TERNARY HYBRID PVDF-HFP/PANI/GO POLYMER ELECTROLYTE MEMBRANE FOR LITHIUM ION BATTERY

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UNIVERSITI SAINS MALAYSIA
2019

TERNARY HYBRID PVDF-HFP/PANI/GO POLYMER ELECTROLYTE MEMBRANE FOR LITHIUM ION BATTERY

by

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Thesis submitted in fulfilment of the requirements
for the degree of
Doctor of Philosophy

April 2019

ACKNOWLEDGEMENT

At first, I would like to thank to almighty Allah for blessing me with such a great opportunity. After that, I would like to show my heartily gratitude to my parents Mr. Mahfooz ur Rehman Farooqui and Miss. Ayesha Begum; also, to my wife Miss. Nikhat Shaikh for their love and support during this whole research journey. Additionally, I am really very thankful to my main supervisor Prof. Dr. Abdul Latif bin Ahmad, and my co-supervisor Dr. Noorashrina binti A. Hamid for their appreciable supervision, valuable guidance and suggestions, and consistent support throughout my research.

I'd like to give special thanks to all the staff from management, laboratories, administration, and technical departments in School of Chemical Engineering for giving me guidance and support, especially to Nor Irwin Basir for sharing his previous experience related to my research and time to time support throughout the period. Also, I am grateful to all of my colleagues, friends and cousins for all of their moral support help and support throughout the research.

At last, but not least, I would like to express my gratitude to the Universiti Sains Malaysia for providing me such an outstanding research environment, facilities and more importantly, the USM fellowship. In addition, I am very grateful to Ministry of Higher Education Malaysia for their financial assistance through Fundamental Research Grant Scheme (FRGS) [203.PJKIMIA.6071355] during this research.

I would like to say Thank You to all of you for your support during this exceptional research experience, your support will be appreciated ceaselessly. Thanks a lot.

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LIST OF ABBREVIATIONS

Al_2O_3	Aluminum oxide
ASTM	American society for testing and materials
CA	Chronoamperometry
DMC	Dimethyl carbonate
DSC	Differential scanning calorimetry
DTGA	Derivate of thermogravimetric
EC	Ethylene carbonate
EIS	Electrochemical impedance spectroscopy
FTIR	Fourier-transform infrared spectroscopy
GO	Graphene oxide
HCl	Hydrochloric acid
$LiFePO_4$	Lithium iron phosphate
$LiPF_6$	Lithium hexafluorophosphate
LPE	Liquid polymer electrolyte
LSV	Linear sweep voltammetry
MSE	Mean square error
NH_4OH	Sodium hydroxide
NMP	N-Methyl-2-pyrrolidone
PANI	Polyaniline
PE	Polyethylene
PMMA	Poly(methyl methacrylate)
PP	Polypropylene
PVAc	Polyvinyl acetate
PVDF	Poly(vinylidene) fluoride

PVDF-HFP	Poly(vinylidene fluoride-co-hexafluoropropylene)
PVDF-TrFE	Poly(vinylidene fluoride-co-trifluoroethylene)
SEM	Scanning electron microscopy
SiO_2	Silicon dioxide
SPE	Solid polymer electrolyte
SPEEK	Sulfonated poly(ether ether ketone)
TGA	Thermogravimetric
TiO_2	Titanium oxide
XRD	X-ray diffraction
ZrO_2	Zirconium oxide

LIST OF SYMBOLS

ρ	Density of membrane (gm/cm^3)
A	Membrane diffusion area (cm^2)
C	capacitor
CPE	constant phase element
D_t	Membrane thickness (μm)
L	Inductor
R	Resistance (ohm)
V_d	Volume of membrane (cm^3)
W	Wardburg constant
W_f	Weight of membrane after dipping it in electrolyte (gm)
W_i	Weight of membrane before dipping it in electrolyte (gm)
Y_f	Experimental values
Y_i	Predicted values

MEMBRAN HIBRID PERTIGAAN ELEKTROLIT POLIMER (PVDF-HFP)/PANI/GO UNTUK BATERI ION LITIUM

ABSTRAK

Poli (vinilidina hexafluropropilina) PVDF-HFP merupakan komponen yang berpotensi sebagai pemisah dalam bateri ion litium kerana ketahanan kimianya yang sangat tinggi, kestabilan mekanikal dan haba yang besar beserta kos yang lebih rendah; walau bagaimanapun, komponen yang asalnya mempunyai ciri-ciri yang terhad dan memerlukan pengubahsuaian lanjut bagi mencapai prestasi yang diinginkan. Oleh itu, dalam penyelidikan ini, hibrid ternari PVDF-HFP/PANI/GO telah dibangunkan dan skop dibahagikan kepada tiga fasa yang pada permulaannya, dos polianilina (PANI) yang berbeza (1% berat, 2% berat, dan 3% berat) telah dicampur ke dalam matriks polimer PVDF-HFP bagi menghasilkan membran elektrolit PVDF-HFP/PANI dengan menggunakan kaedah nafas-bentuk. Penambahan PANI (2% berat) didapati mempengaruhi daya kekonduksian ionik di mana nilainya telah meningkat dari 1.98×10^{-4} S cm^{-1} bagi membran tunggal PVDF-HFP ke 1.04×10^{-3} S cm^{-1}; walau bagaimanapun, kesan pengekstrakannya mengakibatkan kekuatan tegangan membran tunggal PVDF-HFP menurun dari 4.2 MPa hingga 2.8 MPa.

Skop kedua, kesan grafina oksida (GO) dikaji dengan mevariasikan jumlah GO yang berbeza (1% berat, 2.5% berat dan 5% berat) ke dalam matriks polimer PVDF-HFP. Penambahan GO (2.5% berat) meningkatkan kekuatan tegangan membran PVDF-HFP dari 4.2 MPa hingga 12.5 MPa; walau bagaimanapun, ia menyebabkan kekonduksian ionik PEM tunggal diketepikan. Selanjutnya, bagi fasa ketiga, bahan komposit PANI/GO digabungkan atas faktor keunikan kedua-dua pengisi. PVDF-

HFP/ PANI hibrid ternari (2% berat)/GO (10% berat, 25% berat, dan 40% berat) PEM disintesis dan dicirikan untuk bateri ion litium.

Ternari PVDF-HFP/PANI/GO yang diperolehi menunjukkan peningkatan kekuatan tegangan sehingga 8.8 MPa. Tambahan pula, membran ternari PVDF-HFP/PANI/GO menunjukkan kestabilan terma yang luar biasa dengan T_d sehingga 498°C, peningkatan morfologi, pengambilan elektrolit tertinggi (367.5%) dan keliangan yang sangat baik sekitar 89%. Selain itu, PEM bagi PVDF-HFP tunggal, PVDF-HFP/PANI dan PVDF-HFP/PANI/GO yang optimum telah digunakan untuk pencirian elektrokimia dan pemodelan. Selain itu model R-CPE memberikan kualiti yang sesuai dengan nilai MSE sekitar 5% berbanding model R-C dan R-L. Seterusnya, PEM optimum yang disediakan berjaya digunakan dalam bateri ion litium dan menunjukkan kapasiti khusus yang baik untuk 10 pusingan permulaan. Walau bagaimanapun, PEM ternari PVDF-HFP/PANI/GO menghasilkan kestabilan yang lebih baik berbanding dengan PEM lain; oleh itu, ia diuji selanjutnya untuk pengekalan kapasiti dan ia mengekalkan kapasiti melebihi 95% selepas 30 kitaran. Kesimpulannya, penggunaan membran ternari PVDF-HFP/PANI/GO merupakan pemisah yang berpotensi bagi bateri ion litium di masa hadapan.

TERNARY HYBRID PVDF-HFP/PANI/GO POLYMER ELECTROLYTE MEMBRANE FOR LITHIIUM ION BATTERY

ABSTRACT

Poly(vinylidene fluoride-co-hexafluoropropylene) PVDF-HFP is a promising candidate as a separator in lithium-ion batteries owing to its outstanding chemical resistance, high mechanical and thermal stability with lower cost; however, its pristine form has limited characteristics that require further modification to achieve enhanced performance. Therefore, in this research ternary hybrid PVDF-HFP/PANI/GO were develop and the scope were divided into three phase which at first, different dosages of polyaniline (PANI) (1 wt%, 2 wt%, and 3 wt%) are incorporated into PVDF-HFP polymer matrix to fabricate PVDF-HFP/PANI polymer electrolyte membrane by using breath-figure method. The PANI (2 wt%) inclusion influenced the ionic conductivity and enhanced it from 1.98×10^{-4} S cm^{-1} of pristine PVDF-HFP membrane to 1.04×10^{-3} S cm^{-1}; however, its plasticizing effect resulted in tensile strength of pristine PVDF-HFP membrane from 4.2 MPa to 2.8 MPa.

Secondly, the effect of graphene oxide (GO) is investigated by varying different amount of GO (1 wt%, 2.5 wt%, and 5 wt%) into PVDF-HFP polymer matrix. The GO (2.5 wt%) addition remarkably enhanced the tensile strength of PVDF-HFP membrane from 4.2 MPa to 12.5 MPa; however, it showed negligible effect on ionic conductivity of pristine PEM. Therefore, in third phase, PANI/GO composite material is combined for the unique properties of both the fillers. The ternary hybrid PVDF-HFP/PANI (2 wt%)/GO (10 wt%, 25 wt%, and 40 wt%) PEMs are synthesized and characterized for lithium ion batteries.

The obtained PVDF-HFP/PANI/GO ternary membrane showed a remarkable improvement in tensile strength up to 8.8 MPa. Furthermore, the PVDF-HFP/PANI/GO ternary membrane exhibited outstanding thermal stability with T_d up to 498°C, improved morphology, highest electrolyte uptake (367.5%) and an excellent porosity of around 89%. Moreover, the obtained optimum pristine PVDF-HFP, PVDF-HFP/PANI, and PVDF-HFP/PANI/GO PEMs were considered for further electrochemical characterization and modelling. Also, the R-CPE model provided a best quality fit with MSE value of around 5% compared to R-C and R-L model. Further, the prepared optimum PEMs is successfully applied in lithium ion battery and showed good specific capacity for initial 10 cycles. However, PVDF-HFP/PANI/GO ternary PEM resulted in better stability compared to other PEMs; therefore, it is tested for capacity retention and it retained over 95% capacity after 30 cycles. In conclusion, the proposed PVDF-HFP/PANI/GO ternary membrane is a potential candidate as a separator in future lithium-ion batteries.

CHAPTER 1

INTRODUCTION

1.1 Introduction

World economy is highly dependent on fossil fuel and it has a severe impact on world ecology. Global climate impact and air quality are two major concerns about the fossil fuel. In addition, the increasing population in developing countries are enlarging their energy consumption and economies and is increasing dramatically. Therefore, electrochemical energy production has received great attention as an alternative source of energy due to its sustainability and environmentally friendly properties (Brownson et al., 2011; Li et al., 2014; Ntengwe, 2005; Rahman et al., 2014; Scrosati et al., 2011; Yu et al., 2016).

Batteries, fuel cells and supercapacitors are the systems for energy storage and conversion (Bruce et al., 2012; Choi et al., 2012; Han et al., 2014; Kim & Guiver, 2009, Makinouchi et al., 2017). The secondary batteries such as lithium-ion (LIBs), nickel-cadmium and lead-acid, etc. are rechargeable. Each battery has anode and cathode, electrolyte and separator. Anode is the negative electrode where the oxidation process occurs; while, the positive cathode electrode gains electron from external circuit. An electrolyte provides ionic conductivity between negative and positive electrodes. A separator is a physical barrier between electrodes to prevent short circuit while allowing ionic flow (Lu et al., 2015, Poullikkas, 2013; Visco et al., 2009). LIB provides higher operating voltage, lower self-discharge, and higher coulombic efficiency compared to other batteries (Li et al., 2014; Speirs et al., 2014; Wang et al.,

2016; Yong et al., 2015). Some characteristics of the secondary batteries are listed in Table 1.1.

Table 1-1: Characteristics of secondary batteries (Yanilmaz, 2015)

Battery types	**Voltage (V)**	**Energy Density (Wh/kg)**	**Power Density (Wh/kg)**	**Cycle life**
Lithium ion	3.6	100-150	300	400-1.2k
Nickel-Cadmium	1.2	35-57	50-200	1k-2k
Lead acid	2	25-30	75-130	200-400
Nickel-Metal Hydride	1.2	50-80	150-250	600-1.5k

Figure 1.1 shows the schematic diagram of lithium ion battery which includes separator sandwiched in between lithium anode and carbon cathode; it provides superior properties compared to other secondary batteries such as higher working voltage, higher energy density, lower gravimetric density and longer service life. Owing to these properties, LIBs have been used in various devices such as eco-friendly transportation power storage, health care and defence (Lampič et al., 2016; Zhen et al., 2018; Scrosati et al., 2011). In addition, LIBs use lithium ions as the main charge carrier and maintain a high average discharge voltage of 3.7 V. Also, the LIBs are light in weight and can produce much high energy density compared to other batteries; therefore, it has become a promising choice for electric vehicles (EVs) (Yong et al., 2015). Lithium-ion batteries can be designed in various shapes such as prismatic, coin, pouch, and cylindrical depending on the devices and application areas. Cylindrical batteries are used in laptop computers, single-cell coin-shaped batteries are used in small electric appliances and portable IT devices, prismatic cells are common in

portable devices and pouch-shaped cells cased in aluminium plastic composites are good for electric vehicle applications (Lampič et al., 2016; Song et al., 2011). LIBs have received great attention since its introduction in 1990s due to high energy density, low gravimetric density, long cycle life and flexible design. The development of improved electrodes and separators for LIBs is critical to obtain high energy and power densities for electric and hybrid electric vehicles (Wang et al., 2016). Fast charging and discharging at high power rates, energy density, power, cycling, life, charge/discharge rates, safety and cost must be addressed to design advanced lithium-ion batteries.

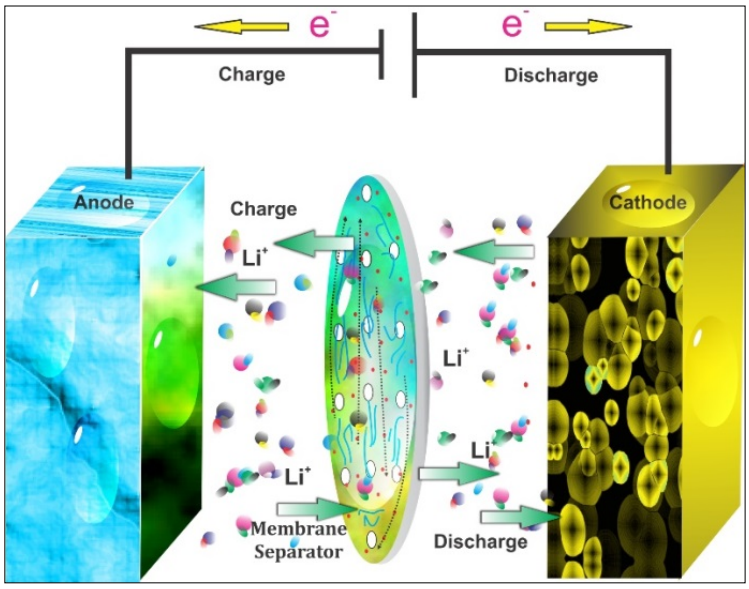

Figure 1-1: Schematic illustrating the mechanism of operation for a lithium-ion battery

1.2 Introduction of separators

A lithium ion battery (LIB) comprises of anode, cathode, separator and electrolyte. Separator is an essential component of LIBs that is placed between two electrodes to provide a physical barrier, while it serves as a medium for ion transfer at

the time of charging and discharging process. In production, some ionically conductive liquid electrolyte is used to fill the pores of the separator (Liu et al., 2017). The separator plays an important role in LIBs; it avoids the electronic contact and serves as a medium for ion transport between negative and positive electrodes; also, it provide and maintain a good support to the electrode, offers better ionic impedance at higher temperatures, and hold the electrolyte effectively for a longer time. For the accomplishment of these features, the separators need to be electrochemically and chemically stable towards the electrolytes and the electrodes; also, it must have an excellent thermal and mechanical stability to withstand at elevated temperature and at high tension during battery assembly and a charge-discharge process (Costa et al., 2013; Deimede & Elmasides, 2015; Jeong et al., 2012). Even though the separator does not participate in any cell reactions, the materials and structure of the separators affect the performance of LIBs. The separator influences internal cell resistance and cell kinetics so that it affects the performance of battery such as cycle life, energy density, power density, and safety.

Polymer electrolyte membranes (PEMs) have been extensively used as a separator in lithium ion batteries. The various types of PEMs such as solid polymer electrolyte membranes (SPEs), liquid polymer electrolyte membranes (LPEs), gel polymer electrolyte membranes (GPEs) etc. have received tremendous attention in the last couple of decade. Each separator is different and has its own merits and demerits and the selection of separators affects the performance of lithium-ion batteries. Many factors must be considered while choosing the separators for LIBs. General requirements are summarized below in Table 2 and detailed description was provided in the upcoming section.