SYNTHESIS AND CHARACTERIZATION OF PVA - METAL COMPLEX COMPOSITES FOR ELECTROCHEMICAL DOUBLE LAYER CAPACITOR (EDLC) DEVICES

BY

MOHAMAD ALI BRZA

A thesis submitted in fulfilment of the requirement for the degree of Doctor of Philosophy (Engineering)

Kulliyyah of Engineering
International Islamic University Malaysia

DECEMBER 2021

ABSTRACT

In the current work, the preparation of the polymer electrolyte (PE) systems consists of PVA polymer matrix, ammonium thiocyanate (NH_4SCN) as ionic source, Cu(II)-, Ce(III)-, and Cd(II)-complex as metal-complexes and glycerol as plasticizer are performed by solution cast technique. The polymer electrolytes are used for application in electrochemical double-layer capacitor (EDLC) device. Due to poor optical, electrical, and electrochemical properties of PVA, it is integrated with the metal-complex and glycerol to increase amorphous phase, electrical conductivity, and decrease optical band gap for the electrolyte to be used for fabricating EDLC device with very high performance. X-ray diffraction (XRD) has shown that the highest conducting plasticized electrolyte with Cu(II)-complexes possess the lowest degree of crystallinity. The possible interactions within the PE elements are verified using Fourier transform infrared (FTIR) spectroscopy. The FESEM images reveal that the surface morphology of the samples showed a uniform smooth surface at high glycerol concentration. This is in good agreement with the XRD and FTIR results. The highest conducting plasticized electrolyte without metal-complexes is found to be 1.82×10^{-5} S cm^{-1} while the conductivity increased up to 2.25×10^{-3} S cm^{-1} by the addition of Cu(II)-complex into the PE. The conductivity is found to be affected by the ionic mobility (μ), diffusion coefficient (D), and number density (n) of ions. From UV-Vis spectroscopy study, the optical parameters (absorption edge, refractive index (N), dielectric constant (ε_r), dielectric loss (ε_i), and optical band gap energy (E_g)) of pure PVA and composite films are measured. Examination of the ε_i optical parameter is carried out to measure the E_g, while types of electronic transition in the films are determined based on the Tauc's method. From transference number measurement (TNM), ions are considered as the dominant charge carrier and the transference number for ions and electrons for the highest conducting electrolyte (PGNC-4) are 0.971 and 0.029, respectively. PGNC-4 is electrochemically stable up to 2.15 V. Galvanostatic charge-discharge (GCD) measurement of the EDLC has been supported with cyclic voltammetry (CV) analysis. CV curves are determined by inserting the plasticized electrolytes between two activated carbon (AC) electrodes, and it shows a nearly rectangular shape at low scan rates. The specific capacitance and energy density of the EDLC for the highest conducting plasticized electrolyte with Cu(II)-complexes (PGNC-4) are nearly constant within 1000 cycles at a current density of 0.5 mA/cm^2 with average of 155.322 F/g and 17.473 Wh/Kg, respectively. The energy density of the EDLC in the current work is in the range of battery energy density. The EDLC performance was found to be stable over 1000 cycles for the PGNC-4 system. The low value of equivalent series resistance shows that the EDLC has good electrolyte-electrode contact. The EDLC for the PGNC-4 system exhibited the initial high power density of 4.960×10^3 W/Kg.

خلاصة البحث

في الدراسة الحالية، تحضير انظمة الكتروليت البوليمرى (PE) يتكون من مصفوفة بوليمر (PVA)، ثيوسيانات الامونيوم (NH_4SCN) كمصدر الأيونى و معقد Cd(II), Ce(III), Cu(II) كالمعدات المعدنية و الجلسيرن كملدن او الملصق و ذلك عن طريق تقنية الصب المحلول. يستخدم البوليمرات الاكترولية فى التطبيق و فبركه متسعه الكتروكيميائية ثنائية الطبقية (EDLC) . بسبب ضعف الخواص البصرية و الكهربائية و الكهروكيمائيه لPVA تم دمجه و تكملته مع المعقد المعدن و الگريسول لزياده الطور الامورفسى اللا البلورى و كذلك التوصيل الكهربائى و تقليل افجوه الطاقه البصرية للالكتروليت لكى تستخدم فبركه EDLC ذات كفاءة العاليه.

تبين من الحيود الاشعة السينية (XRD) ان الكتروليت المعدن ذات التوصيلية العالية مع معقدات Cu(II) تمتلك أقل درجة من التبلور. تم استخدام التحليل الطيفي لتمويل الفوريرى للاشعه تحت الحمراء (FTIR) و ذلك للتحقق من التفاعلات الممكنة للعناصر داخل الالكتروليت البوليمرى. من خلال دراسة اشكال (FESEM) تبين له عند تراكيزه العالية لكليسرين تتميز سطوح الاغشية المستحضرة بأنها وساء و منظم و متوافقه مع نتائج FTIR, XRD. تم الحصول على توصيلة الكتروليت الوصل الملدين بدون معقدات المعدنيه بمقدار 1.82×10^{-5} Scm^{-1} و تزداد هذه القيمة الى 2.5×10^{-3} Scm^{-1} عند اضافة معقد Cu(II) الى اكتروليت البوليمرى (PE). و من خلال الدراسة، تبين ان التوصلية الكهربائية تتأثر بحركية الايونيه (μ) و معامل الانتشار (D) و تركز الايونات (n). من دراسة الطيف الاشعة المرئية وفوق البنفسجية (UV-Vis)، تم قياس البارامترات (حافه الامتصاص، معامل الانكسار (N) و ثابت عزل الكهربات (ε_r) و فقد عزل الكهربائى (ε_i) و كذلك فجوة الطاقه البصرية (E_g)) للاغشيه البوليمريه PVA التميه و الحركيه. من خلال فحص البارامتر الضوئى ε_i تم قياس فجوه طاقه البصريه (E_g)، بينما حددت الانتقالات الالكترونيه بأنواعها للافلام تحت الدراسه اعتمادا على طريقة (Tauc) تاوك. نتائج قياسى الرقم التحويلى TNM، توكد على أن غالبيه حاملات الشحنات هى الايونات، و نتائج TNM للايونات و الاكترونات للاكتروليتات ذات توصليه عاليه لـ PGNC-4 تكون 0.029 و0.971 على التوالى. من خلال الدراسة، تبين أن PGNC-4 مستقر كهربائيا حتى 2.15 فولت، وتم دعم قياسات تفريغ الشحن الكلفانى (GCD) لـ EDLC من خلال تحاليل فولتميرى الدورى (CV)، حيث تم تحديد منحنيات (CV) و ذلك من ادراج الكتروليتات الملدنه (plasticized) تحت الدراسة بين قطبي كاربون المنشط (AC) حيث خمرت شكلا تقريبيا للمستطيل عند معدلات المسح المنخفض .و تظهر من خلال النتائج ان السعة النوعية و كثافه الطاقه للالكتروليتات الملدنية مع معقدات PGNC-4 Cu (II) يمتلك الموصليه عاليه ثابته تقريبا خلال 1000 دورة عند كثافه التيار بمعدل 0.5 mA/cm^2 17.474 Wh/kg 155.332 F/g على التولى في الدراسة الحاليه، الكثافه الطاقيه EDLC عند نطاق كثافة الطاقة البطارية، و اداء EDLC مستقر على مدى 1000 دورة لنظام PGNC-4، و قيمة الواطية للمقاومة المكانية المتواليه دلالة على توصيلية جيدة بين الالكترونيات و القطب. اظهر EDLC لنظام PGNC-4 كثافة لقدرة العالية الأولية لـ 4.960×10^3 W/kg.

APPROVAL PAGE

The thesis of Mohamad Ali Brza has been approved by the following:

_____
Hazleen Bt. Anuar
Supervisor

_____
Shujahadeen B. Aziz
Co-Supervisor

_____
Fathilah Bt. Ali
Co-Supervisor

_____
Mohd Hanafi Ani
Internal Examiner

_____
Mohd Ambri Mohamed
External Examiner

_____
Mohammad Naqib Eishan Jan
Chairman

DECLARATION

I hereby declare that this thesis is the result of my own investigations, except where otherwise stated. I also declare that it has not been previously or concurrently submitted as a whole for any other degrees at IIUM or other institutions.

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ACKNOWLEDGEMENT

Firstly, it is my utmost pleasure to dedicate this work to my dear parents and my family, who granted me the gift of their unwavering belief in my ability to accomplish this goal: thank you for your support and patience.

I wish to express my appreciation and thanks to those who provided their time, effort and support for this project. To the members of my dissertation committee, thank you for sticking with me.

Finally, a special thanks to Professor Dr Hazleen Bt. Anuar, Assistant professor Dr Shujahadeen B. Aziz, and Associate professor Dr Fathilah Bt. Ali and for their continuous support, encouragement and leadership, and for that, I will be forever grateful.

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LIST OF ABBREVIATIONS

Al_2O_3	Aluminium oxide
Al_2SiO_5	Aluminium silicate
BmImBr	1-butyl-3-methylimidazolium bromide
BmImCl	1-butyl-3-methylimidazolium chloride
CB	Conduction band
CH_3COOK	Potassium acetate
NH_4I	Ammonium iodide
NH_4NO_3	Ammonium nitrate
CPE	Constant phase element
CV	Cyclic voltammetry
EDLC	Electrochemical double-layer capacitor
FESEM	Field emission scanning electron microscopy
ESR	Equivalent series resistance
FTIR	Fourier transform infrared spectroscopy
CuI	copper iodide
CuS	Copper monosulfide
DBG	Direct band gap
DMFC	Direct-methanol fuel cell
DOP	Dioctyl phthalate
H_2SO_4	Sulfuric acid
H_3PO_4	Orthophosphoric acid
KOH	Potassium hydroxide
LED	Light-emitting diode
H^+	Hydrogen ion
Li^+	Lithium ion
$LiClO_4$	Lithium perchlorate
LSV	Linear sweep voltammetry
MC	Methylcellulose
NH^{4+}	Ammonium ion
$NH_4CH_3CO_2$	Ammonium acetate