UNIVERSITI TEKNIKAL MALAYSIA MELAKA

DETERMINATION OF IONIC CONDUCTIVITY OF POLYVINYL ALCOHOL-BASED GEL POLYMER ELECTROLYTE CONTAINING PLASTICIZER FOR SUPERCAPACITOR APPLICATION

This report is submitted in accordance with requirement of the Universiti Teknikal Malaysia Melaka (UTeM) for Bachelor Degree of Manufacturing Engineering (Hons.)

by

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I hereby, declared this report entitled "Determination of ionic conductivity of polyvinyl alcohol-based gel polymer electrolyte containing plasticizer for supercapacitor application" is the result of my own research except as cited in references.

Signature :

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Date : 31 August 2021

Approval

This report is submitted to the Faculty of Manufacturing Engineering of Universiti Teknikal Malaysia Melaka as a partial fulfilment of the requirement for the Degree of Manufacturing Engineering (Hons). The member of the supervisory committee is as follow:

....

(Professor Ir. Dr. Mohd Asyadi 'Azam Bin Mohd Abid)- Signature & Stamp

ABSTRAK

Superkapasitor adalah teknologi canggih yang bertindak sebagai mekanisme penyimpanan tenaga yang mengandungi nilai kapasitansi yang lebih disukai ketika dibandingkan dengan kapasitor konvensional. Elektrolit polimer gel (GPE) adalah elemen penting untuk meningkatkan prestasi elektrokimia superkapasitor. Sifat elektrolit polimer gel yang luar biasa telah menarik minat penyelidik untuk mengambil berat tentang topik tersebut. Penyelidikan ini difokuskan untuk menentukan kekonduksian ionik elektrolit polimer gel berasaskan polivinil alkohol (PVA) yang mengandungi pemplastik untuk aplikasi supercapacitor. GPE disediakan dengan menggunakan pelarut, garam KI, PVA dan peratusan berat DEC yang berbeza. Kekonduksian ionik tertinggi yang diperoleh adalah dari 25% DEC dalam PVA GPE dengan nilai 10.99 $mS.cm^{-1}$. Plasticizer dapat mengubah struktur fizikal polimer untuk menjadikan pengangkutan ion lebih mudah melalui polimer yang membantu dalam peningkatan kekonduksian ion. Elektrod berasaskan rGO AC disediakan dan dicirikan. Nisbah I_D/I_G dari spektroskopi Raman menunjukkan nilai 0.992 yang mewakili kualiti struktur grafit yang baik pada elektrod. XRD elektrod menunjukkan dua puncak dengan ketinggian 26.64° dan 43.43° yang sesuai dengan (002) difraksi karbon anorganik dan (100) difraksi karbon grafit. Superkapasitor dibuat menggunakan elektrod GPE dan rGO dengan menggunakan teknik buburan konvensional. Prestasi elektrokimia supercapacitor diuji dengan Cyclic Voltammetry (CV) dan kapasitansi spesifik tertinggi (C_{sp}) yang diperoleh adalah dari 15% DEC PVA GPE dengan nilai 55.56 Fg^{-1}. GPE kemudian menjalani Galvanostatic charge-discharge (GCD) dan memperoleh 0.16 Fg^{-1} dari C_{sp}. Perbezaan nilai C_{sp} yang diperoleh dari CV dan GCD disebabkan oleh penurunan kualiti elektrolit dan elektrod. Oleh kerana kekangan masa, kualiti elektrolit dan elektrod yang lebih baik belum disediakan.

ABSTRACT

The supercapacitor is an advanced technology that act as an energy storage mechanism that contain preferable capacitance value when comparing to a conventional capacitor. Gel polymer electrolyte (GPE) is one of the important elements to improve supercapacitor electrochemical performance. The outstanding properties of gel polymer electrolyte when compared to liquid and solid based electrolyte has attracted the interest of researchers to concern about the topic. The research focused to determine the ionic conductivity of polyvinyl alcohol (PVA) based gel polymer electrolytes containing plasticizer for supercapacitor applications. The GPE was prepared by using solvent, KI salt, PVA and different weight percentage of DEC. The highest ionic conductivity obtained was from 25% DEC in PVA GPE with a value of 10.99 $mS.cm^{-1}$. The plasticizer can amend the physical structure of polymers to make the ions transportation easier through polymer which helps in the improvement of ionic conductivity. The rGO AC-based electrode was prepared and characterized. The I_D/I_G ratio from Raman spectroscopy shown a value of 0.992 which represents the good quality of graphitic structure on the electrode. The XRD of the electrode shown two sharp peaks of the height of 26.64° and 43.43° which corresponds to the (002) diffraction of inorganic carbon and the (100) diffraction of graphitized carbon respectively. The supercapacitor was fabricated using GPE and rGO electrode by using a conventional slurry technique. The supercapacitor electrochemical performance was tested out with Cyclic Voltammetry (CV) and the highest specific capacitance (C_{sp}) obtained is from 15% DEC of PVA GPE with a value of 55.56 Fg^{-1}. The GPE was then undergone Galvanostatic charge-discharge (GCD) and obtained 0.16 Fg^{-1} of C_{sp}. The difference in values of C_{sp} obtained from CV and GCD is due to the degradation of electrolyte and electrode. Due to time constraints, a better quality of electrolyte and electrode are not been prepared.

DEDICATION

To my only

beloved father, Tan Kian Soon

appreciated mother, Tan Siew Yien

adored brother, Tan Jun Qi

and all my helpful friends

for giving me so much supports financially, physically, mentally, encouragement, full cooperation and also understandings towards completing a part of this project.

Thank You So Much & Love You All Forever

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SERS	-	Surface-Enhanced Raman Scattering
CARS	-	Coherent anti-Stokes Raman scattering
CE	-	Counter electrode
CPEs	-	Composite polymer electrolytes
CV	-	Cyclic Voltammetry
EC	-	Ethylene carbonate
EDLC	-	Electric Double Layer Capacitor
EIS	-	Electrochemical Impedance Spectroscopy
FT	-	Fourier Transform
GCD	-	Galvanostatic charge-discharge
GPEs	-	Gel polymer electrolytes system
H_2O	-	Water
ICDD	-	The International Centre for Diffraction Data
JCPDS	-	Joint Committee on Powder Diffraction Standards
KI	-	Potassium iodide
LTS	-	Linear time-invariant
NE	-	Nernst-Einstein

NiO	-	Nickel oxide
PANI/NiO	-	Polyaniline-nickel oxide
PC	-	Propylene carbonate
PEG	-	Polyethylene glycol
PEO	-	Polyethylene oxide
PEs	-	Polymer electrolytes
PPEs	-	Plasticized polymer electrolyte
PTFE	-	Polytetrafluoroethylene
PVA	-	Polyvinyl alcohol
RE	-	Reference electrode
rGO	-	Reduced graphene oxide
RRS	-	Resonant Raman Scattering
RuO_2	-	Ruthenium(IV) oxide
SEM	-	Scanning Electron Microscopy
SPEs	-	Solid polymer electrolytes
SUT	-	Sample under test
WE	-	Working electrode
WSE	-	Working sensing electrode
XRD	-	X-Ray Diffraction

LIST OF SYMBOLS

%	-	Percent
^{o}	-	Degree
^{o}C	-	Degree Celcius
ε	-	Dielectric constant of the electrolyte
δ	-	Distance from the centre of the ion to the electrolyte interface
ΔE	-	Range of cyclic voltammetry operation
θ	-	Incident angle
λ	-	X-ray wavelength
$\lambda_{incident}$	-	Wavelengths (nm) of incident light
$\lambda_{scattered}$	-	Wavelengths (nm) of scattered light
$\pm$	–	upper signs refer to forward anodic sweeps
$\mp$	–	lower signs refer to forward cathodic sweeps
C	-	capacitance
C_{sp}	-	Specific capacitance
cm^{-1}	-	Wavenumber
d	-	Crystal layer spacings
E_{λ}	-	Switching potential

E_i	-	Starting potential
E_{pb}	-	Backward peak potential
$E_{pf.}$	-	Forward peak potential
E_t	-	Electrode potential at time, t
i_{pb}	-	Backward peak current
i_{pf}	-	Forward peak current
I_a	-	Intensities of the armorphous
I_c	-	Intensities of the crystalline
K	-	Boltzmann constant
M	-	Mass of pseudocapacitor material
n	-	Integer
n_i	-	Concentration of the free ions contributing to conductivity
q	-	Charge
q_i	-	Charge of the free ions contributing to conductivity
R_b	-	Bulk resistance obtained from EIS measurement
S	-	Electrode interface surface area
T	-	Time
t_λ	-	Time during switching potential
T	-	Absolute temperature in kelvin
v	-	Sweep rate, constant rate of potential change
X_c	-	Crystallinity
$Z(j\omega)$	-	Complex impedance

CHAPTER 1

INTRODUCTION

1.0 Research Background

There is a global issue that is facing by most parts of the world which is energy shortage and the energy used by 80 % of the world is depending on the use of fossil fuels. The overwhelming fossil fuel usage has caused pollution and catastrophe of the environment such as global warming (Sharma & Kumar, 2020). Other environmental pollution such as air, water, and soil has also been a vital issue to the world. Due to the consequence of the environment and decreasing capacity of fossil fuel, green and renewable energy is needed to replace the high demand for fossil fuel usage. There are two popular green energies been discussed to replace fossil fuels which are solar energy and wind energy. But the problem with these energies is their availability during usage. Sun is not always shining bright and the wind is not always blowing. This causes the energy supply is not stable all time. After all, the best way to solve the problem is using the energy storage mechanisms which are batteries and supercapacitors. Batteries and supercapacitors can act as an energy storage mechanism and used when needed (Bello, et.al., 2020).

Among these two technologies, supercapacitors (Figure 1.1) are more preferable for research purposes due to their properties. Supercapacitors have efficient power performance and their cycling stability is long-term comparing to batteries (Bhat, et.al., 2020). The only property that supercapacitor is incomparable with batteries is the capacity of energy content which supercapacitors have tiny energy content compared to batteries. Supercapacitors also possess electrochemical properties such as efficient charge and discharge rate, great power and energy density that can attract people interest to do research on it, especially from electrochemical specialists. According to Sharma and Kumar (2020), supercapacitors have been categorized into two groups which are Electric Double Layer Capacitor (EDLC) and pseudo-capacitor. For EDLC, there will be no electrochemical reaction in the capacitor and no ionic transport between electrode and electrolyte interface. For pseudo-capacitor, there is an electrochemical reaction takes place which helps to transfer charges between electrode and electrolyte to achieve storage ability. Supercapacitors are building up from electrochemical cell which contains two electrodes with a large surface, electrolytes and porous dielectric.

Fig 1.1 Supercapacitor

Alipoori et al. (2019) pointed out that electrolyte plays an important role in determining the performance of supercapacitors. The ionic conductivity and transport properties of the electrolyte will decide the electrochemical performance of the supercapacitor. Examples of electrochemical properties that will be influenced are stability, power density, energy density and electrical conductivity. Most of the research papers are discussing how to improve the ionic conductivity and transport properties since these two properties will help to increase capacitance and energy density. Thus, the performance of supercapacitors will be improved. Among the research papers, polymer electrolytes are the most compatible with supercapacitors since their properties will help increase the movement of ions and energy density (Li, et.al., 2020)

1.2 Problem Statement

The electrolyte is an important element in supercapacitors, the common electrolytes are mainly composed of electrolyte salts and water solvents or organic molecules solvent. The electrolytic solution formed from the combination is in the liquid state under room temperature. Liquid electrolytes often possess excellent electrochemical properties which are high ionic conductivity and electrochemical stability (Bhat, Yadav, & Hashmi, 2020). However, the are some weaknesses of liquid electrolytes such as toxicity. The toxicity can cause serious effects on the lungs, skin, eyes and mucous membranes (Fitrianingsih, et.al., 2013).

Moreover, liquid electrolytes can lead to a serious risk of fire due to flammable characteristics. Accidents with liquid electrolytes catching fire have made the public aware of their flammability hazard. More research about the replacement and improvement of electrolytes are made to prevent accidents. All these drawbacks of liquid electrolyte have become challenges to apply on electronic devices since the possibility of ignition of fire still exist and more aspect need to be considered before using it (Fitrianingsih, et.al., 2013).

Furthermore, solid electrolytes are utilized to replace liquid electrolyte for their ability in getting promising results for electrochemical applications. (Aziz, et.al., 2018). By using solid electrolytes, the problem facing by utilized liquid electrolytes which is a leakage problem will be fixed. However, the disadvantage of using solid electrolytes is the low ionic conductivity and causing low performance if applied on supercapacitors. The reason for low ionic conductivity properties is due to the crystalline phase of solid polymer electrolytes restrict ions movement. (Fitrianingsih, et.al., 2013)

Based on the research above, the application of liquid electrolytes or solid electrolytes cannot solve the problem perfectly. Therefore, this research will focus on gel polymer electrolytes since this type of electrolytes have both advantages from liquid and solid polymer electrolytes which are high conductivity but safe in use.

1.3 Objectives

The objectives are as follows:

1. To analyze the ionic conductivity of polyvinyl alcohol (PVA) based gel polymer electrolyte containing diethyl carbonate (DEC) plasticizer and potassium iodide salt by using Electrochemical Impedance Spectroscopy.

2. To characterize the morphological and structural properties of reduced graphene oxide (rGO) activated carbon-based electrode by using Scanning Electron Microscopy, Raman Spectroscopy, and X-ray Diffraction.

3. To investigate the electrochemical performance of reduced graphene oxide activated carbon-based supercapacitor with PVA based gel polymer electrolyte by using Cyclic Voltammetry and Galvanostatic Charge Discharge analysis.

1.4 Scopes

The scopes of research are as follows:

1. To achieve objective (1):
    - Prepare PVA based gel polymer electrolytes containing plasticizer with PVA 5.68 weight percentage (wt%); ethylene carbonate 8.52 wt%; propylene carbonate 11.36 wt%; potassium iodide 11.93 wt%; DEC 0 wt% and the weight percentage of DEC plasticizer will vary from 0 to 25%.
    - Characterize PVA based gel polymer electrolytes containing plasticizer using EIS with a frequency range of 1Hz to 100 kHz.

2. To achieve objective (2):
    - Prepare rGO electrode using conventional slurry technique with rGO 40 wt%; activated carbon 50 wt%; CMC/SBR binder 10wt%.
    - Characterize rGO electrode using SEM which operating between 80-120 kV at magnification of 10kx-30kx to see the surface morphology of rGO electrode.

    - Characterize rGO electrode using XRD with 2θ in range of 5^0-55^0 to check crystal phase and phase composition.
    - Characterize rGO electrode using Raman spectroscopy at room temperature and 532nm laser to identify quality of rGO based on G-band and D-band analysis.

3. To achieve objective (3):
    - Fabricate supercapacitor with PVA based gel polymer electrolyte and rGO electrode by using a conventional slurry technique.
    - CV test on supercapacitor will be done with range of 10 to $100mVs^{-1}$ and potential range of 0 to 1.1 V.