsequently improved their capacitance. Graphene or reduced graphene oxide (rGO) is one of the good carbon-based electronic conductive materials. This thesis focuses on the preparation and characterization of Nickel-Cobalt hydroxide/reduced graphene oxide (Ni-Co-OH-rGO) ternary electrode materials for supercapacitor. Ni-Co-OH-rGO was prepared by two-electrode electrodeposition in aqueous electrolyte consist of rGO (0.001g mL^{-1}), $Ni(NO_3)_2 \cdot 6H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$ (molar ratio of Ni to Co is 1:3, fixed to 0.01M metal ions) with Ni foil as both positive and negative electrode. Images and elemental mappings on scanning electron microscopy (SEM) show that Nickel-Cobalt hydroxides (Ni-Co-OH) and rGO uniformly distributed. Beside the peaks of nickel plate, X-ray diffraction (XRD) patterns of Ni-Co-OH-rGO show broad and undefined peaks, indicating the amorphous nature of Ni-Co double hydroxide. Two peaks (anodic and cathodic) are observed in cyclic voltammograms of Ni-Co-OH show redox reaction thus, this material is reversible. Ni-Co-OH with 1:3 Ni to Co ratio has the highest geometric capacitance of 0.25 F cm^{-2} at scan rate of 1 mV s^{-1} which in consistent with computational study where Ni-Co-OH 1:3 has the lowest band gap energy; therefore, it was chosen to be composited with rGO. The presence of rGo has increased the electrochemical performance of Ni-Co-OH; where, Ni-Co-OH-rGO deposited at -1.5 mA cm^{-2} (denoted as Ni-Co-OH-rGO1.5) possessed the best electrochemical performance and has geometrical capacitance of 0.40 F cm^{-2} at 1 mV s^{-1} which is nearly two times as that of Ni-Co-OH thus, chosen as electrode for supercapacitor. Asymmetric supercapacitor (ASC) was fabricated using Ni-Co-OH-rGO1.5 as the cathode and activated carbon cloth as the anode. Galvanostatic charge-discharge (GCD) was performed to Ni-Co-OH-rGO1.5 || AC ASC and it shows that the specific capacitance of the fabricated supercapacitor is 235.7 F g^{-1} and has relatively good cycling stability as it retained 89% of its initial capacitance after 2000 GCD cycles at current density of 2 A g^{-1}. The maximum energy density and power density of Ni-Co-OH-rGO1.5 || AC ASC is 64.2 W h kg^{-1} at 135.9 kW kg^{-1} respectively which is remarkable for application in the field of energy storage such as electronic devices.

ABSTRAK

Superkapasitor adalah peranti elektrokimia yang menarik dalam aplikasi penyimpanan tenaga. Sifatnya yang menonjol seperti kos yang rendah, kestabilan kitaran yang sangat baik, ketumpatan kuasa yang tinggi, dan pengecasan tenaga yang cepat telah menarik perhatian sejak beberapa dekad yang lalu. Superkapasitor boleh dikelaskan kepada tiga jenis; kapasitor dwi-lapisan; iaitu yang berasaskan karbon dan penyimpanan cas secara elektrostatik, kapasitor pseudo; yang kebanyakannya menggunakan polimer dan logam berasaskan oksida dan penyimpanan cas secara elektrokimia, dan kapasitor hibrid; yang menggabungkan kedua-dua bahan dan mekanisma penyimpanan cas kapasitan dwi-lapisan dan kapasitan pseudo. Hidroksida logam peralihan adalah bahan yang sering dikaji dalam superkapasitor hibrid tetapi penggunaan komponen hidroksida secara tunggal mempunyai tahap kekonduksian yang lemah dan resapan jisim yang rendah, mengakibatkan kapasitan yang terhasil juga rendah. Salah satu pendekatan untuk meningkatkan kapasitan adalah dengan menggunakan hidroksida binari atau ternari. Kajian terbaharu juga menunjukkan bahawa menggabungkan bahan konduktif elektronik ke dalam hidroksida binari atau ternari dapat meningkatkan tahap kekonduksiannya dan seterusnya meningkatkan kapasitannya. Grafin atau grafin oksida terturun (rGO) adalah salah satu bahan konduktif elektronik berasaskan karbon yang baik. Tesis ini memfokuskan kepada penyediaan dan pencirian nikel-kobalt hidroksida / grafin oksida terturun (Ni-Co-OH-rGO) bahan elektrod ternari untuk superkapasitor. Ni-Co-OH-rGO disediakan melalui kaedah elektrodeposisi dua elektrod dalam elektrolit akua yang terdiri daripada grafin oksida (0.001g mL^{-1}), $Ni(NO_3)_2 \cdot 6H_2O$ dan $Co(NO_3)_2 \cdot 6H_2O$ (nisbah molar Ni ke Co adalah 1:3, ditetapkan pada 0.01M ion logam) dengan kerajang Ni sebagai positif dan negative elektrod. Imej dan pemetaan unsur pada mikroskopi elektron pengimbasan (SEM) menunjukkan bahawa Ni-Co-OH dan rGO dielektrodeposit secara seragam. Di samping puncak plat nikel, corak belauan sinar-X (XRD) Ni-Co-OH-rGO menunjukkan puncak belauan yang luas dan tidak tentu, yang menunjukkan sifat amorfus hidroksida berganda Ni-Co. Dua puncak (anodik dan katodik) diperhatikan dalam kitaran voltammogram hidroksida berganda Ni-Co menunjukkan tindak balas redoks oleh itu, bahan ini mempunyai tindak balas berbalik. Hidroksida Ni-Co dengan nisbah 1:3 Ni ke Co mempunyai kapasitan geometri tertinggi 0.25 F cm^{-2} pada kadar imbasan 1 mV s^{-1} yang selaras dengan kajian komputasi yang mana Ni-Co 1:3 mempunyai jurang jalur tenaga terendah; oleh itu, ia dipilih untuk digabungkan dengan rGO. Kehadiran rGo telah meningkatkan prestasi elektrokimia hidroksida Ni-Co; yang mana, Ni-Co-OH-rGO yang didepositkan pada -1.5 mA cm^{-2} (dilabelkan sebagai Ni-Co-OH-rGO1.5) memiliki prestasi elektrokimia terbaik dan mempunyai kapasitan geometri 0.40 F cm^{-2} pada 1 mV s^{-1}, iaitu hampir dua kali ganda daripada Ni-Co-OH, dipilih sebagai elektrod untuk superkapasitor. Superkapasitor asimetri (ASC) dihasilkan dengan menggunakan Ni-Co-OH-rGO1.5 sebagai katod dan kain karbon teraktif sebagai anod. Cas-nyahcas galvanostatik (GCD) dilakukan kepada Ni-Co-OH-rGO1.5 || AC ASC dan ia menunjukkan bahawa kapasitan spesifik dari superkapasitor yang dihasilkan adalah 235.7 F g^{-1} dan mempunyai kestabilan kitaran yang baik kerana ia mengekalkan 89% kapasitan awalnya setelah 2000 kitaran GCD pada ketumpatan arus 2 A g^{-1}. Ketumpatan tenaga maksimum dan ketumpatan kuasa Ni-Co-OH-rGO1.5 || AC ASC masing-masing adalah 64.2 W h kg^{-1} pada 135.9 kW kg^{-1}, satu nilai yang tinggi untuk aplikasi dalam bidang penyimpanan tenaga seperti peranti elektronik.

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APPROVAL

The Examination Committee has met on **18th October 2021** to conduct the final examination of **Ainnur-Sherene binti Kamisan** on his degree thesis entitled "**NICKEL-COBALT HYDROXIDE/rGO TERNARY ELECTRODE MATERIALS FOR ASYMMETRIC SUPERCAPACITOR".**

The committee recommends that the student be awarded the Doctor of Philosophy (Physics).

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This thesis was submitted to the Senate of Universiti Pertahanan Nasional Malaysia and has been accepted as fulfilment of the requirements for the degree of **Doctor of Philosophy (Physics)**. The members of the Supervisory Committee were as follows.

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LIST OF ABBREVIATIONS

AC	Activated carbon
ASC	Asymmetric Supercapacitor
ATR-FTIR	Attenuated Total Reflection Fourier Transform Infrared
CAPZ	Ceperley-Alder-Perdew-Zunger
CASTEP	Cambridge Seriel Total Energy Package
CB	Conduction band
CNT	Carbon nanotube
CV	Cyclic voltammetry
DFT	Density Functional Theory
DH	Double hydroxides
DOS	Density of state
EC	Electrochemical capacitor
EDLC	Electric double layer capacitor
EDX	Energy Dispersive X-ray Spectroscopy
EIS	Electrochemical Impedance Spectroscopy
EPD	Electrophoretic deposition
GCD	Galvanostatic charge-discharge
GGA	Generalized gradient approximation
GO	Graphene oxide
HPC	High performance computer
LDA	Localized density abbreviation
LDH	Layered double hydroxides
MS	Materials Studio
ND	Neutron diffraction
NP	Nano-particles
OER	Oxygen evolution activity
PBE	Perdew-Burke-Ernzerhof
PBEsol	Perdew-Burke-Ernzerhof for solids
rGO	Reduced graphene oxide
RSR	Rotor-stator reactor
RT	Room temperature

SC	Supercapacitor
SCE	Saturated calomel electrode
SEM	Scanning Electron Microscopy
TA	Ambient temperature
TMHs	Transition metal hydroxides
VB	Valence band
XRD	X-ray diffraction

CHAPTER 1

INTRODUCTION

1.1 Background

Electrochemical capacitors (ECs) have been regarded as efficient energy storage devices and become the research focus in the field of energy storage due its high power density, fast charge discharge rate, and long life cycles (Chen et al., 2014a; Choudhary et al., 2017; Kim, Sy, Yu, & Zhang, 2015). The urgent need of ECs with high energy density highlights the importance to develop electrode materials with excellent electrochemical performances. Recently, transition metal hydroxide (TMH) has attracted great attentions due to its high theoretical specific capacity. The multiple oxidation states of TMH result in a rich variety of redox reactions (Bai et al., 2016; Eftekhari et al., 2017; Sivakkumar et al., 2007). Up to now, the most studied binary TMHs are Ni-Co double hydroxides (DHs) due to their simple synthesis, low cost, great capacity, high redox activity (providing multiple oxidation states for Faradaic reactions), and higher cycle stability than pure $Ni(OH)_2$ (Chen et al., 2016; Chen et al., 2017). However, the rate capability, the charge transfer efficiency and long-term cycle life of battery-type electrodes based on Ni-Co-OH are usually poor due to their relatively limited accessible surface areas and low electronic conductivity (Chen et al., 2016; Marichi et al., 2016). Incorporating Ni-Co DHs with electronic conductive materials such as nanostructured carbon materials can effectively improve their electrochemical performances (Cai et al., 2017; G. Zhou et al., 2016). Reduced graphene oxide (rGO) has been widely used as the matrix for electrode materials due to its many unusual properties such as its good electronic conductivity and high specific surface area (Kim et al., 2016; Ma et al., 2016; Xiong et al., 2016). With the help of rGO, the capacity of electrode materials is significantly enhanced (Kim et al., 2016; Ma et al., 2016; Xiong et al., 2016). Density Functional Theory (DFT) is a quantum mechanics method that use electron density to predict the properties of a material. The energy, structure and properties of one material varies depending on its geometry and atom arrangements. DFT can be a powerful tool in designing new material where the electrical and physical properties of the designed materials can be calculated instead of the *'guess and check'* method of the experimental approach. Beside of saving time from the *'guess and check'* method, DFT also can reduce the cost of raw materials used in a research by preventing raw materials from being wasted. In this work, Ni-Co-OH-rGO composites electrode for supercapacitor will be prepared by one-step electrodeposition after the optimum ratio of Ni:Co has been determined via Density Functional Theory (DFT).

1.2 Problem Statement

Raw material costs can be a big stressor in research. Although having difficulties in determining the right materials are already time consuming, the raw materials wasted is another problem. Therefore, DFT can be a powerful tool in designing new material where the electrical and physical properties of the designed materials can be calculated instead of the *‘guess and check’* method of the experimental approach.

Pseudocapacitors based on Ni-Co hydroxides have excellent theoretical specific capacitance (~2300 – 3500 F g^{-1})(Chang et al., 2016; Ji et al., 2013) however, due to swelling and shrinkage of the materials caused by reversible redox reaction at electrode surface lead to poor cycling stability. As consequences, pseudocapacitors exhibit lower specific power performance. EDLCs that use wide array of carbonaceous materials, renowned to have rapid charge/discharge rate, low resistance and excellent cycling stability. However, EDLCs suffer from low capacitance hence low energy density. Therefore, hybrid capacitor came into solution where it combines both advantages of pseudocapacitor and EDLC resulting to high energy and high-power density supercapacitor.

Incorporating Ni-Co DHs with electronic conductive materials such as rGO can effectively improve their electrochemical performances however, rGO-based electrodes are commonly binder-enriched by a slurry-coating method. The binder transforms a large portion of the surface of the active material into “dead surface” and decreases the electrical conductivity of electrode materials (Perera et al., 2011; Yuan et al., 2012; Zhang et al., 2012). So far, very few papers have reported the development of binder-free electrodes with transition metal hydroxides as the active materials and graphene as the additive (Bai et al., 2016; Jana et al., 2016).

1.3 Objectives

The aim of this study is to develop a high energy and high power density supercapacitor based on Ni-Co-OH-rGO composites. The objectives of this study are listed below:

1. To determine the optimum ratio of Ni:Co for Ni-Co-OH using Density Functional Theory.
2. To investigate the effect of Co ratio in $Ni(OH)_2$ on its electrochemical, structural and morphological properties.
3. To enhance the electrochemical properties of Ni-Co-OH by introducing novel in-house rGO.
4. To appraise the performance of fabricated Ni-Co-OH-rGO asymmetric supercapacitor.

1.4 Scope of Limitation

First-Principle calculation was implemented only to determine the ideal Ni:Co ratio to be composited with graphene based on optimum Co doping position in each ratio together with its band structures and density of states. There are many factors affecting the yield of electrodeposition such as electrolyte concentration, deposition current or voltage, deposition time, effective area of electrodes and spacing between electrodes. In this research, Ni-Co-OH-graphene composite electrodes were prepared using two-electrode chronoamperometric co-electrodeposition in electrolyte containing 0.01 M Ni-Co ions and 0.001 mg mL^{-1} graphene oxide. Two pieces of nickel foil 20x20 mm were used as both working and counter electrodes fixed by 2 cm apart for all samples depositions. In order to study the effect of Ni:Co ratio on Ni-Co hydroxides physical and electrochemical properties, the deposition current was fixed and limit to -1 mA cm^{-2} for 5 min deposition time. For Ni-Co-OH-graphene composites Ni:Co ratio was fixed to 1:3 and 0.001 mg mL^{-1} of graphene oxide. Graphene oxide will be reduced to rGO and formed composites with Ni-Co hydroxides during electrodeposition process with current limit to -0.5, -1.0, -1.5, and -2.0 mA cm^{-2} to study the effect of deposition current.

1.5 Significance of Research

Supercapacitors are a passive, static energy-storage system, and can store and deliver energy at relatively high rates. Supercapacitors offer high-power density, good operational safety, and long cycling life, so they have been considered to be an excellent energy-storage platform with significant potential. Designing supercapacitor with high power-density i.e., which is how fast it can charge or discharge; and high energy-density i.e., which will determine how long it can run; is the current interest in energy storage area for enormous potential as a portable power supply in practical applications including electric vehicles, smart phones and smart wearable technology.

1.6 Novelty of Research

Ni-Co-OH-rGO composite electrodes were synthesized using one-pot, two-electrode co-electrodeposition with solution of Nickel-cobalt nitrate/graphene oxide (GO) as electrolytes. The preparation method of synthesizing GO completely avoid