SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING

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EFFECT OF HYDROCHLORIC ACID CLEANING ON NICKEL FOAM CURRENT COLLECTOR FOR SUPERCAPACITOR

by

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DECLARATION

I hereby declare that I have conducted, compiled the research work and written the dissertation entitled **“Effect of Hydrochoric Acid Cleaning on Nickel Foam Current Collector for Supercapacitor”**. I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or University.

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LIST OF ABBREVIATIONS

$(NH_4)_2MoO_4$	Ammonium ortomolybdate
AC	Activated carbon
Ag NPs	Silver nanoparticles
Ag/AgCl	Silver-silver chloride
Al	Aluminium
Al_2O_3	Alumina
ANF	Activated nickel foam
ASC	Asymmetric supercapacitor
CE	Counter electrode
CF	Carbon fibre
CNT	Carbon nanotube
Co	Cobalt
$CO(NH_2)_2$	Urea
$CoNi_2S_4$ NFAs	Cobalt-nickel sulphide nanofiber arrays
CPE	Constant phase element
CV	Cyclic voltammetry
DI	De-ionized
EDL	Electric double layer
EDLC	Electric double layer capacitor
EDX	Energy dispersive X-ray
EIS	Electrochemical impedance spectroscopy
E_{pa}	Anodic peak voltage
E_{pc}	Cathodic peak voltage
FESEM	Field emission scanning electron microscopy
FRA	Frequency response analyser
FTIR	Fourier transform infrared
GCD	Galvanostatic charge-discharge
H_2	Hydrogen gas
H_2O	Water
H_2SO_4	Hydrogen sulphate

HCl	Hydrochloric acid
Hg/HgO	Mercury-mercury oxide
ICDD	International centre diffraction data
I_{pa}	Anodic peak current
I_{pc}	Cathodic peak current
KBH_4	Potassium tetrahydroborate
KOH	Potassium hydroxide
Li	Lithium
MnO_2	Manganese(IV) Oxide
NA_2SO_4	Sodium sulphate
NF	Ni foam
$Ni(OH)_2$	Nickel hydroxide
$NiCl_2$	Nickel dichloride
$NiMoO_4$	Nickel molybdates
NiO	Nickel oxide
NiOOH	Nickel oxyhydroxide
NSAs	Nanosheet arrays
O_2	Oxygen gas
OH^-	Hydroxyl ions
PANi	Polyaniline
pG	Porous graphene
Pt	Platinum
PTFE	Poly(1,1,2,2-tetraflouroethylene)
$PVA-H_3PO_4$	Polyvinyl alcohol-phoshoric acid
PVDF	Poly-1,1-diflouroethene
$PVPA/Mo_x$	Poly(vinylphosphonic acid)/molybdenum
PYR_{14} TFSI	1-butyl-1-methylpyrrolidinium bis(triflouromethanesulfonyl)imide
R_{ct}	Charge transfer resistance
RE	Reference elecrode
rGO	Reduced graphene oxide
R_s	Series resistance
S	Sulphur

SCE	Saturated calomel electrode
SEM	Scanning electron microscopy
SiC	Silicon carbide
SS	Stainless steel
VOC	Volatile organic compund
WE	Working electrode
XRD	X-ray diffraction
Z’	Real impedance
Z”	Imaginary impedance
α-MoS_x	Alpha molybdenum sulphate

LIST OF SYMBOLS

α	alpha
δ	bending
β	beta
°	degree
μ	micro
Ω	Ohm
ϴ	tetha
ν	vibration

KESAN PEMBERSIHAN MENGGUNAKAN LARUTAN ASID HIDROKLORIK TERHADAP PENGUMPUL ARUS BUSA NIKEL DI DALAM SUPERKAPASITOR

ABSTRAK

Superkapasitor dikenali sebagai penyimpan tenaga yang mempunyai ketumpatan kuasa yang lebih tinggi daripada bateri dengan jangka hayat kitaran yang lebih lama. Elektrod pengumpul arus adalah salah satu komponen yang memainkan peranan penting dalam superkapasitor. Dalam kajian ini, kesan pembersihan menggunakan kepekatan larutan asid hidroklorik (HCl) yang berbeza terhadap pengumpul arus busa nikel (Ni), dan kesan pembersihan terhadap sifat elektrokimia dalam superkapasitor telah dikaji. Busa Ni berjaya dibersihkan menggunakan kaedah sonikasi selama 10 minit dalam larutan HCl (0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 4.0 and 5.0 M) pada suhu bilik. Hasil pencirian bahan untuk kepekatan pembersihan optimum (larutan HCl 2.5 M) terhadap busa Ni menunjukkan sampel mempunyai ketebalan seragam (0.034 µm) dan pelekatan lapisan oksida (NiO dan $Ni(OH)_2$ yang baik pada permukaan busa Ni. Analisis fasa dan kumpulan berfungsi mengesahkan kehadiran NiO dan $Ni(OH)_2$ tanpa kehadiran bendasing lain. Sifat kitaran busa Ni yang dibersihkan dengan larutan 2.5 M HCl bertindak balas seperti sifat superkapasitor iaitu puncak redoks dengan perbezaan potensi yang kecil (0.398 V pada kadar imbasan 10 mV s^{-1}). Sampel ini juga menunjukkan kapasiti yang luar biasa (1758.2 F cm^{-2} pada ketumpatan arus 8 mA cm^{-2}) dan kebolehbalikan dalam elektrolit kalium hidroksida (KOH) 1.0 M. Kesan elektrokimia disokong oleh analisis impedans. Perbezaan kecil (27.263 Ω) dalam rintangan pemindahan caj menunjukkan bahawa tindak balas elektrokimia telah meresap dengan baik semasa proses interkalasi/de-interkalasi. Oleh itu, kepekatan maksimum untuk pembersihan busa Ni adalah 2.5 M HCl dan ke bawah demi mengelakkan tindak balas superkapasitor.

EFFECT OF HYDROCHLORIC ACID CLEANING ON NICKEL FOAM CURRENT COLLECTOR FOR SUPERCAPACITOR

ABSTRACT

Supercapacitors are well known as energy storage that have higher power density than battery with longer cycling life. Current collector electrode is one of the important components that plays a vital role in performance of supercapacitor. In this work, effects of cleaning with different concentrations of hydrochloric (HCl) solution on nickel (Ni) foam current collector, and the effect after cleaning on electrochemical properties in supercapacitor were studied. The Ni foams were successfully cleaned using sonication method for 10 minutes in HCl solution (0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 4.0 and 5.0 M) at room temperature. The results of material characterization for optimum cleaning concentration (2.5 M HCl solution) of Ni foam showed the sample has uniform thickness (0.034 μm) and good attachment of oxide (NiO and $Ni(OH)_2$) layers on the surface of the Ni foam. Phase and functional group analysis confirmed the presence of the NiO and $Ni(OH)_2$ with no other impurities. The cycle behaviour of Ni foam cleaned with 2.5 M HCl solution responsed with supercapacitor characteristic such as redox peaks with small potential difference (0.398 V at scan rate of 10 mV s^{-1}). The performance of this concentration also showed an outstanding areal discharge capacity (1758.2 F cm^{-2} at current density of 8 mA cm^{-2}) and reversibility in 1.0 M potassium hydroxide (KOH) electrolyte. The effect in the electrochemical performance was supported by the impedance analysis. A small difference (27.263 Ω) in the charge transfer resistance indicates that the electrochemical reaction was well-diffused during the intercalation/de-intercalation process. Thus, the maximum concentration for Ni foam cleaning should be less than 2.5 M HCl solution in order to avoid supercapacitor responses.

CHAPTER 1

INTRODUCTION

1.1 Background

Interest towards energy storage technologies has grown significantly as the technologies are evolving rapidly. In order to enable varieties of application ranging from electrical grid level storage to powering vehicles and mobile devices, a lot of energy storage mechanisms have been developed and suited to the particular applications based on the specific technical requirements [1, 2]. Besides, electrochemical storage devices are gaining more intentions from the researchers nowadays to improve the electrochemical behaviour and capacity. The electrochemical devices includes battery, capacitor and supercapacitor.

Supercapacitor is known as high-capacity capacitor that possesses a lower energy density than battery but has higher power density [3, 4]. Supercapacitor consists of two components which are electrodes and electrolyte. There are two electrodes used for supercapacitor such as cathode and anode. In electrode, current collector electrode used to support active materials and to collect the current produced from the surface of anode or cathode. Commonly, metal (aluminium, copper, stainless steel and nickel) is used as current collector in the supercapacitor. Amongst the metal stated, Nickel (Ni) is chosen to be the current collector electrode due to higher corrosion resistance and economically [5]. There are three types of Ni that been used commercially, Ni foil, Ni mesh and Ni foam. Amongst the three designs, Ni foam is well-known as the best current collector due to having high surface area which can provide more intercalation and de-intercalations of ions [6]. Generally, Ni foam used as substrate where active material is paste on it. Therefore, the cleanliness of the Ni foam need to be considered as the contaminants that can influence the performance of these electrodes.

A few cleaning method had been done by researcher such as washing, washing and rinsing, centrifugation, stirring, soaking and sonication. Amongst all methods, sonication method is believed to be high promising method for cleaning [7]. Eventually, type and material of the cleaning agent plays a vital role in cleaning process. Contaminants such as grease and oil (obtain from fabrication process or handling) cannot be cleaned by only alcohols or distilled water because these contaminants will not dissolved in these medium. Aqueous acid such as hydrochloric acid (HCl) can be used to remove this type of contaminants.

Therefore, during manufacturing, it is critical to ensure the cleanliness of the current collectors as it may affect the quality of the supercapacitor. Here, maintaining the quality of the supercapacitor is very crucial in terms of aesthetic, cleanliness, and performance. As a result, a study about effect of cleaning towards nickel foam as current collector for supercapacitor has been conducted.

1.2 Problem statements

Cleaning is necessary in order to make sure dirt, oils and fingerprints are removed from the surface of Ni foam. Owing to the fact that dirt and fingerprints may introduce impurities to the Ni foam. Whereas oils will reduce the electrochemical reactions between Ni foam and electrolyte. Cleaning Ni foam with HCl solution may result in the formation of oxide layer on the surface of the Ni foam. This layer can become a barrier to the electrochemical reaction or otherwise, it can improve the intercalation and de-intercalation of ions during diffusion since the surface becomes more porous. Therefore, study regarding the cleaning was conducted.

Formation of oxide/hydroxide layer after cleaning with HCl solution may affect the electrochemical reaction, performance and the life cycle of the Ni foam. The Ni foam with presence of oxide/hydroxide layer is predicted to contribute to the performance of the supercapacitor. Cyclic voltammetry, galvanostatic charge-discharge and electrochemical impedance spectroscopy were performed to study the electrochemical behaviour of Ni foam. If the electrochemical are enhanced, meaning that there is contribution from these oxide/hydroxide layer (which should be avoided).

1.3 Objective

Two objectives are concerned in this project research. The objectives are as stated:

i. To investigate the effect of cleaning with different concentrations of HCl acid towards Ni foam current collector.
ii. To analyse the electrochemical properties of bare and cleaned Ni foams as the current collector electrode in supercapacitor

1.4 Scope of research

Ni foam was chosen as current collector electrode material for this research. Overall, this research work was divided into five chapters. Chapter 1 comprises on general background and major issue associated in current collector of supercapacitor. Possible approaches to improve the issue are presented. Chapter 2 describes the comprehensive literature review on current collector in supercapacitor and the effect of cleaning towards the current collector.

Chapter 3 discusses the overall methodology and the details of the materials and equipment used in this research work. The result on morphology, elemental, phase, functional group analysis and electrochemical behaviour of bare and cleaned Ni foam with different concentration of HCl solution are presented in the Chapter 4. Conclusion of the results and discussions in Chapter 4 is summarized in Chapter 5.