Faculty of Manufacturing Engineering

SYNTHESIS AND MECHANICAL ANALYSIS OF ELECTROCONDUCTIVE HIGH DENSITY POLYETHYLENE/POLYANILINE-DODECYLBENZENESULFONIC ACID/ALUMINA COMPOSITE

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DECLARATION

I declare that this thesis entitled "Synthesis and Mechanical Analysis of Electroconductive High Density Polyethylene/Polyaniline-Dodecylbenzenesulfonic Acid/Alumina Composite" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature :…………………………..

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APPROVAL

I hereby declare that I have read this thesis and in my opinion this thesis is sufficient in terms of scope and quality for the award of Doctor of Philosophy.

Signature :……………..

Supervisor Name :……………………….....................................

Date :………………………...

ABSTRACT

Polyaniline (PANI) based composites have become of great interest in supercapacitor electrode application due to its high conductivity (13.37 Scm^{-1}) and capacitance (501.31 Fg^{-1}). Some researchers have established excellent capacitance of PANI based electrodes. Yet pseudo-capacitive nature of the PANI electrodes causes swelling, shrinking and cracking during doping/ dedoping of charged ions that have resulted in poor cycle stability thus limits its application. This study aims to enhance the PANI properties to be used as a supercapacitor electrode. PANI doped with dodecylbenzene sulfonic acid (PANI-DBSA) was synthesized through oxidative polymerization by varying concentrations of dopant (DBSA) and concurrently nano alumina (Al_2O_3) was synthesized and functionalized with silane. Later, high density polyethylene/PANI-DBSA/ Al_2O_3 (HDPE/PANI-DBSA/Al_2O_3) composite was fabricated via a statistical approach to optimize the level of DBSA, PANI-DBSA and nano alumina in HDPE in order to incorporate comparable mechanical strength and conductivity. The application of conductive composite of HDPE/PANI-DBSA/Al_2O_3 towards supercapacitor electrode performance has been verified. As the result, the DBSA doping of PANI produces the protonation of amine nitrogen atoms of PANI. This redox reaction creates charge carrier in form of bipolarons and polaron species in PANI structure thus has enhanced the conductivity of PANI. However, over-doping leads to a decrease of polaron population, due to its conversion to bi-polarons which decrease the conductivity of PANI. Afterwards, through RSM study, the recommended optimum formulation of HDPE/PANI-DBSA/Al_2O_3 composite is made by controlling the concentration of DBSA at 2.00 mmol, composition of PANI-DBSA at 20 wt%, and composition of nano alumina at 5wt %. This recommended formulation yielded a desirability of confident level at 86.65% which is well above the accepted of 80 %. It demonstrates the improved compatibility between PANI-DBSA, nano alumina and HDPE through intermolecular forces from the interactions between two organic molecules. The hydrophobic effect of the organic substitution in DBSA and silane could be linked with the free energy transfer of hydrocarbon molecules from an aqueous phase (hydrophilic substitution in PANI molecule and nano alumina surface) to a homogeneous hydrocarbon phase. As a final point, the results demonstrate the fabrication of a promising electrode material derived from HDPE filled PANI-DBSA and nano alumina particles have improved the electrochemical performance of HDPE/PANI/Al_2O_3 ‖ MWCNT asymmetric supercapacitors in Na_2SO_4, KOH, and H_2SO_4 aqueous electrolytes. Among the electrolytes, KOH exhibited better specific gravimetric capacitance (145.58 Fg^{-1}) and good capacitance retention (101%) after 10,000 charge-discharge cycles. In brief, HDPE/PANI/Al_2O_3 ‖ MWCNT asymmetric supercapacitor has maximum energy density of 0.55 $Whkg^{-1}$ with a power density of 0.33 $kWkg^{-1}$. Thus, the asymmetric supercapacitor is well-suited for power storage since it has a high power density, then it can output large amounts of energy based on its volume.

ABSTRAK

Komposit berasaskan polyanilina (PANI) telah menarik minat di dalam penggunaan aplikasi elektrod superkapasitor kerana kekonduksian (13.37 Scm^{-1}) dan kapasitannya yang tinggi (501.31 Fg^{-1}). Beberapa penyelidik telah menghasilkan kapasitan yang sangat baik daripada elektrod berasaskan PANI. Walau bagaimanapun, sifat pseudokapasitif elektrod PANI menyebabkan berlakunya pembengkakan, penyusutan dan keretakan semasa process pendopan/pendedopan ion sekaligus menyebabkan kemerosotan dalam kestabilan kitarannya dan mengehadkan aplikasinya. Kajian ini bertujuan untuk meningkatkan sifat PANI untuk digunakan sebagai elektrod bagi superkapasitor. PANI didopkan dengan asid dodesilbenzena sulfonik (PANI-DBSA) disintesiskan melalui pempolimeran oksidatif dengan kepekatan dopan (DBSA) yang berbeza-beza dan aluminium oksida nano telah disintesis dan difungsikan dengan silane. Kemudian, komposit polietilena berketumpatan tinggi/PANI-DBSA/aluminium oksida nano (HDPE/PANI-DBSA/Al_2O_3) dihasilkan melalui kaedah statistik bagi mengoptimumkan tahap komposisi DBSA, PANI-DBSA dan aluminium oksida nano dalam HDPE untuk mendapatkan kekuatan mekanikal dan kekonduksian yang seimbang. Seterusnya, penggunaan komposit berkonduktif HDPE/PANI-DBSA/Al_2O_3 untuk melihat prestasi sebagai elektrod superkapasitor disahkan. Kesannya, pendopan DBSA-PANI menghasilkan protonasi atom nitrogen amina dari PANI. Tindak balas redoks ini mewujudkan pembawaan caj dalam bentuk spesies polaron di dalam struktur PANI dan meningkatkan kekonduksian PANI. Walau bagaimanapun, pendopan yang berlebihan menyebabkan pengurangan populasi polaron, kerana penukarannya kepada bi-polaron telah mengurangkan kekonduksian PANI. Melalui kajian RSM, formulasi optimum yang disyorkan bagi komposit HDPE/PANI-DBSA/Al_2O_3 telah dibuat dengan mengawal kepekatan DBSA, komposisi PANI-DBSA, dan komposisi aluminium oksida nano yang ditetapkan masing-masing pada 2.00 mmol, 20% berat dan 5wt %. Nilai formulasi yang disarankan ini menghasilkan tahap keyakinan yang terbaik (86.65%), iaitu melebihi nilai ambang 80%. Ini menunjukkan berlakunya keserasian antara PANI-DBSA, aluminium oksida nano dan HDPE melalui daya intermolekul daripada interaksi antara dua molekul organik. Kesan hidrofobik bagi penggantian organik pada DBSA dan silane boleh dikaitkan dengan pemindahan tenaga bebas molekul hidrokarbon dari fasa akueus (penggantian hidrofilik pada molekul PANI dan di permukaan aluminium oksida nano) ke fasa hidrokarbon homogen. Kajian menunjukkan fabrikasi bahan elektrod dari HDPE diisi dengan PANI-DBSA dan zarah aluminium oksida nano telah meningkatkan prestasi elektrokimia pada superkapasitor asimetri HDPE/PANI/Al_2O_3║MWCNT dalam elektrolit akueus Na_2SO_4, KOH dan H_2SO_4. Diantara kesemua elektrolit, KOH mempamerkan kapasitan gravimetrik spesifik yang lebih baik (145.58Fg^{-1}) dan pengekalan kapasitan selepas 10,000 kitaran dengan caj-pelepasan caj yang baik (101%). Ringkasnya, superkapasitor asimetri HDPE/PANI/Al_2O_3║MWCNT mempunyai ketumpatan tenaga maksimum 0.55Whkg^{-1} dengan ketumpatan kuasa 0.33 kWkg^{-1}. Oleh itu, superkapasitor asimetri sesuai untuk penyimpanan kuasa kerana ia mempunyai ketumpatan kuasa yang tinggi, yang membolehkan ia mengeluarkan jumlah tenaga yang besar berdasarkan isipadunya.

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LIST OF ABBREVIATIONS

PANI	-	Polyaniline
DBSA	-	Sodium dodecylbenzene sulfonic acid
HDPE	-	High density polyethylene
MWCNT	-	Multi walls carbon nano tube
PANI-DBSA	-	Polyaniline doped with Sodium dodecylbenzene sulfonic acid
Al_2O_3	-	Alumina
KOH	-	Potassium hydroxide
Na_2SO_4	-	Sodium sulfate
H_2SO_4	-	Sulfuric acid
HCl	-	Hydrochloric acid
CPC	-	Conductive polymer composite
COP	-	Chemical oxidative polymerization
SEM	-	Scanning electron microscope
TEM	-	Transmission electron microscopy
FTIR	-	Fourier-transform infrared spectroscopy
TGA	-	Thermal gravimetric analysis
XRD	-	X-ray powder diffraction
DSC	-	Differential scanning calorimetry
mmol	-	Mili mol
CV	-	Cyclic voltammograms
CD	-	Charge-discharge
THF	-	Tetrahydrofuran
APS	-	Ammonium persulfate
wt %	-	Weight percent

MPa	-	Mega pascal
ALN	-	Aluminum nitrate nanohydrate
ALP	-	Aluminium phosphide
MPS	-	3-methacryloxypropyltrimethoxysilane
NMP	-	N-Methyl-2-pyrrolidone
SDBS	-	Sodium dodecylbenzene sulfonate
RSM	-	Response surface method
CCD	-	Central composite design
ASTM	-	American Society for Testing Materials
EDLC	-	Electric double layer carbon
C_{sp}	-	Capacitance

LIST OF PUBLICATIONS

1. Mustaffa., N.A., Ahsan, Q., Azam, M.A. and Abdullah, L.C., 2018. Effect of Dodecylbenzene Sulfonic Acid Dopant Concentration on the Synthesis of Polyaniline. *Journal of Advanced Manufacturing Technology*, 12 (2), pp. 197–208.

2. Mustaffa., N.A., Ahsan, Q., Azam, M.A. and Abdullah, L.C., 2017. Dodecylbenzene Sulfonic Acid Concentration Effect on Electrical and Thermal Properties of Polyaniline. *Malaysian Journal of Analytical Sciences*, 21(4), pp.950–957.

LIST OF AWARDS

1. Bronze Medal for Invention of Asymmetric HDPE/PANI and CNT Electrode for Hybrid Pseudocapacitor in Malaysian Technology Expo 2017

2. Silver Medal for Invention of Novel Asymmetric Supercapacitor Electrode from HDPE/ PANI – CNT Hybrid Materials in mini UTeMEX 2016

CHAPTER 1

INTRODUCTION

1.1 Background

Over the last few decades, a rapid progress occurred in polymer composite production for various applications in the electronic and packaging industries. Of which, the conductive polymer composite material has been a noteworthy field to be discovered in the energy storage engineering and its applications. In the world market, conductive composites have been identified to hold major contributions in various applications such as electronics, telecommunications, aerospace, security, medical, special construction, consumer products and defense (Wang and Li, 2013). It has also been proven that the conductive polymer composites have more benefits compared to other materials used in other industry produced cases & enclosures, conduit and cable, antenna, reflectors, molded components, integration products, lightning strike protection and electrostatic discharge protector (Koul *et al.*, 2000; Narkis *et al.*, 1999; Clingerman, 2001). A conductive polymer composite contains components which possess chemically and /or physically distinct phases which are distributed within each continuous phase and exhibits properties that are different from the individual components, such as electrical conductivity (Müller *et al.*, 2017). In addition, composites are conventionally designed as structural materials. Theoretically, the conductive composite is a two-phase system containing an insulating phase (polymer matrix) and a conductive phase (filler/particle) (Nelson, 2010). Several kinds of materials which can be used as conductive fillers include dispersed metals, carbon black, metalized mineral particles, carbon and metallic fibers, carbon nanotubes, conductive