

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

USAID UR REHMAN FAROOQUI

**UNIVERSITI SAINS MALAYSIA
2019**

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

by

USAID UR REHMAN FAROOQUI

**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.

TABLE OF CONTENTS

ACKNOWLEDGEMENT	ii
TABLE OF CONTENTS	iii
LIST OF TABLES	xiii
LIST OF FIGURES	xvi
LIST OF ABBREVIATIONS	xix
LIST OF SYMBOLS	xv
ABSTRAK	xvi
ABSTRACT	xviii
CHAPTER 1: INTRODUCTION	
1.1 Introduction	1
1.2 Introduction of separators	3
1.3 Problem Statement	5
1.4 Research objective	7
1.5 Scope of research and limitations	8
1.6 Organization of thesis	8
CHAPTER 2: LITERATURE REVIEW	
2.1 Overview of separators	10
2.2 Polymer electrolyte membranes for lithium ion battery	11
2.2.1 Liquid polymer electrolyte membranes (LPEs)	14
2.2.2 Solid polymer electrolyte membranes (SPEs)	15
2.2.3 Gel-polymer electrolyte membranes (GPEs)	16
2.2.4 Composite membranes	19
2.3 Requirements of the separator	23
2.4 Preparation methods for GPEs (PEMs)	26
2.4.1 Casting technique	27
2.4.2 In situ polymerization	28
2.4.3 The inversion technique/phase separation	29
2.4.4 Electrospinning technology	30
2.4.5 Breath figure method	32

2.5	Introduction of the inorganic fillers	35
2.6	Electrochemical methods	41
2.6.1	Electrochemical impedance spectroscopy	41
2.6.2	EIS for battery equivalent circuit models	43
(a)	Electrical double layer capacitance, Cdl	43
(b)	Polarization resistance (Rp)	43
(c)	Diffusion and Warburg impedance (W)	44
(d)	Ohmic resistance (Ro)	44
(e)	Inductance (L)	45
2.7	Definitions	46
2.7.1	Internal resistance	46
2.7.2	Battery capacity	46
2.7.3	Current rate (C-rate)	46
2.7.4	Ionic conductivity	46
2.7.5	Energy density	47
2.8	Conclusions	47

CHAPTER 3: METHODOLOGY

3.1	Introduction	49
3.2	Chemicals and materials	49
3.3	Flow chart of experimental work	51
3.4	Description of major equipment	52
3.4.1	Glove box	52
3.4.2	Split test cell	54
3.4.3	Universal tensile strength tester	55
3.4.4	The electrochemical cell	56
3.5	Synthesis of particle and composite	58
3.5.1	Synthesis of Polyaniline (PANI) particles	58
3.5.2	Synthesis of PANI/graphene oxide (GO) composite	58
3.6	Synthesis of various PVDF-HFP membranes	59
3.6.1	Preparation of pristine PVDF-HFP membranes	59
3.6.2	Preparation of PVDF-HFP/PANI polymer electrolyte membrane	60
3.6.3	Preparation of PVDF-HFP/GO composite membrane	61
3.6.4	Preparation of PVDF-HFP/PANI/GO polymer electrolyte membrane	

		62
3.7	Physical Characterization	63
3.7.1	Membrane morphology	63
3.7.2	Porosity	64
3.7.3	Electrolyte Uptake (EU)	64
3.7.4	Functional Group Analysis	65
3.7.5	Thermal stability	65
3.7.6	Differential Scanning Calorimetry (DSC) Analysis	66
3.7.7	X-ray Diffraction (XRD) analysis	66
3.7.8	Membrane thickness and viscosity measurement	67
3.7.9	Mechanical stability	67
3.8	Electrochemical Characterization	68
3.8.1	Ionic conductivity	68
3.8.2	Linear sweep voltammetry (LSV) analysis	69
3.8.3	Chronoamperometry (CA) Analysis	70
3.8.4	Coin cell assembly	70
3.8.5	Coin cell testing	71
3.9	Electrochemical modelling through equivalent circuit models	72
3.9.1	Model validation and analysis	72

CHAPTER 4: RESULT AND DISCUSSION

4.1	Introduction	75
4.2	Effect of thickness and solvent variation on the performance of PVDF HFP membranes	76
4.2.1	Morphology of various PVDF-HFP membranes	76
4.2.2	Mechanical Strength Analysis	79
4.2.3	Conclusion	80
4.3	Effect of PANI addition on the performance of PVDF-HFP PEMs	81
4.3.1	Porosity and EU of PANI based PVDF-HFP PEMs	81
4.3.2	Scanning Electron Microscope (SEM) Analysis	82
4.3.3	Functional group analysis of PVDF-HFP/PANI membranes	84
4.3.4	Thermal stability of PANI based PVDF-HFP membranes	86
4.3.5	Mechanical strength of PANI based PVDF-HFP membranes	91
4.3.6	Ionic conductivity of PANI based PVDF-HFP membranes	92

4.3.7	Conclusion	93
4.4	Effect of graphene oxide on the performance of PVDF-HFP PEMs	94
4.4.1	Functional group analysis of PVDF-HFP/GO PEM	95
4.4.2	Porosity and EU of GO based PVDF-HFP PEMs	96
4.4.3	Thermal stability of GO based PVDF-HFP membranes	97
4.4.4	Mechanical strength of GO based PVDF-HFP membranes	101
4.4.5	Ionic conductivity of GO based PVDF-HFP membranes	102
4.4.6	Conclusion	103
4.5	Effect of PANI/GO on the performance of PVDF-HFP PEMs	104
4.5.1	Functional group analysis of PANI/GO membranes	105
4.5.2	Porosity and EU of PANI/GO based PVDF-HFP PEMs	107
4.5.3	Morphology of GO based PVDF-HFP PEMs	108
4.5.4	Thermal stability of PANI/GO based PVDF-HFP ternary membranes	110
4.5.5	Mechanical strength of PANI/GO based PVDF-HFP membranes	115
4.5.6	Ionic conductivity of PANI/GO based PVDF-HFP membranes.	117
4.5.7	Conclusion	118
4.6	PVDF-HFP/PANI/GO ternary hybrid polymer electrolyte membrane for lithium ion battery	119
4.6.1	Linear sweep voltammetry of optimum membranes	120
4.6.2	Chronoamperometry analysis of optimum membranes	121
4.6.3	Cycling performance of optimum PVDF-HFP PEMs	122
4.6.4	Electrochemical modelling of optimum PVDF-HFP PEMs	126
4.6.5	Conclusion	133

CHAPTER 5: CONCLUSION AND FUTURE PROSPECTS

5.1	Conclusions	134
5.2	Recommendations for future work	135

REFERENCES 137

APPENDICES

Appendix A: Pore size graphs/data obtained by Porolux

Appendix B: Different parametric values obtained for prepared PEMs

Appendix C: FTIR spectra of PVDF-HFP/GO

Appendix D: Screenshot of series IX software for tensile strength calculation

Appendix E: Pore size analysis

Appendix F: Sample calculations

LIST OF PUBLICATIONS

LIST OF TABLES

		Page
Table 1-1	Characteristics of secondary batteries	2
Table 1-2	General requirements of separators for LIBs	5
Table 2-1	The requirement of separator with brief explanations	24
Table 3-1	List of chemicals utilized for this research	50
Table 3-2	List of equipment utilized for membrane preparation and battery assembly	51
Table 4-1	Effect of solvent variation on porosity, thickness and viscosity of PVDF-HFP membrane	79
Table 4-2	Effect of thickness variation on porosity and mechanical strength of PVDF-HFP membrane	80
Table 4-3	Porosity and electrolyte uptake of pristine and PVDF-HFP/PANI membranes	82
Table 4-4	Characteristic peaks and possible assignments pristine PVDF-HFP and PVDF-HFP/PANI membranes	85
Table 4-5	T_m , T_d and X_c values of pristine and PANI based PVDF-HFP membranes	90
Table 4-6	Porosity and Electrolyte uptake of Pristine and PVDF-HFP/GO membranes	97
Table 4-7	T_m , T_d and X_c values of pristine and GO based PVDF-HFP membranes	100
Table 4-8	Porosity and Electrolyte uptake of Pristine and PVDF-HFP/PANI/GO ternary hybrid membranes	107
Table 4-9	T_m , T_d and X_c values of pristine and PANI/GO based PVDF-HFP membranes	114
Table 4-10	Different EC models used for the EIS data obtained for pristine PVDF-HFP PEM	127
Table 4-11	The parameters obtained from R-CPE model fitting of optimum PVDF-HFP PEMs	131

LIST OF FIGURES

		Page
Figure 1-1	Schematic illustrating the mechanism of operation for a lithium ion battery	3
Figure 2-1	Various types of polymer electrolyte membranes	14
Figure 2-2	Schematic diagram and SEM image of an organic/inorganic trilayer separator. Reproduced with permission (Kim et al., 2010).	20
Figure 2-3	Sequence of stages resulting in the breath-figures self-assembly. A-D formation of the first row of pores. E-C Formation of the second row of pores. Reproduced with permission (Bormashenko, 2017).	34
Figure 2-4	Thermogravimetric curves of various polymer electrolyte membranes. Reproduced with permission (Kelley et al., 2012).	38
Figure 2-5	Electrochemical system of lithium ion battery at charging and discharging process	45
Figure 3-1	Schematic diagram of whole experimental work	52
Figure 3-2	The argon glove box	53
Figure 3-3	The split test cell coin cell assembly kit without crimping	55
Figure 3-4	Instron 3366 universal mechanical strength tester	56
Figure 3-5	The electrochemical cell (VMP3 analyzer)	57
Figure 3-6	Flow chart for synthesis of PVDF-HFP/PANI membrane	61
Figure 3-7	Schematic diagram of PVDF-HFP/GO membrane preparation	62
Figure 3-8	The schematic diagram of PVDF-HFP/PANI/GO ternary membrane preparation	63
Figure 3-9	Simple Randles's equivalent circuit	72
Figure 4-1	The SEM images of membrane surface and cross section 40:60 (a & b), 50:50 (c & d), 60:40 (e & f), 100:00 (g & h) of PVDF- HFP membranes	78

Figure 4-2	SEM images of surfaces (a & c) and (b & d) and cross sections (e) and (f) of pristine PVDF-HFP and PVDF-HFP/PANI membrane respectively	83
Figure 4-3	The FTIR spectra of pristine PVDF-HFP and PVDF-HFP/PANI membrane	86
Figure 4-4	Thermogravimetric (TGA) curves of PANI based PVDF-HFP membranes	87
Figure 4-5	Derivative of TGA curves (DTGA) of PANI based PVDF-HFP membranes	88
Figure 4-6	DSC curves of pristine and PANI based PVDF-HFP membranes	89
Figure 4-7	The XRD spectra of various PANI based PVDF-HFP membranes	91
Figure 4-8	Mechanical strength of PANI based PVDF-HFP PEMs	92
Figure 4-9	EIS complex graphs obtained for PANI based PVDF-HFP membranes	93
Figure 4-10	FTIR spectra of pristine PVDF-HFP and PVDF-HFP/GO membrane	96
Figure 4-11	Thermogravimetric (TGA) curves of GO based PVDF-HFP membranes	98
Figure 4-12	Derivative of Thermogravimetric (DTGA) curves (b) stability up to 400°C of pristine and GO based PVDF-HFP membranes	98
Figure 4-13	DSC curves of pristine and GO based PVDF-HFP membranes	99
Figure 4-14	XRD spectra of various GO based PVDF-HFP membranes	101
Figure 4-15	Mechanical strength of GO based PVD-HFP membranes	102
Figure 4-16	EIS complex graphs obtained for GO based PVDF-HFP membranes	103
Figure 4-17	FTIR spectra of various particles and different PVDF-HFP membranes	107
Figure 4-18	Pore size data of various PVDF-HFP PEMs	109

Figure 4-19	SEM images of surfaces (a)-(b), (d)-(e) and (g)-(h) and cross sections (c), (f) and (i) of pristine PVDF-HFP, PVDF-HFP/PANI and PVDF-HFP/PANI/GO membranes respectively	110
Figure 4-20	Thermogravimetric (DTGA) curves of PANI/GO based PVDF- HFP membranes	112
Figure 4-21	Derivative of Thermogravimetric (DTGA) curves of PANI/GO based PVDF-HFP membranes	112
Figure 4-22	The DSC analysis of pristine and PANI/GO based PVDF-HFP membranes	113
Figure 4-23	XRD spectra of various PANI/GO based PVDF-HFP membranes	115
Figure 4-24	Mechanical strength of PANI/GO based PVDF-HFP membranes	116
Figure 4-25	Ionic conductivity of PANI/GO based PVDF-HFP membranes	117
Figure 4-26	Linear sweep voltammetry analysis of optimum PVDF-HFP membranes	121
Figure 4-27	Lithium ion transference number Li^+ of optimum PVDF-HFP membranes	122
Figure 4-28	Charge-discharge curves of (a) pristine and (b) PANI based PVDF-HFP PEMs	124
Figure 4-29	Charge-discharge curves of (a) PVDF-HFP/GO and (b) PVDF- HFP/PANI/GO PEMs	125
Figure 4-30	Charge discharge curves of (a) charge discharge curve of PVDF-HFP/PANI/GO PEM and (b) rate performance of optimum PVDF-HFP PEMs	126
Figure 4-31	The Nyquist and Bode plot of R-C model fitting of pristine PVDF-HFP PEM	128
Figure 4-32	The Nyquist and Bode plot of R-L model fitting of pristine PVDF-HFP PEM	128
Figure 4-33	The Nyquist and Bode plot of R-CPE model fitting of pristine PVDF-HFP membrane	129

Figure 4-34	The Nyquist and Bode plots of PVDF-HFP/PANI membrane	130
Figure 4-35	The Nyquist and Bode plots of PVDF-HFP/GO membrane	131
Figure 4-36	The Nyquist and Bode plots of PVDF-HFP/PANI/GO membrane	132

LIST OF ABBREVIATIONS

Al ₂ O 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 ₄ OH	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	Warburg 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 hexafluoropropilina) 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 $1.98 \times 10^{-4} \text{ S cm}^{-1}$ bagi membran tunggal PVDF-HFP ke $1.04 \times 10^{-3} \text{ S cm}^{-1}$; walau bagaimanapun, kesan pengestrakannya 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 LITHIUM 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 developed and the scope was divided into three phases 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 $1.98 \times 10^{-4} \text{ S cm}^{-1}$ of pristine PVDF-HFP membrane to $1.04 \times 10^{-3} \text{ S cm}^{-1}$; 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, Poullickas, 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.

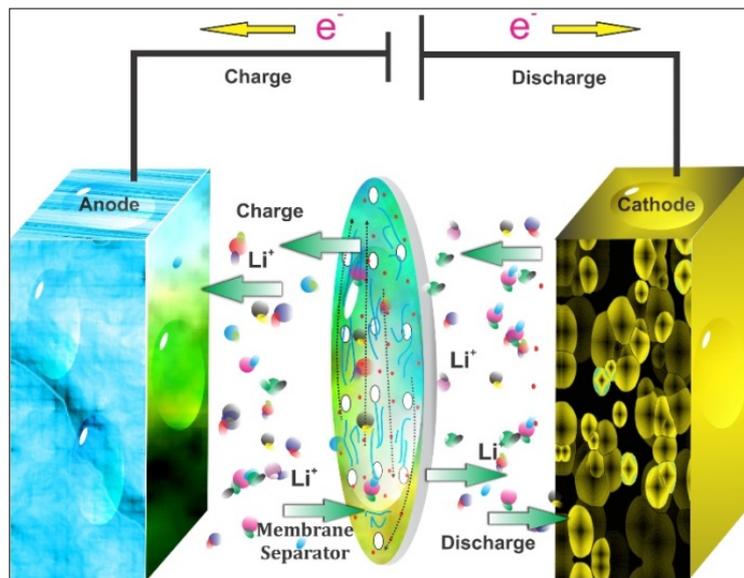


Figure 1-1: Schematic illustrating the mechanism of operation for a lithium-ion battery

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.

Table 1-2: General requirements of separators for LIBs (Arya et al., 2017)

Parameter	Requirement
Wettability	The separator must completely wet out rapidly
Pore size	< 1 μm
Dimensional stability	The separator must not bend and remain flat
Shutdown	The separator must shut down the battery at higher temperature
Electrochemical & Chemical stability	Must have good stability over the longer period
Thermal stability	Must be thermally stable even at higher temperatures
Porosity	Porosity must be between 40-60%
Mechanical stability	Must avoid a significant elongation under tension to prevent from width contraction

1.3 Problem Statement

The battery explosions and fires occur quite frequently and its causes are of major concern (Ma et al., 2018; Zhang et al., 2014). The commercially available separators and the liquid electrolytes are an important source of this flammability in LIBs. Generally, the commercial separators are polyolefins that possess poor mechanical stability and are combustible due to low melting points; it shrinks and melt at higher temperature ($>100^{\circ}\text{C}$) or if overcharged and leads to short circuit in LIBs (Costa et al., 2018; Steiger et al., 2014). Most of the LIB systems continue to use liquid electrolytes; therefore, the separator must be essentially wettable and suitable with most of the commercial and novel electrolytes. However, the low surface energy and

hydrophobic nature of the commercial polyolefin separators such as polypropylene (PP) and polyethylene (PE) results in poor electrolyte uptake that affects the cyclic retention capacity of LIBs. In addition, the poor wettability slows down the wetting process that can increase the battery manufacturing and production time (Liu et al., 2018; Zhang, 2007).

Polymer electrolyte membranes (PEMs) have received more attention and become a promising alternative in liquid electrolytes for some important applications such as lithium batteries (Li et al., 2018; Makinouchi et al., 2017; Wang et al., 2017; Yuan et al., 2014). A popular approach is to functionalize the separators by incorporating inorganic fillers into the host polymer matrix. In this regard, Polyaniline (PANI) is one of the emerging filler in energy devices due to its better conductivity, low cost, easy and flexible synthesis etc.; however, its electrical conductivity must be minimized before its addition to the host polymer to avoid short-circuit in LIBs. Deka et al., (2009) studied the influence of insulating PANI (base form) nanofibers on the ionic conductivity and interfacial stability of poly(vinylidene fluoride-hexafluoropropylene (PVDF-HFP) PEM; however, the study doesn't report the effect of PANI on the mechanical stability of proposed PEM. Besides that, Kumar and Deka (2010) reveal that the higher concentration of plasticizer may lead to poor mechanical strength due to lower dispersion and higher viscosity. This suggestion supports the findings of Wan et al., (2015), where the author has found no contribution of PANI to improve the tensile strength of polyimide (PI) membrane separator.

To overcome this problem, graphene oxide (GO) has been introduced to PANI particles and the PANI/GO composite has incorporated into PVDF-HFP polymer

matrix. Both the fillers i.e. PANI and GO have proven their worth in energy applications (Ludmila et al., 2017; Beydaghi et al., 2015; Cao et al., 2015; Cao et al., 2011; Weiss et al., 2012). PANI insertion is expected to provide better ionic conductivity to PVDF-HFP PEM; whereas, graphene oxide may add thermal, insulator and more importantly mechanical support to PVDF-HFP polymer matrix. Therefore, the proposed PVDF-HFP/PANI/GO ternary hybrid PEM can enhance the thermal, mechanical, morphological and electrochemical properties of pristine PVDF-HFP PEM that leads can lead to enhance the performance of lithium ion battery.

1.4 Research objective

The aim of this work is to develop a porous (PVDF-HFP/PANI/GO) ternary hybrid polymer electrolyte membrane for lithium ion battery. To accomplish the mentioned aim, the objectives are as follows:

1. To study the effect of thickness and solvent variation on the performance of PVDF-HFP polymer membrane.
2. To investigate the effect of individual addition of PANI and GO on the chemical, thermal, mechanical and electrochemical properties of PVDF-HFP PEM.
3. To analyse the effect of PANI/GO composite on thermal, mechanical, chemical and electrochemical properties of PVDF-HFP PEM.
4. To identify the performance of pristine PVDF-HFP, PVDF-HFP/PANI, PVDF-HFP/GO and PVDF-HFP/PANI/GO ternary membrane in lithium ion battery

1.5 Scope of research and limitations

The separators have a significant impact on the cell performance, battery life, cell production time, safety and reliability of LIBs. The internal short circuits develop due to cell failure, which is mostly attributed to the properties of separator material. The approach of this research provides direction for further improvements for marketable separators of LIBs. PANI and PANI/GO composite have synthesized by polymerization method and incorporated individually and as composite into PVDF-HFP polymer matrix. The various PVDF-HFP PEMs have prepared by using breath figure method. The different dosages of PANI (1 wt%, 2 wt%, and 3 wt%), GO (1 wt%, 2.5 wt%, and 5 wt%), and PANI/GO (GO=10 wt%, 20%, and 40 wt%) have prepared and characterized. The characterization involves SEM, FTIR, TGA, DSC, XRD, LSV, CA, ionic conductivity, mechanical strength, porosity, electrolyte uptake, and lithium ion battery performance test. The proposed PANI/GO composite can enhance the thermal and mechanical stability while retaining the high ionic conductivity of PVDF-HFP PEMs. However, some important performance limitations are recognized that are inherent to the preparation of this ternary membrane; it arises from the polymer selection to composite preparation and membrane fabrication method. Also, significant improvements in wettability, thermal stability and permanent porosity are in due need.

1.6 Organization of thesis

The thesis consists of 5 chapters that follow the order of summaries as described below:

Chapter 1 gives an overview of the thesis that includes introduction of batteries, lithium ion battery and separators. The main objectives of the research are also listed in this chapter.

Chapter 2 presents the related background information from the literature essential to understand this research and its significance. More specifically, it reviews the available literature about various types of PEMs, the requirement for PEMs and preparation of PEMs for lithium ion battery.

Chapter 3 describes the materials, methods, equipment and experimental techniques used for the subsequent studies. Also, it includes the flow chart of experimental work; synthesis and characterization of particle, composite and different membranes.

Chapter 4 portrays the findings of this research, with physical, chemical, and electrochemical data of the prepared PEMs for lithium ion battery followed by their discussion.

Chapter 5 includes the conclusion of this research and brings a final evaluation of the performance of pristine and modified PVDF-HFP PEMs for lithium ion battery. In addition, it provides future recommendations to optimize the performance of proposed PEMs for energy devices.

CHAPTER 2

LITERATURE REVIEW

2.1 Overview of separators

Over the years, various developments have been achieved in battery technology. Specifically, the developments are mainly attributed to optimized electrochemical systems as well as the advancement and foundation of new battery chemistries (Kim et al., 2015; Venugopal et al., 1999). However, despite such achievements, there is still a considerable gap that needs an extensive research, which can offer the best performance when operating it in different conditions. Likewise, there many other separator alternatives receiving good response as far as their chemistries and geometries are concerned.

A separator as referred in this context implies a membrane that is porous and is located between the electrodes, which have contrasting polarity and permeable to the ionic movement though blocking electric connection of the electrodes. Over the years, various kinds of separators have been used in batteries. Among others, some of these separators comprises of sausage casing and cedar shingles, separators that are made from cellophane and cellulosic papers to nonwoven fabrics, microporous flat sheet membranes, ion exchange membranes, foams that are produced from polymeric items (Deimede & Elmasides, 2015; Ye et al., 2015). Advancement of the batteries resulted to the separator function also been more challenging and intricate. Separator plays a vital role in rechargeable batteries; specifically, the separators ensures that both the negative and positive electrodes are separated to protect from electrical short

circuits. Also, the separator allows the swift movement of ionic charge carriers, which is required to make sure that the circuit needed at the path of current in the electrochemical cell is completed. Moreover, the separators are also expected to be perfect electronic insulators and have the ability to conduct the ions through the intrinsic ionic conductor or through the soaking in the electrolyte. Additionally, the separators should reduce any procedures that greatly impact the electrochemical energy efficacy of batteries (Zhang, 2007). Currently, most of the separators used in batteries are mainly advanced as by-products of present technologies. These separators haven't mainly advanced particularly for these batteries and for that reason, they cannot be fully augmented for the specific systems that they are applied in. A key benefit of employing prevailing technologies is that it has made it possible to produce the separators in large quantity at very low costs (Costa et al., 2013). On the other hand, the low cost of production for the separators has made it possible to battery manufactures to make good profits in their operations. The objective of this chapter is to illustrate the different kinds of separators according to their uses in lithium ion batteries (LIBs); also, it includes the detailed discussion about their preparation method and functionalization, chemical, mechanical, and electrochemical performance in LIBs. The separator needs, elements, and classification methods are explained in perspective of lithium-ion batteries. Irrespective of the prevalent use of separators, there is still a need to extend the life cycle, minimize the cost and to optimize the performance of separators.

2.2 Polymer electrolyte membranes in lithium ion battery

During the 1970s, a type of materials known as polymer electrolytes (PEs) were introduced and became a potential candidate for ion conducting material in

energy storage devices; it has shown high ion conductivity, enhanced stability features, and safety as contrasted with organic liquid electrolytes (Arora & Zhang, 2004). The polymer electrolytes comprise of a macromolecule matrix with minimal lattice energy salt put in a low viscosity and high dielectric constant organic solvent that provides good ionic conductivity, impressive chemical constancy, minimal costs, and a safety to PEs. The principle of ionic conduction in the polymer electrolytes includes the creation of covalent bond among the polymer backbones with ionizing groups. To begin with, the electron donor panel in the polymer creates redemption to the cation aspect in the dopant salt, which enables the separation of ion resulting to ionic hopping system that enables the ionic conductivity (Costa et al., 2013; Sohn et al., 2009). In order to achieve ideal multifaceted creation of polymer and salt, the lattice energy of the salt has to be lower while the dielectric constant of the host polymer is required to be higher.

On the other hand, the ionic conduction in polymer was found to be increased by the addition of cationic and anionic species (Lewis acid-base) which improves the acid base interaction in between polymer chains. Nevertheless, addition of Li-based metal ions in mixture of polymers leads to the production of unbalanced metal deposition at interface charge-discharge which leads to the formation of Li dendrite. (Brissot et al., 1999; Kang et al., 2013; Yamaki et al., 1998). These dendrites can result to internal short circuits because of the thread resembling structure among the electrons; also, it might result in swift discharge that can lead to thermal runaway. The application of lithium ion conducting polymer electrolytes might eradicate a few of the safety challenges faced; it can minimize the flammability as well as the higher resistance to dendrite creation. However, the ionic conductivity might be much lesser

than those of liquid electrolytes when at room temperature. Polymer electrolytes have various benefits which includes an impressive ionic conductivity, good levels of energy density, structural robustness, solvent-free feature, wide electrochemical stability window, easy to form, and light in weight (Lee et al., 2006; Li et al., 2007). Polymer electrolytes comprises of solutions of salts that are detached in the polymer host with the electron donor group. Since the polymer electrolytes are responsible for two roles as they act as separators and as electrolyte in a solid-state formation, it can address most of the shortcomings that are common in the liquid electrolytes such as adaptability of shape, scope, and even weightiness (Raghavan et al., 2011). The swift ion movement takes place in amorphous stage with either 2 or 3 orders of size greater conductivity as compared to crystalline stage (Kimura et al., 2014; Li et al., 2004). From an intensive review of the existing literature, it has been found that polymer electrolytes are categorized in three different groups, as shown in Figure 2-1. The liquid polymer electrolyte membranes (LPEs) that used ionic liquid with lithium salt and incorporated in host polymer, solid polymer electrolytes (SPEs) that do not soaked in lithium salt before assembly, and gel polymer electrolyte (GPEs) that soaked in lithium salt i.e. liquid electrolyte before assembly.

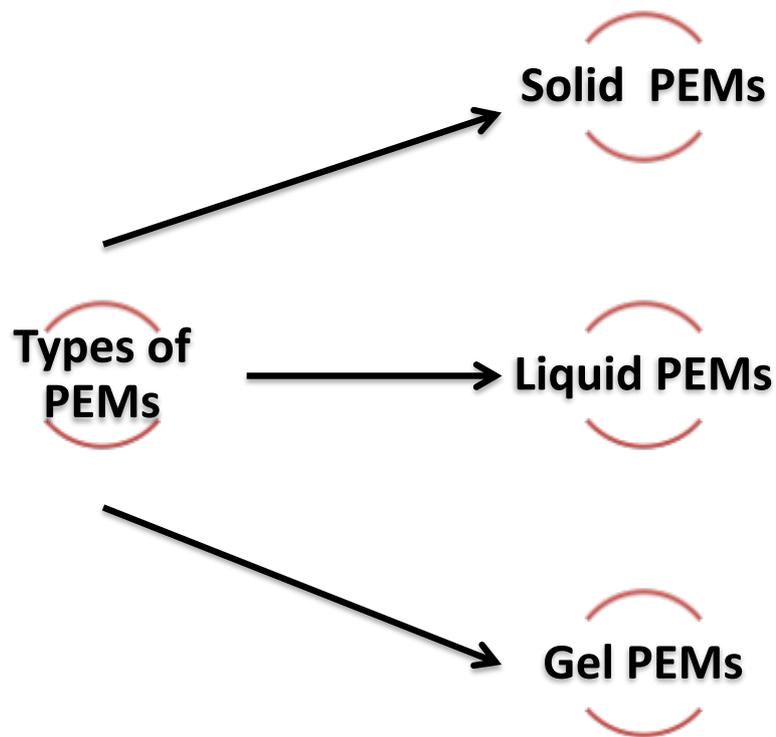


Figure 2-1: Various types of polymer electrolyte membranes

2.2.1 Liquid polymer electrolyte membranes (LPEs)

The first group comprises of the Liquid Polymer Electrolytes (LPEs) that entails a lithium salt that is dissolved in an organic solvent and a separator that ensures that the electrodes are protected from short circuiting (Tang et al., 2016; Wang et al., 2016). The polymer electrolytes in this group has lithium ions moving inside the cell among both positive and negative electrodes particularly during charge and discharge of LIB. The lithium salts such as LiClO_4 , LiPF_6 , and LiBF_4 are most commonly used in LIBs. Based on the solvent used, there is a possibility to separate it further into non-aqueous liquid (NALE) and aqueous liquid electrolyte (ALE). The non-aqueous liquid features high ionic conductivity when compared to solid polymer electrolyte and is

attained when alkali salts are dissolved in solvents like propylene carbonate (PC), ethylene carbonate (EC), dimethyl carbonate (DMC), and diethyl carbonate (DEC) (Xu et al., 2015). The liquid polymer electrolytes have various features for example high ionic conductivity, good thermal stability at both ambient and sub-ambient environments, high electrochemical window, and easy to handle (Aurbach et al., 2002; Chen, et al., 2014). The aqueous liquid electrolytes have shown higher ionic conductivity and safety compared to non-aqueous liquid electrolyte, which makes it a promising choice to use even at higher temperatures. On the other hand, ionic liquids (ILs) are the novel groups of purely organic salt like materials and are usually in liquid form at room temperatures due to poor ion management of atoms; it act as a plasticizer in polymer electrolytes with a melting point over a broad range of 300⁰C to 400⁰C (Zhang, 2007). The features of and broad electrochemical stability these ionic liquids makes the polymers ideal candidates to substitute organic electrolyte for the advancement of specialized electrochemical gadgets such as batteries, high-level capacitors, and fuel cells etc (Shin et al., 2005; Silvester, 2011; Ye et al., 2011; Zhang & Shen, 2012). Ionic liquids tend to be quite flexible as the ratio of cation to anion can be easily changed.

2.2.2 Solid polymer electrolyte membranes (SPEs)

The other group of polymer electrodes comprises of solid polymer electrodes (SPEs). This category of polymer electrolyte comprises of disbanding of salt in a polymer matrix with electron donor category and possesses different benefits like high durability, extended shelf life, high energy density, light weight, high flexibility of cell design, less reactive towards the electrodes, addresses the leakage challenges of solvent and dangerous gases for operations at ambient temperature, and minimizes the

packaging cost; moreover, it also exhibits broader electrochemical, and thermal stability with lesser volatility (Chen et al., 2011; Ye et al., 2011). Additionally, an ionically conducting polymer membrane must have an ideal balance among its conductivity and the mechanical strength under for electrochemical devices. Solid polymer electrodes have improved stability in ambient and sub-ambient conditions that could be anticipated to possess the ability for their uses in solid-state ionic gadgets such as the high energy-density lithium ion batteries, high value capacitors, and fuel cells (Fattah et al., 2016; Lehtinen et al., 1998). Once the lithium salt is introduced to the polymer system, it is going to be detached by the exchanges with the polar group of polymers as lithium ions migrate together with the polymer chains through hopping procedure in the amorphous stage (Ulaganathan et al., 2013). However, the SPEs have found to have lower ionic conductivity compared to its other counterparts i.e. the liquid electrolytes (discussed earlier) and gel-polymer electrolytes (GPEs) (Kim et al., 2005), which will be discussed in detail next.

2.2.3 Gel-polymer electrolyte membranes (GPEs)

The different types of separators filled with liquid electrolyte enhance the lithium ion transportation between the electrodes in LIBs (Masoud, 2015; Raghavan et al., 2011). Usually, the GPEs are created once the polymer matrix swells with the liquid electrolyte and could function as separators and electrolytes concurrently. They display broad electrochemical operating windows, ideal compatibility with electrodes, and high ionic conductivity. On the other hand, the mechanism of ionic conduction in GPEs must be uniform to the ionic conduction in liquid electrolytes and segmental mobility of polymer chain shown a great impact on it (Li et al., 2014). It is crucial to highlight that it is above the scope of this chapter to entirely compile the broad variety

of gel-polymer electrolytes; however, the brief information about most of these GPEs such as PMMA, PEO, PAN, and PVDF will be discussed. Various techniques for instance electrospinning, casting of the solvent, phase inversion, and liquid removal or stimulation method have used to prepare GPEs. Nevertheless, unfortunately, the homopolymers are not able to perform to the expected levels of commercial lithium batteries especially in perspective of mechanical strength, electrochemical stability, and ionic conductivity (Arora & Zhang, 2004). Therefore, a substitute approach to address these shortcomings to some extent involves preparing copolymers by using copolymerization and in other cases cross-linking with various purposeful monomers.

For example, a numerical copolymer consisting oligo methyl ether methacrylate and cyclic carbonate methacrylate (OEGMA/CCMA) was preferred as a matrix for the production of gel-polymer electrolytes because both monomers make it possible to deal with the liquid electrolyte. As a matter of fact, the prepared gel-polymer electrolyte exhibited high liquid electrolyte holding capacity, impressive ionic conductivity (2.3 mS cm^{-1} at 258°C), ideal C-rate ability, and persistent cycling output (Tillmann et al., 2014). In a different study, a gel-polymer electrolyte was discussed to consist of a copolymer mixed with another polymer as a host and displayed high ionic conductivity (3.5 mS cm^{-1} at 30°C), outstanding lithium transference number, enhanced output and steady cycling performance (Wang et al., 2014). Chemical cross-linking can be discussed as a technique that can greatly improve the thermal as well as the dimensional stability of GPEs (Lian et al., 2014; Lu et al., 2015). By using UV-cured technology, a semi-interpenetrating polymer network gel-polymer membrane founded on the cross-linked poly[diacrylate-co-poly(vinylene carbonate)] [P(EGDA-co-VC)] and PVDF–HFP polymer was produced effectively.

The gel polymer electrolyte featured a superb mechanical, interfacial and thermal stability to the lithium-metal electrode; also, it provides higher electrolyte holding capacity, which ultimately improves the ionic conductivity. Additionally, the use of GPEs displayed an outstanding cycling and rate performance as compared to the normal liquid electrolyte (Lu et al., 2015). In another study, the cross-linked GPEs were produced by in situ chemical cross-linking of the liquid electrolyte with good volume of cross-linking agent. In results, the gel-polymer electrolytes have shown an improved electrolyte holding capacity and a stable cyclic performance due to the robust interfacial bond among the electrodes and the electrolyte together with the conquest of the dendritic advancement of the lithium powder electrode (Choi et al., 2014). Similarly, the polyoxyethylene (PEO) network was cross linked by a polyacrylonitrile-interpenetrated that acts as a separator and a gel-polymer electrolyte and exhibited good electrolyte acceptance and high ionic conductivity ($1.06\text{--}8.21\text{ mS cm}^{-1}$ at 25°C) (Kuo et al., 2014).

A blending is another approach to manage the issues related with mechanical and electrochemical stability. The polymer blends for instance PVdF/ poly(dimethyl siloxane) (Li et al., 2011), PAN/PMMA (Rao et al., 2012), PVdF/[lithium poly(4-styrene sulfonyl (phenylsulfonyl) imide)] (PSSPSI) (Rohan et al., 2014), PVdF/PEO-b-PMMA (Xiao et al., 2009), PVdF/polysulfone (PSF) (Cheng et al., 2014), PVdF/lithium poly(pyromellitic acid borate) (PPAB) (Xu et al., 2014), and PAN/PVdF (Gopalan et al., 2008) have employed as GPEs. In the study by Gopalan et al., (2008), the authors mixed PAN with PVDF with the resultant GPEs showing sufficient dimensional stability, higher liquid electrolyte uptake, improved ionic conductivity (7.8 mS cm^{-1} at 25°C), low interfacial resistance, and a larger electrochemical window

unlike pure PVdF. In a different report, PVdF/PSSPSI mixtures have been formulated through solution casting technique with PSSPSI acting as a single-ion-conducting electrolyte; the particular GPEs exhibited excellent mechanical and thermal stability, impressive ionic conductivity (1.1 mScm^{-1} at 25°C), and remarkable lithium cation transference number (0.87) due to broader electrochemical window and stopping of the bis (sulfonyl imide) anions inside the polymer chains (Rohan et al., 2014).

2.2.4 Composite membranes

The mixing of inert particles to the absorbent or separators that are nonwoven result in the creation of composite separators that have enhanced features. Particularly, the ceramic compounds for instance SiO_2 , Al_2O_3 , and TiO_2 etc. are introduced to the host polymer to enhance the wettability, ionic conductivity, mechanical strength, and thermal stability (Stephan et al., 2006). Currently, the composite membranes are coated with ceramic particles or powders comprise of SiO_2 , Al_2O_3 , TiO_2 etc., which are commercially available and can easily get dissolved in a polymer/solvent solution. The prepared solution then can be covered on the microporous membrane separators of PP and PE; in this case, the polymer usually acts as an adhesive to join the inert particles to the porous surface of the separator (Aravindan & Vickraman, 2008; Leng et al., 2015; Stolarska et al., 2007). For instance, a practical ceramic-glazed separator was prepared by covering the core-shell structured silica-poly sub-microspheres onto one side of a porous PE separator (Yang et al., 2015). The existence of the PPMA shell makes it possible for the liquid to have absorption and retention features. In addition, the prepared separator exhibited enhanced thermal shrinkage reaction, ideal electrolyte wettability, and better electrolyte uptake. Also, the cycling performance together with the C-rate competence was improved by addition of ceramic particles. Dip-coating

method was also used to prepare a trilayer composite membrane with inorganic fillers on both sides of PMMA polymeric membrane (Kim et al., 2010). The solution was prepared for coating by incorporation of Al_2O_3 and PVdF-HFP binder with a ratio of nine units of filler and one unit of binder. In Figure 2-2, the schematic figure and SEM images of the organic and inorganic trilayer separator have presented. The trilayer separator displayed and improved thermal integrity due to presence of inorganic layers and sufficient retention ability with increasing C-rate.

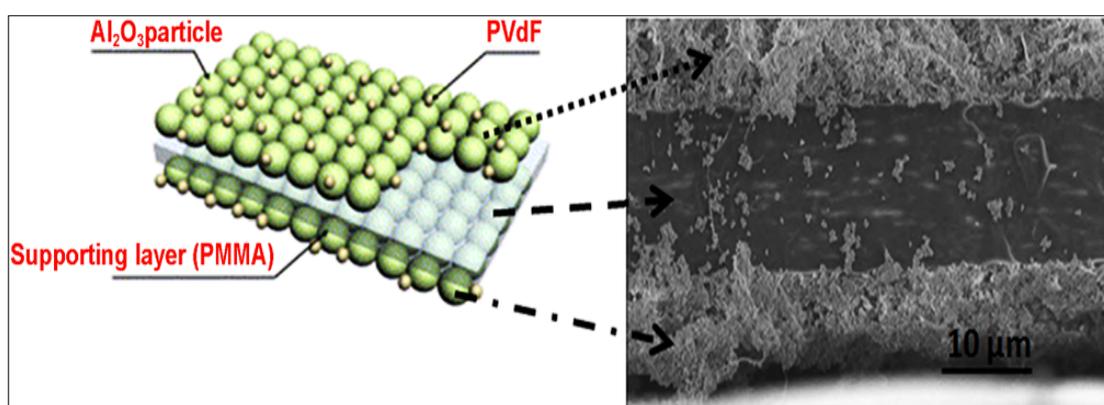


Figure 2-2: Schematic diagram and SEM image of an organic/inorganic trilayer separator. Reproduced with permission (Kim et al., 2010).

In another work, a ceramic layer prepared with the bilayer separator was coated directly to the anode to enhance the thermal stability of counter electrode (Huang, 2011). This separator was resulted in constant cyclic output and greatly enhanced the rate capabilities compared to normal polyolefin separators. The resultant composite membranes in all cases displayed a good thermal stability and improved thermal capacity retention; however, it had some limitations to the coating layer thickness. The consequences such as decrease in porosity and increase in thickness have found to increase the cell resistance. The inorganic particles must be filled directly to the

polymer matrix to form an improved composite membrane. PVDF-HFP membranes filled with ZrO₂ (Puguan et al., 2016), TiO₂ (Kim et al., 2006), and SiO₂ (Aravindan & Vickraman, 2008) were developed and has shown uniform pore size, improved wettability, excellent electrochemical and interfacial stability, and higher ionic conductivity as compared to pristine PVDF-HFP membranes. Recently, the montmorillonite (MMT) was used to functionalize poly(vinylidene-co-trifluoroethylene) PVDF-TRFE membrane. Nunes-Pereira et al., (2012) prepared MMT/PVDF-TRFE microporous membrane for battery application. An optimum dose of MMT (4%) was added to the PVDF-TRFE polymer matrix, which has resulted in improved electrochemical and mechanical stability of the composite membrane.

Moreover, the fabrication of electrospun PAN (Choi et al., 2005), PVDF-HFP (Li et al., 2007; Raghavan et al., 2008), PET (Lee et al., 2012; Xiaofei et al., 2014), Nylon 6,6 (Yanilmaz et al., 2014), polyetherimide-polyurethane (PEI-PU) (Zhai et al., 2015), and polyimide (Lee et al., 2014) nonwoven mats with inorganic fillers has also been explained. For example, PVDF-HFP/SiO₂ coated PET non-woven separators have produced for lithium-ion batteries, where the uniformly linked interstitial gaps existed among closely packed SiO₂ nanoparticles and linked by PVDF-HFP binders (Jeong et al., 2012). The obtained nonwoven composite separator resulted in better cell performance compare to conventional PE separator due to facile movement of ions; also, it retarded the cell impedance growth during cycling.

The basic phase isolation procedure could also be used to fabricate PVDF-HFP membranes for lithium ion batteries since a sponge resembling porous structure can be obtained. As far as the ionic conductivity of the electrolyte is concerned, it is $1.76 \times$

$10^{-3} \text{ S cm}^{-1}$ while the stability of the electrochemical oxidation can reach up to 4.7 V (vs. Li/Li⁺). The apparent activation energy for the transfer of ions is 10.35 kJ mol⁻¹ indicating that this type of porous gel polymer can be practically used in different applications. Moreover, approaches like coating of the surface, embedding, blending, and grafting are potential methods to increase the ionic conductivity together with the mechanical strength. In addition, (VDF-HFP) copolymer can be mixed with sulfonated aromatic agents and used in fuel cells as proton exchange membranes. In order to graft these specific types of membranes, di-amines and amines with aromatic compounds have been applied, while bisulfonic acid groups have been functionalized to enhance the proton conductivity. Despite the fact of the lower ionic conductivities especially when compared to that of Nafion (Shi et al., 2014), it was found that the conductivities increased with increasing the ion exchange capacity; also, the decomposition temperature increased to 170⁰C at highly oxidative condition.

A different alternative to functionalize PVDF-HFP involves the grafting of para-sulfonic phenolate or its modification by sulfonic acid group, which eventually lead to improved protonic conductivity (Choi et al., 2010). Because blending is a basic technique to adjust the aspects of polymeric membranes; polymers like ethylene carbonate (EC)/propylene carbonate(PC), poly(methyl methacrylate) (PMMA), and poly(vinyl acetate) (PVAc) together with the inorganic particles such as ceramics (Al₂O₃, SiO₂ and TiO₂) and lithium ions (LiClO₄, LiAsF₆, LiBF₄, LiPF₆) can be introduced to the polymer matrix to enhance the mechanical stability as well as the ionic conductivity (MacGlashan et al., 1999; Masoud, 2016; Masoud et al., 2016; Saikia & Kumar, 2004; Tang et al., 2016; Thiam et al., 2017; Zhang et al., 2014a). Since PMMA is compatible with PVDF-HFP and N-butyl-N-methyl-imidazolium

hexafluoro phosphate (BMIPF₆), the plasticizer BMIPF₆ ends up being trapped in situ, therefore enhancing the electrochemical stability of the resultant SPE (Shi et al., 2014), whereas, CTFE addition to PVDF-HFP polymer matrix has resulted in improved amorphous content and melting point of the composite membrane.

2.3 Requirements of the separator

When deciding a suitable separator for a battery, there are various factors that need to be taken into consideration according to its functions and role in LIBs (Dong & Cao, 2014). The features of any available separator have to be assessed against the needs so that the selected optimum separator will not only meet the identified needs but to also surpass them. Thus, there are different features that have to be considered when deciding the separators for LIBs. Some of the features to consider for a separator selection in LIBs are as follows: Similarity in thickness as well as other features

- a) Must be electric insulator
- b) Successful in averting movement of particles or colloidal or particles that are soluble among the two electrodes
- c) Minimum electrolyte resistance
- d) The dimensional and mechanical stability
- e) Adequate physical strength to make sure easy handling
- f) Chemical resistance to electrolyte degradation
- g) High electrolyte uptake

The sequence of criteria differs significantly according to different battery applications. The specified list features a wide spectrum of the needs for battery separators. In most of the applications, separator requirements need to be compromised

to enhance the performance, cost, safety and many other aspects. For instance, batteries with lesser internal resistance and tend to use less power need thin and porous separators, even though the higher thickness is in high demand as a requirement for sufficient physical strength (Zhang, 2007). Moreover, each type of battery has different separator requirements, which are important for safety and improved performance. For instance, separators made for nickel-metal (NiMH) batteries and sealed nickel-cadmium (NiCd) must have good gas permeation to avoid overcharging; likewise, the separators in the lithium-ion cells must have shut-down property to enhance safety (Poullikkas, 2013). On the other hand, separators for the alkaline battery must be quite flexible to be wrapped easily around the electrodes; while, the separator for a starting, lighting, and ignition (SLI) battery should have capability to act as mechanical-shock preventer.

Table 2-1: The requirement of separator with brief explanations

Parameter	Brief explanation
Ionic conductivity	The internal cell resistance can be increased by using separator; therefore, the separator resistance must be lower to enhance the ionic movements, which can improve the ionic conductivity.
Dimensional stability	The separator should maintain its size and shape when dipped it in liquid electrolyte; also, the shrinkage must be avoided while storage or during battery usage as it might lead to safety issues.
Chemical and electrochemical stabilities	The separator should possess electrochemical and chemical stabilities with electrodes and electrolytes in LIBs; it must not take part in any unwanted chemical reaction at the time of charge/discharge process. Moreover, the separators must be inert and chemically stable even at higher temperatures; also, it must avoid any interference due to impurities.