BIOPOLYMER ELECTROLYTES BASED ON THE BLEND OF KAPPA-CARRAGEENAN AND CELLULOSE DERIVATIVES FOR SOLID STATE DYE SENSITIZED SOLAR CELL APPLICATION

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INSTITUTE OF GRADUATE STUDIES UNIVERSITY OF MALAYA KUALA LUMPUR

2016
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INSTITUTE OF GRADUATE STUDIES
UNIVERSITY OF MALAYA
KUALA LUMPUR

2016
UNIVERSITY OF MALAYA
ORIGINAL LITERARY WORK DECLARATION

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BIOPOLYMER ELECTROLYTES BASED ON THE BLEND OF KAPPA-CARRAGEENAN AND CELLULOSE DERIVATIVES FOR SOLID STATE DYE SENSITIZED SOLAR CELL APPLICATION
Field of Study: APPLIED SCIENCE (ADVANCED MATERIALS)

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ABSTRACT

The main objective of this study was to develop novel biopolymer electrolytes for application in solid state DSSC obtained from the blend of $k$-carrageenan and cellulose derivatives. The new biopolymer electrolytes were prepared using solution casting technique. The cellulose derivative, CMCE was produced from cellulose extracted from kenaf fiber. The cellulose derivative was blended with different wt % of $k$-carrageenan derivative, CMKC to obtain free standing films. The properties of the prepared blend films were subjected to various characterizations, such as FTIR, tensile measurement, SEM, DMA, EIS, and LSV to investigate their structural, mechanical, viscoelastic and electrical properties. The detailed FTIR characterizations demonstrated that both polymers are compatible with each other. The mechanical properties of CMKC were enhanced after blending with CMCE. The polymer blend with wt % ratio of 60:40 yielded the most conductive film with conductivity of $3.25 \times 10^{-4}$ S cm$^{-1}$. This blend ratio was selected as polymer host for developing biopolymer electrolytes system. LiI, NaI, NH$_4$I and DNH$_4$I were used as the dopant salts. The effects of these four dopant salts to the conducting, thermal and optical properties of CMKC/CMCE blend were investigated. Impedance study showed that the ionic conductivity increased with increase in salt concentration. The highest ionic conductivities achieved for CMKC/CMCE blend system containing LiI (30 wt %), NaI (30 wt %), NH$_4$I (30 wt %) and DNH$_4$I (40 wt %) are $3.89 \times 10^{-3}$ S cm$^{-1}$, $4.55 \times 10^{-3}$ S cm$^{-1}$, $2.41 \times 10^{-3}$ S cm$^{-1}$ and $6.68 \times 10^{-3}$ S cm$^{-1}$ respectively. The highest ionic conductivity among the four systems were exhibited by CMKC/CMCE-40 wt % of DNH$_4$I. The temperature-dependent conductivity study revealed that all of the CMKC/CMCE blend based electrolytes followed VTF model conductivity-temperature behavior. The fabricated DSSC using the CMKC/CMCE-40 wt % of DNH$_4$I electrolyte showed good response under light intensity of 100 mW cm$^{-2}$ and exhibited a highest efficiency of 0.21 %, which
confirmed that the blend biopolymer systems can potentially be applied for the fabrication of efficient dye sensitized solar cells.
ABSTRAK

Objektif utama kajian ini adalah untuk membangunkan elektrolit biopolimer novel untuk aplikasi sel suria terpeka pewarna keadaan pepejal diperolehi daripada adunan terbitan k-carrageenan dan selulosa. Elektrolit biopolimer baru telah disediakan dengan menggunakan teknik penuangan larutan. Terbitan selulosa, CMCE telah dihasilkan daripada selulosa yang di ekstrak daripada serabut kenaf. Terbitan selulosa telah diadun dengan perbezaan peratus berat terbitan k-carrageenan, CMKC untuk mendapatkan kedudukan bebas filem. Sifat-sifat adunan filem yang dihasilkan telah disubjekkan kepada pelbagai pencirian seperti spektoskopi inframerah, pengujian ketegangan, mikroskop pengimbasan elektron, analisis dinamik mekanikal, elektrokimia spektroskopi impedans and voltammetri sapuan linear untuk menyiasat struktur, sifat mekanikal, sifat viskoelastik dan sifat elektrik. Pencirian inframerah menunjukkan bahawa kedua-dua polimer sepadan antara satu sama lain. Sifat mekanikal CMKC telah meningkat selepas diadun dengan CMCE. Adunan polimer dengan nisbah peratus berat 60:40 menghasilkan filem yang paling beraliran dengan kekonduksian iaitu $3.25 \times 10^{-4}$ S cm$^{-1}$. Nisbah adunan ini telah dipilih sebagai perumah polimer untuk memajukan sistem elektrolit biopolimer. LiI, NaI, NH$_4$I and DNH$_4$I telah digunakan sebagai dopan. Kesan-kesan penambahan ke empat-empat garam terhadap sifa kekonduksian, sifat haba dan optik adunan CMKC/CMCE telah disiasat. Kajian spektroskopi impedans menujukkan kekonduksian ionik bertambah dengan penambahan dalam kepekatan garam. Kekonduksian ionik yang paling tinggi dicapai untuk sistem adunan CMKC/CMCE yang mengandungi LiI (30 % berat), NaI (30 % berat), NH$_4$I (30 % berat) dan DNH$_4$I (40 % berat) masing-masing adalah $3.89 \times 10^{-3}$ S cm$^{-1}$, $4.55 \times 10^{-3}$ S cm$^{-1}$, $2.41 \times 10^{-3}$ S cm$^{-1}$ dan $6.68 \times 10^{-3}$ S cm$^{-1}$. Kekonduksian ionik tertinggi di antara empat sistem ditunjukkan oleh CMKC/CMCE-40 % berat DNH$_4$I. Kajian terhadap kebergantungan kekonduksian terhadap suhu menunjukkan bahawa
semua elektrolit berasaskan adunan CMKC/CMCE mengikuti sifat model kekonduksian-suhu VTF. Sel suria terpeka pewarna yang telah difabrikasi menggunakan elektrolit CMKC/CMCE-40 % berat DNH₄I telah menunjukkan tindakbalas yang baik di bawah keamatan cahaya 100 mW cm⁻² dan mempamerkan kecekapan tertinggi sebanyak 0.21 %, yang mengesahkan bahawa sistem adunan biopolimer berpotensi digunakan untuk fabrikasi didalam sel suria terpeka pewarna cekap.
ACKNOWLEDGEMENTS

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TABLE OF CONTENTS

Abstract ............................................................................................................................ iii
Abstrak .............................................................................................................................. v
Acknowledgements ......................................................................................................... vii
Table of Contents ........................................................................................................... viii
List of Figures ................................................................................................................. xii
List of Tables ................................................................................................................... xv
List of Symbols .............................................................................................................. xvi
List of Abbreviations .................................................................................................... xviii

CHAPTER 1: INTRODUCTION .................................................................................. 1
1.1 Introduction .............................................................................................................. 1
1.2 Problem statement ................................................................................................... 3
1.3 Scope and objectives of the study ............................................................................ 4
1.4 Significance of the study ......................................................................................... 6
1.5 Organization of the thesis ........................................................................................ 7

CHAPTER 2: LITERATURE REVIEW ...................................................................... 9
2.1 Introduction .............................................................................................................. 9
2.2 Dye sensitized solar cell ........................................................................................ 9
2.3 Operational principal of a DSSC .......................................................................... 10
2.4 Fluorine-doped tin oxide glass ............................................................................. 13
2.5 Titanium oxide photoelectrode ............................................................................ 13
2.6 Ditetrabutylammonium cis-bis (isothiocyanato)bis(2,2’-bipyridyl-4,4’-dicarboxylato) ruthenium (II) ........................................................................................ 14
2.7 Platinum counter electrode .................................................................................... 15
2.8 Electrolytes ............................................................................................................ 15
  2.8.1 DSSCs employing liquid electrolytes .............................................................. 16
  2.8.2 DSSCs employing gel electrolytes ................................................................. 17
  2.8.3 DSSCs employing solid polymer electrolytes ............................................. 18
2.9 Solid polymer electrolytes ..................................................................................... 22
2.10 Biopolymer ............................................................................................................ 24
  2.10.1 k-carrageenan ........................................................................................... 25
  2.10.2 Cellulose .................................................................................................... 26
  2.10.3 Carboxymethylation of k-carrageenan and cellulose ................................ 27
2.11 Doping salt ......................................................................................................... 32
2.12 Biopolymer electrolytes .................................................................................... 34
2.13 Biopolymer blend electrolytes ......................................................................... 36
2.14 CMKC and CMCE blend based electrolytes .................................................. 40
2.15 Summary ............................................................................................................. 41

CHAPTER 3: EXPERIMENTAL METHOD ............................................................... 42
3.1 Introduction ........................................................................................................... 42
3.2 Materials ............................................................................................................... 44
3.3 Sample preparation .............................................................................................. 44
  3.3.1 Extraction of cellulose from kenaf fiber ...................................................... 44
  3.3.2 Preparation k-carrageenan and cellulose derivatives ................................ 45
  3.3.3 CMKC/CMCE blend film preparation ...................................................... 46
  3.3.4 CMKC/CMCE blend electrolytes film ...................................................... 47
3.4 Characterization of samples .............................................................................. 49
  3.4.1 Fourier transform infrared spectroscopy ................................................... 49
  3.4.2 Scanning electron microscopy and energy dispersive X-ray spectroscopy.. 50
3.4.3 X-ray diffraction ................................................................. 50
3.4.4 Dynamic mechanical analysis ............................................. 51
3.4.5 Electrochemical impedance spectroscopy ......................... 51
3.4.6 Transference number and linear sweep voltammetry .......... 52
3.4.7 Mechanical properties ........................................................ 53

3.5 Fabrication and characterization of dye sensitized solar cell .... 54

CHAPTER 4: K-CARRAGEENAN AND CELLULOSE DERIVATIVES ....... 57

4.1 Introduction ........................................................................... 57

4.2 Characterization of carboxymethyl k-carrageenan and carboxymethyl cellulose powder ........................................................................................................... 57

4.2.1 Result of FTIR analysis ....................................................... 57
4.2.2 SEM-EDX studies .............................................................. 59
4.2.3 XRD study ........................................................................ 63

4.3 Summary ................................................................................ 66

CHAPTER 5: STUDIES ON CMKC/CMCE BLEND SYSTEM ............ 67

5.1 Introduction ........................................................................... 67

5.2 Characterization of CMKC/CMCE films ................................ 67

5.2.1 FTIR analysis ................................................................. 67
5.2.2 SEM study ................................................................. 70
5.2.3 DMA study ............................................................... 72
5.2.4 Impedance study at room temperature ......................... 74
5.2.5 LSV study ............................................................... 78
5.2.6 Mechanical studies ..................................................... 79

5.3 Summary ................................................................................ 80
CHAPTER 6: STUDIES ON CMKC/CMCE BLEND ELECTROLYTE SYSTEMS AND THEIR PERFORMANCE IN SOLID STATE DSSC .......... 81

6.1 Introduction ............................................................................................................. 81

6.2 Characterization of CMKC/CMCE-electrolyte films ............................................. 81

6.2.1 Result of FTIR Analysis ............................................................................... 81

6.2.2 Result of DMA .............................................................................................. 87

6.2.3 Result of ionic conductivity at room temperature ......................................... 92

6.2.4 Result of ionic conductivity study at various temperatures .................. 104

6.2.5 Result of transference number .................................................................... 108

6.2.6 Result of LSV ............................................................................................... 111

6.2.7 Performance of solid state DSSCs employing CMKC/CMCE based electrolytes .................................................................................................................. 113

6.3 Summary ............................................................................................................. 118

CHAPTER 7: CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK ................................................................. 120

7.1 Conclusions ......................................................................................................... 120

7.2 Suggestions for further work ........................................................................... 122

References .................................................................................................................. 124

List of Publications ..................................................................................................... 136
LIST OF FIGURES

Figure 2.1: Schematic structure of DSSC ................................................................. 10
Figure 2.2: Working principle of DSSC operation ................................................... 12
Figure 2.3: The molecular structure of N719 dye .................................................... 15
Figure 2.4: Structure of $k$-carrageenan ................................................................. 25
Figure 2.5: Structure of cellulose ........................................................................... 26
Figure 2.6: Overall reaction of carboxymethylation process on $k$-carrageenan ....... 28
Figure 2.7: Difractograms of samples (a) cellulose and (b) cellulose treated by % 46 monochloroacetic acid, % 25 NaOH with neutral pH .......................................... 30
Figure 2.8: Structure of CMKC ............................................................................. 31
Figure 2.9: Structure of CMCE .............................................................................. 32
Figure 3.1: Flow chart of experimental work ......................................................... 43
Figure 3.2: Photo of (a) kenaf fiber and (b) $k$-carrageenan .................................. 45
Figure 3.3: Flow chart for the preparation of biopolymer electrolytes based on CMKC/CMCE blend ................................................................. 48
Figure 3.4: Schematic diagram of DSSC ................................................................. 54
Figure 3.5: The fabricating procedure of FTO-$\text{TiO}_2$-dye/CMKC/CMCE- electrolytes+$\text{I}_2$/Pt-FTO .................................................................................. 56
Figure 4.1: FTIR spectra of $k$-carrageenan and CMKC ......................................... 58
Figure 4.2: FTIR spectra of kenaf-cellulose and CMCE ......................................... 59
Figure 4.3: Cross-sectional SEM images of $k$-carrageenan and CMKC at 100× magnification ............................................................................. 61
Figure 4.4: Cross-sectional SEM images of cellulose and CMCE at 100× magnification ............................................................................. 62
Figure 4.5: XRD spectra of $k$-carrageenan and CMKC powder ......................... 64
Figure 4.6: XRD spectra of kenaf-cellulose and CMCE powder ......................... 65
Figure 5.1: FTIR spectra of BO, B1, B2, B3 and B4 films ............................................. 69
Figure 5.2: Cross-sectional SEM images of CMKC and CMKC/CMCE blend films .... 70
Figure 5.3: Tan δ versus temperature curves for B0, B2, B4 and B5 ......................... 73
Figure 5.4: Typical impedance plot for B4 (0 wt % salt) blend film ........................... 74
Figure 5.5: Model of equivalent circuit for B4 film .................................................... 75
Figure 5.6: Variation of log conductivity of CMKC/CMCE blend as a function of CMCE concentration ....................................................................................... 76
Figure 5.7: H⁺ conduction mechanism and intermolecular interaction in CMKC/CMCE blend ........................................................................................................ 77
Figure 5.8: Linear sweep voltammetry curve ............................................................... 78
Figure 6.1: FTIR spectra for (a) LiI and CMKC/CMCE- LiI films containing (b) 0, (c) 10, (d) 20 and (e) 30 wt % of LiI ................................................................. 83
Figure 6.2: FTIR spectra for (a) NaI and CMKC/CMCE-NaI films containing (b) 0, (c) 10, (d) 20 and (e) 30 wt % of NaI ................................................................. 84
Figure 6.3: FTIR spectra of (a) NH₄I and CMKC/CMCE containing (b) 0, (c) 10, (d) 20 and (e) 30 wt % of NH₄I ................................................................. 85
Figure 6.4: FTIR spectrum of (a) DNH₄I and CMKC/CMCE containing (b) 0, (c) 10, (d) 20, (e) 30 and (f) 40 wt % of DNH₄I ................................................................. 86
Figure 6.5: Possible interactions between CMKC and CMCE with iodide salts ........ 87
Figure 6.6: Tan δ versus temperature for CMKC/CMCE films containing (a) LiI, (b) NaI, (c) NH₄I and (d) DNH₄I salt ................................................................. 90
Figure 6.7: Impedance plots for the films of CMKC/CMCE containing (a) LiI, (b) NaI, (c) NH₄I and (d) DNH₄I ................................................................. 96
Figure 6.8: Model of equivalent circuit for CMKC/CMCE electrolytes .................... 97
Figure 6.9: The plots of real part of dielectric constant versus temperature at various frequencies for CMKC/CMCE blend films containing (a) LiI, (b) NaI, (c) NH₄I and (d) DNH₄I films ............................................................................................................................................................................. 103

Figure 6.10: VTF plots for CMKC/CMCE blend films containing (a) LiI, (b) NaI, (c) NH₄I and (d) DNH₄I............................................................................................................................................................................. 107

Figure 6.11: Polarization current versus time for the CMKC/CMCE blend films containing (a) 30 wt % LiI, (b) 30 wt % of NaI, (c) 30 wt % of NH₄I and (d) 40 wt % of DNH₄I. ................................................................................................................................................................................. 110

Figure 6.12: Linear sweep voltammograms for the highest conducting CMKC/CMCE electrolyte films............................................................................................................................................................................. 113

Figure 6.13: Photocurrent density-voltage of DSSCs with different iodide salt in CMKC/CMCE electrolyte............................................................................................................................................................................. 117
LIST OF TABLES

Table 2.1: The photovoltaic performance of some DSSCs using liquid electrolyte........16
Table 2.2: The photovoltaic performance of some DSSCs based on gel polymer electrolyte..........................................................................................................................18
Table 2.3: The photovoltaic performance of some DSSCs based on solid polymer electrolyte..........................................................................................................................20
Table 2.4: The photovoltaic performance of some DSSCs based on solid biopolymer electrolyte..........................................................................................................................22
Table 2.5: Some solid polymer electrolytes reported in the literature .......................24
Table 2.6: Some characteristics of iodide salts used in this study...............................34
Table 2.7: Ionic conductivities of some solid biopolymer electrolytes .........................36
Table 2.8: Ionic conductivities of some biopolymer blend electrolytes .........................39
Table 3.1: The designation of the CMKC:CMCE (wt/wt%) blend samples .................46
Table 4.1: Elemental data of κ-carrageenan, cellulose and their derivatives .................63
Table 4.2: Crystallinity index of κ-carrageenan, kenaf-cellulose and their derivatives .. 65
Table 5.1: Glass transition temperatures for CMKC and CMKC/CMCE blend films ...73
Table 5.2: Mechanical properties of CMKC and CMKC/CMCE blend films..............79
Table 6.1: Glass transition temperatures for CMKC/CMCE blend electrolytes.........91
Table 6.2: Conductivity and relative number of charge carriers for the CMKC/CMCE blend electrolyte films at room temperature .................................................................101
Table 6.3: The activation energy of CMKC/CMCE blend films containing LiI, NaI, NH₄I and DNH₄I ..................................................................................................................108
Table 6.4: J-V performance of FTO-TiO₂/Electrolyte+I₂/Pt-FTO...............................118
LIST OF SYMBOLS

$E_a$ - Activation energy

$A$ - Area of blocking electrode

$N_o$ - Avogadro number

$R_b$ - Bulk resistance

$q$ - Charge of ion

$\varepsilon^*$ - Complex dielectric constant

$\sigma$ - Conductivity

$\sigma_e$ - Conductivity contributed by electrons

$\sigma_i$ - Conductivity contributed by ions (cations/anions)

$A_c$ - Crystalline area

$X_c$ - Crystalline index

$\varepsilon$ - Dielectric constant

$U_o$ - Dissociation energy

$S$ - Dye molecule

$e^-$ - Electron

$e$ - Electronic charge

$\eta \%$ - Energy conversion efficiency

$S^*$ - Energy excited

$E_g$ - Energy gap

$a_o$ - Equilibrium distance

$T_o$ - Equilibrium glass transition

$ff$ - Fill factor

$T_g$ - Glass transition

$Z$ - Highest common factor of the ionic charges

$Z''$ - Imaginary impedance

$\Gamma$ - Iodide ion

$r_+$ - Ionic radius of cation

$r_o$ - Ionic radius of the anion

$t_i$ - Ionic transference number
<table>
<thead>
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<th>Symbol</th>
<th>Term</th>
<th>Definition</th>
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<tbody>
<tr>
<td>$U$</td>
<td>Lattice energy</td>
<td></td>
</tr>
<tr>
<td>$A_0$</td>
<td>Madelung constant</td>
<td></td>
</tr>
<tr>
<td>$n$</td>
<td>Mobile charge carriers density</td>
<td></td>
</tr>
<tr>
<td>$\mu$</td>
<td>Mobility of the charge carriers</td>
<td></td>
</tr>
<tr>
<td>$V_{oc}$</td>
<td>Open-circuit voltage</td>
<td></td>
</tr>
<tr>
<td>$S^+$</td>
<td>Oxidized dye</td>
<td></td>
</tr>
<tr>
<td>$%$</td>
<td>Percent</td>
<td></td>
</tr>
<tr>
<td>$h\nu$</td>
<td>Photon energy</td>
<td></td>
</tr>
<tr>
<td>$\sigma_0$</td>
<td>Pre-exponential factor</td>
<td></td>
</tr>
<tr>
<td>$Z'$</td>
<td>Real impedance</td>
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<tr>
<td>$\varepsilon_r$</td>
<td>Real part of the dielectric constant</td>
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<tr>
<td>$n/n_o$</td>
<td>Relative number of charge carriers</td>
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<tr>
<td>$n_i$</td>
<td>Repulsion exponent</td>
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<td>$i_e$</td>
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<tr>
<td>$J_{sc}$</td>
<td>Short-circuit current density</td>
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<tr>
<td>$l$</td>
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<td>$A_T$</td>
<td>Total area under the diffraction curve</td>
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<tr>
<td>$i_T$</td>
<td>Total current</td>
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<tr>
<td>$I_3^-$</td>
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<tr>
<td>$C_o$</td>
<td>Vacuum capacitance</td>
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<tr>
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<td>Volume</td>
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<tr>
<td>$w$</td>
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<td>$wt%$</td>
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# LIST OF ABBREVIATIONS

<table>
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<tr>
<th>Abbreviation</th>
<th>Definition</th>
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<tbody>
<tr>
<td>[Bmim][TfO]</td>
<td>1-n-butyl-3-methylimidazolium trifluoromethane sulfonate</td>
</tr>
<tr>
<td>Ag⁺</td>
<td>Silver ion</td>
</tr>
<tr>
<td>BATS</td>
<td>Butyltrimethyl ammonium bis (trifluoromethyl sulfonyl) imide</td>
</tr>
<tr>
<td>CA</td>
<td>Cellulose acetate</td>
</tr>
<tr>
<td>CB</td>
<td>Conduction band</td>
</tr>
<tr>
<td>CMCE</td>
<td>Carboxymethyl cellulose</td>
</tr>
<tr>
<td>CMKC</td>
<td>Carboxymethyl k-carrageenan</td>
</tr>
<tr>
<td>CMKGM</td>
<td>Carboxymethyl konjac glucomannan</td>
</tr>
<tr>
<td>Cu⁺</td>
<td>Copper ion</td>
</tr>
<tr>
<td>DC</td>
<td>Direct current</td>
</tr>
<tr>
<td>DMA</td>
<td>Dynamic mechanical analysis</td>
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<tr>
<td>DMC</td>
<td>Dimethyl carbonate</td>
</tr>
<tr>
<td>DNH₄⁺</td>
<td>N-N-Dimethyl-N-(methyl-sulfanylmethylene) ammonium ion</td>
</tr>
<tr>
<td>DNH₄I</td>
<td>N-N-Dimethyl-N-(methyl-sulfanylmethylene) ammonium iodide</td>
</tr>
<tr>
<td>DS</td>
<td>Degree substitution</td>
</tr>
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<td>DSC</td>
<td>Differential scanning calorimetry</td>
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<td>DSSC</td>
<td>Dye sensitized solar cell</td>
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<td>DTAB</td>
<td>Dodecytrimethyl ammonium bromide</td>
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<td>1-ethyl-3-methylimidazolium dicyanamide</td>
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<tr>
<td>EMImI</td>
<td>1-ethyl-3-methylimidazolium iodide</td>
</tr>
<tr>
<td>EMImTFO</td>
<td>1-Ethyl-3-methylimidazolium trifluoromethanesulfonate</td>
</tr>
<tr>
<td>EVII</td>
<td>Ethenyl(phenyl)methyl-3-vinyl-imidazolium iodide</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform Infrared spectroscopy</td>
</tr>
<tr>
<td>FTO</td>
<td>Fluorine-doped tin oxide</td>
</tr>
<tr>
<td>Chemical Symbol</td>
<td>Name</td>
</tr>
<tr>
<td>-----------------</td>
<td>---------------------------------------</td>
</tr>
<tr>
<td>H⁺</td>
<td>Hydrogen ion</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>Sulfuric acid</td>
</tr>
<tr>
<td>H₃PO₄</td>
<td>Phosphoric acid</td>
</tr>
<tr>
<td>HPMC</td>
<td>Hydroxypropylmethylcellulose</td>
</tr>
<tr>
<td>I⁻</td>
<td>Iodide ion</td>
</tr>
<tr>
<td>I₂</td>
<td>Iodine</td>
</tr>
<tr>
<td>ᵢ⁻ carrageenan</td>
<td>Iota-carrageenan</td>
</tr>
<tr>
<td>IL</td>
<td>Ionic liquid</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium tin oxide</td>
</tr>
<tr>
<td>K⁺</td>
<td>Potassium ion</td>
</tr>
<tr>
<td>k⁻ carrageenan</td>
<td>Kappa-carrageenan</td>
</tr>
<tr>
<td>KClO₄</td>
<td>Potassium perchlorate</td>
</tr>
<tr>
<td>KGM</td>
<td>Konjac glucomannan</td>
</tr>
<tr>
<td>KI</td>
<td>Potassium iodide</td>
</tr>
<tr>
<td>Li⁺</td>
<td>Lithium ion</td>
</tr>
<tr>
<td>LiBF₄</td>
<td>Lithium tetrafluoroborate</td>
</tr>
<tr>
<td>LiCF₃SO₄</td>
<td>Lithium trifluoromethanesulfonate</td>
</tr>
<tr>
<td>LiClO₄</td>
<td>Lithium chloride</td>
</tr>
<tr>
<td>LiI</td>
<td>Lithium iodide</td>
</tr>
<tr>
<td>LiNO₃</td>
<td>Lithium nitrate</td>
</tr>
<tr>
<td>LiTf</td>
<td>Lithium trifluoromethanesulfonate</td>
</tr>
<tr>
<td>LSV</td>
<td>Linear sweep voltammetry</td>
</tr>
<tr>
<td>Mac</td>
<td>Maleic acid</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>Magnesium ion</td>
</tr>
<tr>
<td>MG49</td>
<td>49% poly(methyl methacrylate) grafted natural rubber</td>
</tr>
<tr>
<td>MPII</td>
<td>1-Methyl-3-propylimidazolium iodide</td>
</tr>
<tr>
<td>MVII</td>
<td>1-vinyl-3-methylimidazolium iodide</td>
</tr>
<tr>
<td>N719</td>
<td>Ditetrapentammonium cis-bis (isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato) ruthenium</td>
</tr>
<tr>
<td>Na⁺</td>
<td>Sodium ion</td>
</tr>
<tr>
<td>NaCl</td>
<td>Sodium chloride</td>
</tr>
</tbody>
</table>
NaI - Sodium iodide
NaOH - Sodium hydroxide
NH₄⁺ - Ammonium ion
NH₄BF₄ - Ammonium tetrafluoroborate
NH₄CF₃SO₄ - Ammonium triflate
NH₄I - Ammonium iodide
NH₄I - Ammonium iodide
NH₄NO₃ - Ammonium nitrate
O - Oxygen
OA - Oxalic acid
P-4VI - Poly(4-vinyl-imidazole)
PAA - Poly(acrylic acid)
PAN - Peroxyacetyl nitrate
PANI - Polyaniline
PBSU - Poly(butylene succinate)
PC - Propylene carbonate
PDMS - Polydimethylsiloxane
PEG - Poly(ethylene glycol)
PEGME - Poly(ethylene glycol) methyl ether
PEM - Polymer electrolyte membrane
PEMA - Poly(ethyl methacrylate)
PEO - Poly(ethylene oxide)
PEOMA - Polyethyleneoxide-maleic anhydride
PHEMA - Poly(2-hydroxyethyl methacrylate)
PMMA - Poly(methyl methacrylate)
PMVE - Perfluoromethylvinyl ether
POEM - Poly((oxyethylene) methacrylate)
PPFEMO - Poly(perfluorinated ethylenmethylenoxide)
Pt - Platinum
PTMG - Polytetramethylene glycol
PVA - Polyvinyl alcohol
PVC - Poly(vinyl chloride)
PVDF - Poly(vinylidene fluoride)
PVDF-HFP - Poly(vinylidene fluoride hexafluoro propylene)
PVK - Poly(N-vinylcarbazole)
PVP - Poly(N-vinylpyrrolidone)
Rb⁺ - Rubidium ion
RS - Rice starch
RT - Room temperature
SEM-EDX - Scanning electron microscopy-energy dispersive X-ray spectroscopy
SnO₂ - Tin dioxide
SPI - Soy protein isolate
TBAI - Tetrabutylammonium iodide
TCO - Transparent conducting glass
TiO₂ - Titanium oxide
TNM - Transference number measurement
TPAI - Tetrapropylammonium iodide
TS - Tensile strength
VB - Valency band
VTF - Vogel-Tamman-Fulcher
XRD - X-ray diffraction
ZnO - Zinc oxide
λ-carrageenan - Lambda-carrageenan
CHAPTER 1: INTRODUCTION

1.1 Introduction

Direct utilization of solar radiation in producing electricity is close to an ideal way in utilizing the nature’s renewable energy flow. Despite significant development, the most well-known and studied unconventional photovoltaic system is the dye-sensitized nanostructured solar cell. In 1991, Grätzel and co-workers developed the most well-known unconventional photovoltaic system which is the dye-sensitized nanostructured solar cell using organic liquid electrolytes (Chen et al., 2013; Grätzel, 2004). This type of solar cell has attracted large attention due to their low production cost, simple structure and high power conversion efficiency. However, DSSCs using liquid electrolytes have drawbacks such as less long-term stability due to the volatility organic solvent in the electrolytes (Nogueira et al., 2001). In addition, the liquid electrolyte in dye sensitized solar cell (DSSC) introduces risks of evaporation and solvent leakage (de Freitas et al., 2008). In order to overcome this problem, many researchers have looked for other alternatives to replace liquid electrolyte such as solid polymer electrolytes, hole conductor and gels electrolytes.

The gel electrolytes show better conductivity as well as higher efficiency although the liquid encapsulated inside the gel pores creates problem during solar cells sealing and hence affects long term stability (Grätzel, 2004; Nogueira et al., 2001). The solid polymer electrolyte seems novel alternative electrolyte in DSSCs due to its completely solid in nature, excellent properties such as good conducting property, easy to fabricate, low cost and good stability. They have obtained growing interests from the point of practical applications. Lee and co-workers (2008) studied poly(ethylene oxide)/poly(dimethylsiloxane) (PEO/PDMS) blend solid polymer electrolyte and its dye-
sensitized solar cell applications. Their DSSCs employing PEO/PDMS blend complexed with LiI showed photoconversion efficiencies of 0.48% and 1.35% at 100 and 10 mW cm\(^{-2}\) respectively (Lee et al., 2008). Meanwhile, Roh et al. (2010) reported that DSSC fabricated using PVC-g-POEM/(LiI+MPII)/PEG electrolyte possessed energy conversion efficiency of ~5.0% at 100 mW cm\(^{-2}\) (Roh et al., 2010). It has been proven that application of polymer electrolytes resolves the problems related to leakage of liquid electrolytes (Wu et al., 2007). The DSSCs employing polymer electrolytes show low performance as compared to cells using liquid electrolytes. The reasons for this are low ionic conductivity of the polymer electrolytes, unfavourable polymer electrolyte morphology that results in poor contact with electrode materials. Furthermore, most studies were done on synthetic based polymers, which are associated to the environmental issues and high cost (Siracusa et al., 2008). In order to reduce the dependence of synthetic based polymer for electrolytes, biopolymers as polymer hosts may be applied.

Biopolymers have widely investigated due to being environmental friendly, nontoxic, and abundant in nature. Furthermore, it could overcome the main shortcoming of synthetic polymer, which is mostly insoluble in solvents (Ma et al., 2007). Biopolymer materials show good potential to act as polymer hosts in polymer electrolytes due to their good biocompatibility and biodegradability. Biodegradable biopolymer are attracted more attention as representative water-soluble polysaccharide in many research fields (Barbucci et al., 2000; Samsudin et al., 2012).

As an effort to reduce dependency on petrochemical based electrolytes, this study focuses on developing electrolytes based on biopolymer blend by using modified
natural polymers namely of carboxymethyl kappa-carrageenan (k-carrageenan), CMKC and carboxymethyl cellulose, CMCE for potential use as electrolytes in DSSC.

1.2 Problem statement

(a) There are several renewable resource-based biopolymers that are suitable to be used as host polymers in the polymer electrolytes. These include starch, cellulose, chitosan, etc. (Kumar et al., 2012; Lu et al., 2009; Ramesh et al., 2011; Samsudin et al., 2012; Shukur et al., 2013). However, recent advance in development of polymer electrolytes has driven the need to identify promising resources. So that, chemical modification on the natural polymers can be considered to enhance their properties and is expected to bring about quite promising results.

(b) The bio-based polymers are also promising candidates that meet different requirements. However, single biopolymers do not offer good mechanical, physical or chemical properties to meet wide range of device applications. Incorporation with other natural bio-based polymer, producing biopolymer blend, has shown favourable result such as improving their good conductive and mechanical properties. However, the challenge is to identify suitable blend ratio that will yield good polymer electrolytes.

(c) Recently, the development of solid polymer electrolytes based on synthetic polymer and biopolymers has shown impressive results. However, limited understanding on the effect of different iodide salts (different cation size) to the properties of solid polymer electrolytes have been reported. Therefore, it is very
interesting to investigate the effect of different cation size of salts and suitability of the salts to the properties of biopolymer.

(d) Until today, DSSSSs employing liquid electrolytes have shown the best photovoltaic performance. However, some issues related to DSSCs liquid electrolytes exist such as the volatility organic solvent in the electrolytes (Nogueira et al, 2001), risks of evaporation and solvent leakage (Freitas, 2008). Therefore, solid state DSSCs employing solid polymer electrolytes based on biopolymers seem to be new alternative and thus needs to be researched to replace liquid state DSSCs. The biopolymers also offer the possibility of producing green polymer electrolytes and DSSCs.

1.3 Scope and objectives of the study

The objectives of this study are as follows:

1. To obtain carboxymethyl k-carageenan, CMKC and carboxymethyl cellulose, CMCE from k-carrageenan and kenaf fiber.
   - In this study, CMKC and CMCE were synthesized from k-carrageenan and kenaf fiber. The new derivatives of k-carrageenan and cellulose are expected to have more oxygen number in the structures compared to their original structure. This means that they can provide more vacancies for coordination with cations or anions from the dopant salts leading to high ionic conductivity.
2. To identify the most suitable CMKC/CMCE blend composition to be used as host polymer electrolytes.
   - In this study, four polymer blends ratio were prepared. The study was carried out in order to identify suitable blend ratio for use as host in developing polymer electrolytes. For this purpose CMKC/CMCE blends were prepared and characterized using Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX), dynamic mechanical analysis (DMA), electrochemical Impedance spectroscopy (EIS), linear sweep voltammetry (LSV) and tensile measurement. Only one composition which had the optimum properties was chosen. For the blend system, CMKC was chosen as the first polymer and CMCE as the second polymer.

3. To prepare and characterize biopolymer electrolytes of CMKC/CMCE blend doped with different iodide salts for potential application in dye sensitized solar cells.
   - To obtain CMKC/CMCE blend based polymer electrolyte with > \(10^{-4}\) S cm\(^{-1}\), the optimum polymer blend system was doped with 10 to 50 wt % of salt. The prepared films were characterized using FTIR, DMA, EIS, LSV and transference number (TNM). The dopant used are lithium iodide (LiI), sodium iodide (NaI), ammonium iodide (NH\(_4\)I) and N-N-Dimethyl-N-(methyl-sulfanymethylene) ammonium iodide (DNH\(_4\)I).

4. To fabricate solid state dye sensitized solar cells and study their performance
   - The prepared solid electrolytes were then used to fabricate solid state dye sensitized solar cells and characterized under light intensity of 100 mW cm\(^{-2}\).
Their short-circuit current density \( (J_{sc}) \), open-circuit voltage \( (V_{oc}) \), fill factor \( (ff) \) and energy conversion efficiency \( (\eta \%) \) were then analyzed.

### 1.4 Significance of the study

With increasing trend to reduce the environmental impact, special attention has been paid to explore biopolymer-based materials to replace conventional synthetic-based materials. Biopolymer materials are therefore widely studied because of these environmental concerns and supply limitations of synthetic polymer. Therefore, much effort has been made to develop the biopolymer electrolytes by using natural polymer.

In this study, CMKC/CMCE blend was used as hosts in polymer electrolytes for potential application in DSSCs. The CMKC and CMCE have more number of oxygens as compared to the pristine polymers and thus, both can provide more vacancy for cations or proton to coordinate (Mobarak et. al, 2012). Even though, these carboxymethyl polymers have attracted interests of industrial and scientific organizations in recent years, the ability to conduct electricity and their potential application in DSSCs, have not been explored. In comparison to conventional PEO, these polysaccharide matrices are expected to show much lower crystallinity at room temperature. For instance, they are expected to form polymer electrolytes with higher conductivity, more favorable morphology and better contact with electrode materials which in turn will improve DSSCs efficiency.
1.5 Organization of the thesis

The thesis is divided into seven chapters.

Chapter 1 provides a brief description which summarizes the research study. The objectives and scopes of this study are also included in this chapter.

Chapter 2 describes an overview of literature on DSSCs and biopolymer electrolytes is presented in this chapter. This includes the overview DSSC working principle and reviews of previous works related to electrolytes for DSSCs application.

Chapter 3 describes the sample preparation methods such as synthesis, blending, doping, film preparation and cell fabrication. The experimental techniques for the structural, thermal, optical, electrical and solar cell characterizations of the electrolyte systems are also presented in this chapter. The results of these studies are presented in Chapter 4, Chapter 5 and Chapter 6.

Chapter 4 presents the results of FTIR, XRD, SEM-EDX, degree of substitution and elemental analyses of the synthesized CMKC and CMCE.

Chapter 5 demonstrates the detailed studies on CMKC/CMCE blend systems. In this study, four blend systems of different CMKC to CMCE wt % ratios were prepared. The effects of different wt % of CMCE to the properties of CMKE were studied using FTIR, SEM, tensile measurement, DMA, EIS and LSV to obtain information of their structural, mechanical, viscoelastic and electrical behavior. Based on these results, the most optimum CMKC/CMCE blend composition was identified and then used for the preparation of biopolymer electrolytes based on CMKC/CMCE blend.
Chapter 6 presents the results of the biopolymer electrolytes of CMKC/CMCE blend containing different cation of iodide salts (LiI, NaI, NH4I and DNH4I) are revealed and discussed in this chapter. The electrolytes properties were investigated using FTIR, DMA, EIS, LSV and TNM studies. The performance characteristics ($J_{sc}$, $V_{oc}$, $ff$ and $\eta$ %) of the solar cells fabricated using selected CMKC/CMCE electrolytes are presented in this chapter.

Chapter 7 provides an overall conclusion of the thesis. In addition, the future prospects of presented work is also discussed in this chapter.
CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

This chapter focuses on the review of dye sensitized solar cell, its operational mechanism, polymer electrolytes commonly use in DSSCs and their applications in DSSC. This chapter also includes some basic properties of biopolymer, k-carrageenan, kenaf-cellulose, CMKC, CMCE, dopant salts (LiI, NaI, NH\(_4\)I and DNHI\(_4\)) and polymer blend electrolytes.

2.2 Dye sensitized solar cell

DSSC or commonly known as Grätzel cell was developed by O’Regan and Grätzel (1991) is a semiconductor photovoltaic device that directly converts solar radiation into electric current. This cell, received more attention recently due to its high power conversion efficiency, low energy production cost, easy fabrication and environmentally friendly operation. It consists of two main electrodes namely transparent photoelectrode which is made up from a glass sheet treated with conducting oxide layer and counter electrode. They are separated by an electrolyte containing redox mediator. Figure 2.1 shows a schematic diagram for standard DSSC.
2.3 Operational principal of a DSSC

When a DSSC is illuminated by sunlight, the dye molecule on TiO₂, S absorbed energy from the sunlight and are excited, S*. Since the excited electrons of the dye are in an energy level above the conduction band (CB) of the TiO₂, the electrons are injected into the conduction band of the TiO₂.

Excitation: \( \text{TiO}_2 \mid S + hv \rightarrow \text{TiO}_2 \mid S^* \)  

Injection: \( \text{TiO}_2 \mid S^* \rightarrow \text{TiO}_2 \mid S^+ + e^-_{(\text{CB})} \)
The excited dye will be oxidized. The oxidized dye molecules will be reduced by an iodide ion which in turn becomes a triiodide ion.

Regeneration: TiO$_2$ | 2S$^+$ + 3I$^-$ → TiO$_2$ | 2S + I$_3^-$ \hspace{1cm} (2.3)

The electron in the conduction band of TiO$_2$ flows through the external circuit while at the counter electrode.

Reduction: I$_3^-$ + 2e$^-$ (Pt) → 3I$^-$ \hspace{1cm} (2.4)

The iodide ion is recaptured and the difference between the Fermi level of the electron in the semiconductor photoelectrode and the redox potential of the electrolyte gives the voltage generated under illumination.

In order to generate high current, the reactions from equation (2.5) and equation (2.6) must effectively compete with the recombination reactions (Calogero & Di Marco, 2008).

Recaption: I$_3^-$ + 2e$^-$$_{(CB)}$ → 3I$^-$ \hspace{1cm} (2.5)

Recombination TiO$_2$: | S$^+$ + e$^-$$_{(CB)}$ → TiO$_2$ | S \hspace{1cm} (2.6)

The working principle of DSSC is illustrated in Figure 2.2.
Figure 2.2: Working principle of DSSC operation
2.4 **Fluorine-doped tin oxide glass**

In DSSC, transparent conducting glass (TCO) is used to deposit the TiO$_2$ photoelectrode and platinum counter electrode. This TCO functions both as a current collector and as a support for the electrodes (Ngamsinlapasathian et al., 2006). It must have low sheet resistance, highly transparent, high transmittance and high heat stability to ensure good cell performance (Hara and Arakawa, 2003). Most commonly used TCO are fluorine-doped tin oxide (FTO) and indium-tin-oxide (ITO) glass. In this work, FTO glass is used as TCO due to its stable heat resistance temperature compared to the ITO glass (Kawashima et al., 2004; Sima et al., 2010).

2.5 **Titanium oxide photoelectrode**

The photoelectrode comprises of a porous network of metal oxides like TiO$_2$, ZnO, and SnO$_2$. They have widely used due to their wide bandgap whereas the porous network is used to get high surface area for good sensitizer binding and efficient solar harvesting (Vlachopoulos et al., 1988). Metal oxides performance as electron acceptor and electronic conduction path to facilitate photoexcited electrons because of their conductive electronic structure, referred to as valence band (VB) and conduction band (CB) (Gong et al., 2012; O'regan & Grätzel, 1991).

The most popular choice as photoelectrode is TiO$_2$ since it has a large energy bandgap, $E_g$ of $\sim$3 eV and can be efficiently sensitized by a dye (Vlachopoulos et al., 1988). TiO$_2$ is found as stable photoelectrode in photoelectrochemical system even under extreme operating conditions. It is cheap, non-toxic, inert, biocompatible, has strong oxidizing ability, long term stability, good optical and electrical properties.
In this study, TiO$_2$ was applied on FTO glass by the doctor blade method using commercially available TiO$_2$ paste.

2.6 Ditetrabutylammonium cis-bis (isothiocynato)bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium (II)

The function of dye sensitizer is to absorb light for the generation of electrons and holes into the semiconductor conduction band and then accepts electron from the redox mediator in the electrolytes. Thus, a dye sensitizer should absorb light optimally over a wide wavelength range of the electromagnetic spectrum from visible light to near infrared region (400 - 900 m). The excited state of dye must be slightly above the conduction band of TiO$_2$ whereas its ground state level is slightly below the redox potential. It should also adhere well to TiO$_2$ surface, must have several =O and -OH groups. In addition, the life time of a dye must consistent with the device life. The widely used dye sensitizer in DSSCs is ruthenium(II) complexes.

Among the ruthenium complexes, ditetrabutylammonium cis-bis (isothiocynato)bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium (II) (N719) dye is a common choice due to its unique characteristics as listed below;

(a) High stability to enable good absorption to TiO$_2$
(b) Excellent redox properties
(c) Broad absorption spectrum in visible region

Figure 2.3 shows the molecular structure of a N719 dye.
2.7 Platinum counter electrode

The counter electrode plays important role in electrons transfer. The use of a suitable catalyst helps in the reduction of the charge transfer resistance at counter electrode and pushing the reaction toward a forward direction (Su’ait et al., 2015; Thomas et al., 2014). There are several types of counter electrode studied by researchers such as platinum, carbon based materials, conducting polymers, nitride and sulfide based material (Su’ait et al., 2015). In the present work, platinum is selected as the catalyst (coated on FTO) due to its high catalyst activity and high power conversion efficiency. Platinum coating is also very compatible to I/I₃⁻ (Caramori et al., 2010).

2.8 Electrolytes

Electrolytes play an important role in the photovoltaic performance of the DSSCs. In fact, all electrochemical devices required electrolytes. The electrolytes should meet the requirements of having a long-term stability including chemical, optical, electrochemical, thermal and interfacial stability to prevent the degradation of the dye. The electrolyte should have excellent interfacial properties with both

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**Figure 2.3: The molecular structure of N719 dye**
photoelectrode and counter electrode. The electrolytes also should be compatible with the dye (Bella & Bongiovanni, 2013; Wu et al., 2008). Many efforts have been done to develop DSSCs using different kinds of electrolytes.

### 2.8.1 DSSCs employing liquid electrolytes

DSSCs employing liquid electrolytes typically consist of a redox mediator dissolved in an organic solvent. Liquid electrolytes show high ionic conductivity which is an important characteristic to obtain good performance of DSSC. Various metal salts based liquid electrolytes and ionic liquids are being used together with redox couple in DSSC such as triiodide (I$_3^-$/I$^-)$). Some of the DSSCs developed using liquid electrolytes are listed in Table 2.1.

**Table 2.1: The photovoltaic performance of some DSSCs using liquid electrolyte**

<table>
<thead>
<tr>
<th>DSSCs based liquid electrolytes system</th>
<th>DSSC performance ($J_{sc}$ (mA cm$^{-2}$), $V_{oc}$ (V) and $\eta$ (%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>EMImDCA + I/I$_3^-$</td>
<td>$J_{sc}$ = 7.8, $V_{oc}$ = 0.70 and $\eta$ % = 3.8</td>
<td>Kawano et al., 2004</td>
</tr>
<tr>
<td>EMImBF4 + I/I$_3^-$</td>
<td>$J_{sc}$ = 9.9, $V_{oc}$ = 0.60 and $\eta$ % = 3.3</td>
<td>Kawano et al., 2004</td>
</tr>
<tr>
<td>1.5 M EMImI + 0.05M I$_2$ + acetonitrile</td>
<td>$J_{sc}$ = 19.0, $V_{oc}$ = 0.67 and $\eta$ % = 0.92</td>
<td>Hara et al., 2005</td>
</tr>
<tr>
<td>MVII+0.6M LiI + I$_2$</td>
<td>$J_{sc}$ = 9.4, $V_{oc}$ = 0.55 and $\eta$ % = 2.4</td>
<td>Wang et al., 2008</td>
</tr>
<tr>
<td>EVII+0.6M LiI + I$_2$</td>
<td>$J_{sc}$ = 9.9, $V_{oc}$ = 0.60 and $\eta$ % = 3.3</td>
<td>Wang et al., 2008</td>
</tr>
<tr>
<td>EC + PC</td>
<td>$J_{sc}$ = 16.86, $V_{oc}$ = 0.73 and $\eta$ % = 7.76</td>
<td>Subramania et al., 2013</td>
</tr>
</tbody>
</table>
Although conversion efficiencies of DSSCs employing liquid electrolytes are quite high, they exhibit poor long-term stability due to the volatility which introduces risks of evaporation and solvent leakage (de Freitas et al., 2008). This problem can be overcome by replacing liquid electrolytes with gel electrolytes or solid polymer electrolytes.

2.8.2 DSSCs employing gel electrolytes

Gel electrolytes are proposed as alternative to replace liquid electrolytes in dye sensitized solar cell. Yang et al. (2008) replaced liquid electrolytes with gel polymer electrolytes. They reported that a polymer gel electrolyte PMMA–EC/PC/DMC–NaI/I$_2$ with ionic conductivity of 6.89 mS cm$^{-1}$ was optimized at 12wt% PMMA, 0.6M NaI, 0.06M I$_2$ and 0.5M TBP. Based on this gel polymer electrolyte, a quasi-solid-state dye-sensitized solar cell was fabricated. The quasi-solid-state DSSC exhibited a light-to-electrical energy conversion efficiency of 4.74% under irradiation of 100 mW cm$^{-2}$ simulated sunlight, which is almost equal to that of DSSC with a liquid electrolyte (Yang et al., 2008).

Similar observation has been reported by Tang et al. (2012). They synthesized a microporous hybrid polymer of poly(acrylic acid)/gelatin/polyaniline (PAA/Gel/PANI) for application in quasi-solid-state DSSCs. The gel electrolytes showed high conductivity of 14.38 mS cm$^{-1}$ and achieved a light-to-electric energy conversion efficiency of 6.94% (Tang et al., 2012). However, in the viewpoint for commercialization, this gel electrolyte cannot be used because they have poor mechanical strength. Table 2.2 lists some of DSSCs employing gel polymer electrolytes.
Table 2.2: The photovoltaic performance of some DSSCs based on gel polymer electrolyte

<table>
<thead>
<tr>
<th>DSSCs based gel polymer electrolytes system</th>
<th>DSSC performance $J_{sc}$ (mA cm$^{-2}$), $V_{oc}$ (V) and $\eta$ (%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA – EC/PC/DMC – NaI/I$_2$</td>
<td>$J_{sc} = 11$, $V_{oc} = 0.55$ and $\eta % = 4.78$</td>
<td>Yang et al., 2011</td>
</tr>
<tr>
<td>PAA/Gel/PANI/I$_2$</td>
<td>$J_{sc} = 5.3$, $V_{oc} = 0.69$ and $\eta % = 6.94$</td>
<td>Tang et al., 2012</td>
</tr>
<tr>
<td>Agarose + KI/I$_2$</td>
<td>$J_{sc} = 3.27$, $V_{oc} = 0.67$ and $\eta % = 0.54$</td>
<td>Singh et al., 2013</td>
</tr>
<tr>
<td>Micro Cellulose + LiI/I$_2$ + MPII/EMISCN</td>
<td>$J_{sc} = 8.39$, $V_{oc} = 0.59$ and $\eta % = 3.33$</td>
<td>Paolo Salvado et al., 2014</td>
</tr>
<tr>
<td>MFC + NaI/I$_2$ + MPII + TBP</td>
<td>$J_{sc} = 15.2$, $V_{oc} = 0.76$ and $\eta % = 7.03$</td>
<td>Bella et al, 2014</td>
</tr>
<tr>
<td>CMCE + NaI/I$_2$ + MPII + TBP</td>
<td>$J_{sc} = 10.03$, $V_{oc} = 0.75$ and $\eta % = 5.18$</td>
<td>Bella et al, 2014</td>
</tr>
<tr>
<td>P(VP-co-VAc) + TPAI/I$_2$</td>
<td>$J_{sc} = 6.86$ mA, $V_{oc} = 0.73$ and $\eta % = 3.07$</td>
<td>Ng et al., 2015</td>
</tr>
</tbody>
</table>

2.8.3 **DSSCs employing solid polymer electrolytes**

A novel alternative to gel electrolytes is solid polymer electrolyte, since it is completely solid in nature with good conducting properties. In fact, they mechanically, behave like solids but internal structure and consequently the conductivity behavior closely resembles liquid state (MacCallum and Vincent, 1987; 1989). Most of solid state devices need materials with high ionic conductivity in the range of $10^{-3}$ to $10^{-2}$ S cm$^{-1}$ which is definitely available in polymer electrolyte. Moreover, the advantage properties, such as the ability to form thin films, flexibility, light weight, elasticity and high energy density make them suitable candidate for many
electrochemical devices including solid state DSSCs (Li et al., 2006; Nogueira et al., 2001).

A new solid polymer electrolyte system consisting of polyvinylpyrrolidone (PVP) and KI for DSSC application has been developed by Singh et al. (2013). They found that the ionic conductivity enhanced by doping KI and the highest ionic conductivity value obtained was $4.69 \times 10^{-5}$ S cm$^{-1}$ at 30 wt % KI concentration. Meanwhile, the fabricated DSSC using maximum conducting film showed 0.14 % efficiency at 1 sun condition (Singh et al., 2013). Similar effort has been reported by Singh et al. (2015). They successfully prepared solid polymer electrolyte films based on PEMA doped with NH$_4$I salt at different compositions by solution casting technique and tested them for DSSC application. Their TNM measurement results suggested that the PEMA/NH$_4$I films have ionic conductivity. They found that the efficiency of DSSC fabricated using film at maximum ionic conductivity of $1.80 \times 10^{-5}$ exhibited maximum efficiency of 0.43 % at 1 sun condition. They observed that the $J_{sc}$ values of the dye-sensitized solar cells increased with increasing amount of salt in the electrolyte, which was in good agreement with the changes of the ionic conductivity result. The increase of $J_{sc}$ was attributed to the improved transportation of redox couple in less viscous matrix (more amorphous) provided by salt, which would certainly improve the interfacial contact between electrode/electrolyte and better ion mobility.

Lee and co-workers (2008) studied poly(ethylene oxide)/ poly(dimethylsiloxane) (PEO/PDMS) blend solid polymer electrolyte and its DSSC applications. Their PEO/PDMS blend complexed with LiI showed conductivity close to $10^{-3}$ S cm$^{-1}$ at 303 K. The addition of PDMS in PEO reduced the crystallinity of the matrix. The conductivity was found to depend on the number of charge carriers. The dye sensitized
solar cells fabricated using the nanoporous TiO$_2$ electrode and the solid polymer blend showed photoconversion efficiencies of 0.48% and 1.35% at 100 and 10 mW cm$^{-2}$, respectively. Meanwhile, Roh et. al (2010) studied PVC-g-POEM comprised of a PVC backbone and POEM side chains synthesized via atom transfer radical polymerization and complexed with a salt for DSSC applications. They reported that the ion conducting POEM domains were well interconnected, resulting in high ionic conductivity of $\sim$10$^{-4}$ S cm$^{-1}$ at 25 $^\circ$C and energy conversion efficiency of $\sim$5.0% at 100 mW cm$^{-2}$. Table 2.3 lists some of DSSCs employing solid polymer electrolytes.

### Table 2.3: The photovoltaic performance of some DSSCs based on solid polymer electrolyte

<table>
<thead>
<tr>
<th>DSSCs based solid polymer electrolytes system</th>
<th>DSSC performance $J_{sc}$ (mA cm$^{-2}$), $V_{oc}$ (V) and $\eta$ (%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO + KI/I$_2$</td>
<td>$J_{sc} = 0.06$, $V_{oc} = 0.68$ and $\eta$ % = 0.01</td>
<td>Lee et al., 2008</td>
</tr>
<tr>
<td>PEO/PDMS + LiI/I$_2$</td>
<td>$J_{sc} = 3.05$, $V_{oc} = 0.54$ and $\eta$ % = 0.48</td>
<td>Lee et al., 2008</td>
</tr>
<tr>
<td>PVC-g-POEM + LiI</td>
<td>$J_{sc} = 2.3$, $V_{oc} = 0.68$ and $\eta$ % = 0.8</td>
<td>Roh et al., 2010</td>
</tr>
<tr>
<td>PVC-g-POEM/MPPII</td>
<td>$J_{sc} = 5.3$, $V_{oc} = 0.69$ and $\eta$ % = 2.2</td>
<td>Roh et al., 2010</td>
</tr>
<tr>
<td>POEM6-qP$_4$VP$_4$ + LiI/I$_2$</td>
<td>$J_{sc} = 11.1$, $V_{oc} = 0.49$ and $\eta$ % = 3.0</td>
<td>Seo et al., 2012</td>
</tr>
<tr>
<td>PVP + KI/I$_2$</td>
<td>$J_{sc} = 0.97$, $V_{oc} = 0.48$ and $\eta$ % = 0.14</td>
<td>Singh et al., 2013</td>
</tr>
<tr>
<td>PEMA + NH$_4$I/I$_2$</td>
<td>$J_{sc} = 1.52$, $V_{oc} = 0.56$ and $\eta$ % = 0.43</td>
<td>Singh et al., 2015</td>
</tr>
<tr>
<td>PVP + NH$_4$I/I$_2$</td>
<td>$J_{sc} = 0.1$, $V_{oc} = 0.35$ and $\eta$ % = 0.025</td>
<td>Singh et al., 2015</td>
</tr>
</tbody>
</table>
According to Wang (2009), the photoelectrical performance of the DSSCs based on solid polymer electrolytes was affected by the type of polymer used (Wang, 2009). Recently, much effort has been made to develop polymer electrolytes by using natural polymer due to their richness in nature, very low cost, high conductive properties and principally biodegradation properties. It could also overcome the main shortcoming of synthetic polymer, which was mostly insoluble in the solvents (Ma et al., 2007). Therefore, biopolymer electrolytes were further studied for electrochemical applications such as dye sensitized solar cells

Su’aït et al. (2013) developed solid state DSSC from bio based polyurethane (PU), solid polymer electrolyte with lithium iodide as conducting material. They found ionic conductivity of PU increased with the addition Li and the highest conductivity of $7.6 \times 10^{-4} \text{ S cm}^{-1}$ was achieved at 25 wt % of LiI. They also reported a DSSC consists of FTO/TiO_2-dye/PU-LiI-I_2/Pt showed the photovoltaic response with the $J_{sc}$ of 0.06 mA cm$^{-2}$, $V_{oc}$ of 0.14V, $ff$ of 0.26 and $\eta$ % of 0.003 respectively, under light intensity of 100 mW cm$^{-2}$. Meanwhile, Khanmirzaei et al. (2013) prepared biopolymer rice starch electrolyte for solid state DSSC. They reported that electrolytes conductivity of $3.63 \times 10^{-4} \text{ S cm}^{-1}$ was obtained by introducing 30 wt % of 1-methyl-3-propylimidazolium iodide (MPII) as ionic liquid and 2 wt % of TiO_2 and exhibited $\eta$ % of 0.17 %. Some of DSSCs employing solid biopolymer electrolytes reported in literature are listed in Table 2.4.
### Table 2.4: The photovoltaic performance of some DSSCs based on solid biopolymer electrolyte

<table>
<thead>
<tr>
<th>DSSCs based solid biopolymer electrolytes system</th>
<th>DSSC performance $J_{sc}$ (mA cm$^{-2}$), $V_{oc}$ (V) and $\eta$ (%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chitosan + NH$_4$I/I$_2$ - BMII</td>
<td>$J_{sc} = 0.07$, $V_{oc} = 0.23$ and $\eta% = NA$</td>
<td>Buraidah et al., 2010</td>
</tr>
<tr>
<td>Arrowroot + KI</td>
<td>$J_{sc} = 5.68 \times 10^{-4}$, $V_{oc} = 0.56$ and $\eta% = 0.63$</td>
<td>Singh et al., 2014</td>
</tr>
<tr>
<td>RS + LiI + 30 wt.% MPII + 2 wt % TiO$_2$</td>
<td>$J_{sc} = 0.49$, $V_{oc} = 0.45$ and $\eta% = 0.17$</td>
<td>Khanmirzaei &amp; Ramesh, 2014</td>
</tr>
<tr>
<td>PU + Li/I$_2$</td>
<td>$J_{sc} = 0.06$, $V_{oc} = 0.14$ and $\eta% = 0.003$</td>
<td>Su'ait et al., 2014</td>
</tr>
</tbody>
</table>

### 2.9 Solid polymer electrolytes

Generally, polymers are known as insulators. These insulating materials are made to conduct by introducing a quantity of ions into the polymer structure to form polymer-salt complexes, i.e. the polymer electrolytes. Fenton and Wright were the first to study polymer electrolytes in the 1970’s (Fenton et al, 1973; Wright, 1975). They discovered the first ion conducting polymer which is poly(ethylene oxide) (PEO) dissolved with alkali metal salts. The first potential application of polymer electrolytes was realized by Armand et al. (1979), when he and co-workers discovered the solid state battery using PEO-Li salt. Since then, a large number of polymer electrolytes containing different mobile ions like NH$_4^+$, Li$^+$, Na$^+$, K$^+$, Ag$^+$, Cu$^+$, Mg$^{2+}$ etc were reported in the literature. It has obtained growing interests from the point of practical applications due to several advantageous properties like easy to fabricate, flexible in nature, good electrode-electrolyte contact, cost effective and good mechanical stability.
Polymer-salt complexes are also called as solvent free or dry solid polymer electrolytes. The dry systems use the polymer host as the solid solvent and do not include any organic liquids. This type of polymer electrolytes are formed by dissolving suitable ionic salts like $\text{NH}_4\text{CF}_3\text{SO}_3$, $\text{LiClO}_4$, $\text{NaI}$, $\text{LiNO}_3$, etc in suitable solvents. Most commonly, they are prepared by the solution casting technique in which the solution of polar polymers and ionic salts are mixed, thoroughly stirred and cast onto glass or petri dishes. The solution are slowly evaporated and followed by further drying to form solvent free film. Due to the absence of solvent in such system, the polymers themselves act like a solvating agent. Therefore, complexations occur by the interaction of salt cation with polar polymer having sufficient donor ability. The lower values of the parameters namely lattice energy and cohesive energy of the polymer can facilitate the formation of stable polymer salt complex (Armand, 1990; Croce et al., 1993).

Bhattacharya and co-workers (2009) reported the comparative study on solid polymer electrolyte and solar cell properties of the PEO based polymer electrolytes with different cation iodide salts namely $\text{Li}^+$, $\text{Na}^+$, $\text{K}^+$, $\text{NH}_4^+$, $\text{EMI}^+$, and $\text{HMI}^+$ with wide variation in their ionic radii. They reported that the ionic conductivity of the PEO:PEG blend solid polymer electrolyte increase as the size of the salt cation increases. They indicated that the change in conductivity was found due to the change in crystallinity (Bhattacharya et al., 2009). Table 2.5 shows some of the previously studied solid polymer electrolytes.
Table 2.5: Some solid polymer electrolytes reported in the literature

<table>
<thead>
<tr>
<th>Solid polymer electrolyte system</th>
<th>Conductivity, $\sigma$ (S cm$^{-1}$)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO/NaI:I$_2$ + EMImTFO</td>
<td>$4.72 \times 10^{-5}$</td>
<td>Singh et al., 2009</td>
</tr>
<tr>
<td>MG49/PMMA + LiBF$_4$</td>
<td>$8.6 \times 10^{-6}$</td>
<td>Su’ait et al., 2011</td>
</tr>
<tr>
<td>PEO/PVP + NaCl</td>
<td>$1.66 \times 10^{-7}$</td>
<td>Kumar et al., 2012</td>
</tr>
<tr>
<td>PVC/NH$_4$CF$_3$SO$_3$ + BATS</td>
<td>$1.56 \times 10^{-4}$</td>
<td>Deraman et al., 2013</td>
</tr>
<tr>
<td>PVDF-HFP/PEMA/NH$_4$CF$_3$SO$_3$ + TiO$_2$</td>
<td>$1.32 \times 10^{-3}$</td>
<td>Rudhzhia et al., 2013</td>
</tr>
<tr>
<td>PVP + KI</td>
<td>$4.69 \times 10^{-5}$</td>
<td>Singh et al., 2013</td>
</tr>
<tr>
<td>PEMA/Li CF$_3$SO$_3$ + BmimTfO</td>
<td>$1.17 \times 10^{-4}$</td>
<td>Ramesh et al., 2014</td>
</tr>
<tr>
<td>PEO/PVP + LiClO$_4$</td>
<td>$0.23 \times 10^{-5}$</td>
<td>Kesavan et al., 2014</td>
</tr>
<tr>
<td>PVDF/PMMA + EC-TBAI</td>
<td>$5.10 \times 10^{-3}$</td>
<td>Theerthagiri et al., 2015</td>
</tr>
</tbody>
</table>

Even though many studies on polymer electrolytes have been done, most of the studies reported in the literature used petrochemical based polymers, which are associated to the environmental issues and high cost. In order to reduce the dependence of petrochemical based polymer for electrolytes, bio based polymers are applied as hosts.

2.10 Biopolymer

Nowadays, the bio based polymers from polysaccharides are attracted much attention in research due to the increasing demand for environment protection, as well as rising costs and supply of fossil fuels. It is predicted that biopolymers, as one of primary importance resources of renewable energy, will provide the major raw material
for the progress of industry in the future. There are several renewable resource-based biopolymers suitable to be used as host polymers in the polymer electrolytes. These include starch, cellulose, carrageenan, chitosan and others.

2.10.1 *k*-carrageenan

Natural polymer of carrageenan has attracted a lot of interests since they are abundant in nature, renewable, biodegradable, non-toxic and cost effective. Carrageenan is an anionic polymer which is extracted from certain red algae and consists of linear-sulfated polysaccharides of D-galactose and 3, 6-anhydro-D-galactose (Tranquilan-Aranilla et al., 2012; Fan et al., 2011). Three types of carrageenan with different position and number of ester sulfate group are kappa-carrageenan (*k*-carrageenan), iota-carrageenan (*i*-carrageenan) and lambda-carrageenan (*λ*-carrageenan). All carrageenan are soluble in water and insoluble in organic solvents. *k*-carrageenan is the most generally known and commercially explored members of this polysaccharide family. It has one negative charge per disaccharide unit and is a good film forming materials (Sánchez-García et al., 2010; Zarina & Ahmad, 2014). Figure 2.4 presents the chemical structure of *k*-carrageenan.

![Figure 2.4: Structure of *k*-carrageenan](image)
2.10.2 Cellulose

Cellulose is a linear and high molecular weight polymer that can be described the most abundant renewable and biodegradable polymer (Heydarzadeh et al., 2009; Mohkami & Talaeipour, 2011). Due to hydrogen bonds that are associated with the structure of the molecular cellulose, it neither melts nor dissolves readily in common solvents (Adinugraha & Marseno, 2005). In general, cellulose is made up of glucose rings connected by –C(1)–O–C(4) ether bonds, known as β-1,4 glycosidic linkages, with extensive intramolecular hydrogen (Biswal & Singh, 2004) as shown in Figure 2.5. Cellulose can be extracted from a variety of sources such as woods, annual plants, microbes and animals (Mohkami & Talaeipour, 2011).

![Figure 2.5: Structure of cellulose](image)

In this study, cellulose was extracted from kenaf (Hibiscus cannabinus) which is a plant that belongs to the Malvaceae family. It has grown commercially in many places, including Malaysia. Kenaf is divided into two parts, which are the bast and the core. Generally, fibers are derived from the bast because it has attractive mechanical properties. Kenaf fiber is derived from the outer fibrous bark, the bast, contains about 30% to 63% cellulose (Bismarck et al., 2005; Kargarzadeh et al., 2012; Rowell & Stout, 1998). The high percentage of cellulose makes kenaf suitable for cellulose extraction.
2.10.3 Carboxymethylation of $k$-carrageenan and cellulose

Chemical modification or introduction of new functional group to polysaccharides is considered as one of the most important method to enhance the properties of these biopolymers. Recently, many researches are geared towards functionalization of known materials and carboxymethylation of polysaccharides is one of the widely studied conversions that lead to development of new biomaterials with very promising properties. The carboxymethylation of pristine polymers employed Williamsons’s ether synthesis process, a consecutive two-step reaction (Lawal et al., 2007; Leong et al., 2011). Chemical modification of pristine polymers include the reaction proceeds with a strong base such as sodium hydroxide (NaOH) that deprotonates the hydroxyl groups in pristine polymer to form alkoxides, thereby increasing their nucleophilicity. The carboxymethyl groups are then formed in a reaction between the pristine polymer alkoxides and monochloroacetic acid. Figure 2.6 depicts an example of overall reaction of carboxymethylation process on pristine polymer such as $k$-carrageenan.
Figure 2.6: Overall reaction of carboxymethylation process on $k$-carrageenan (Mobarak et al., 2012)
Other than carrageenan, carboxymethylation process has been used for modification of cellulose (Mohkami & Talaeipour, 2011), starch (Ragheb et al., 1997), chitosan (Abreu & Campana-Filho, 2005; de Abreu & Campana-Filho, 2009; Mobarak et al., 2013), guar gum (Dodi et al., 2011) and gellan (Miyamoto et al., 1996) as starting materials.

Fan and friends (2011) synthesized and characterized carboxymethyl derivatives of $k$-carrageenan, in order to develop a wound healing material possessing anticoagulant activity, antimicrobial activity and moisture absorbability and moisture retention capacity by the reaction of $k$-carrageenan with monochloroacetic acid. They reported that the CMKC exhibited good antimicrobial properties against Escherichia coli and Staphylococcus aureus, and the antibacterial activity of CMKC enhanced as the DS increased. CMKC displayed better moisture absorption and water retention ability than $k$-carrageenan and as the DS increased. This result indicated that the properties of CMKC increased when chemical modification on $k$-carrageenan was done.

Meanwhile, Mohkami & Talaeipour (2011) investigated the chemical structure of carboxymethylated fiber from waste paper and evaluated the prepared material by FTIR and XRD analysis. They found that the carboxymethyl functional groups had increased in the carboxymethylated fiber as shown by the FTIR results. Besides that, the crystallinity of cellulose had decreased in the carboxymethylated fiber as indicated by the XRD result in Figure 2.7. This was due to the cleavage of the hydrogen bonds in the crystalline part of cellulose chain during alkali treatment with NaOH.
Figure 2.7: Difractograms of samples (a) cellulose and (b) cellulose treated by % 46 monochloroacetic acid, % 25 NaOH with neutral pH (Mohkami & Talaepour, 2011)
Furthermore, Mobarak et al. (2012) found that the percentage of oxygen content in CMCK increased as compared to oxygen content in the pristine $k$-carrageenan which means that the large number of monochloroacetic acid moiety was reacted with the $k$-carrageenan. They obtained the degree of substitution of carboxymethyl $k$-carrageenan of 1.76. This new $k$-carrageenan derivatives have been substituted with more oxygen atoms thus it provided more vacancy for cation to coordinate. The increase in amount of oxygens also enhanced conductivity of $k$-carrageenan derivatives as the oxygen atoms carried lone pairs of electron that coordinated with the cations of the doping salt (Noor et al., 2010).

Recently, due to the good biodegradable, CMKC and CMCE are attracted more attention as representative water soluble polysaccharide in many researches fields (Liuyun et al., 2009; Mishra et al., 2010; Tranquilan-Aranilla et al., 2012). They contain a hydrophobic polysaccharide backbone and many hydrophilic carboxyl groups, and hence show amphiphilic characteristics. Besides that, they can form cross-linking networks with other components in polymer electrolytes because of their rich hydroxyl group in their molecule structure (Yang et al., 2011). Polymers that show extensive hydrogen bonding appear to be more conductive than those having few hydrogen bonds (Finkenstadt, 2005). The structure of CMKC and CMCE are shown in Figure 2.8 and Figure 2.9 respectively.

![Figure 2.8: Structure of CMKC](image-url)
Since, CMKC and CMCE are semicrystalline and contain many oxygen atoms in their structure, they are expected to produce electrolytes with high conductivity and good morphology and subsequently show good photoelectrochemical performance once applied in DSSC.

### 2.11 Doping salt

The incorporation of salts into polymer hosts makes the polymers conductive. The salt with low lattice energy should be taken into consideration (Bamford et al., 2001; Scrosati, 1993). According to the lattice energy, $U$ in principal, is proportional to the reciprocal of the ionic radius,

$$U = \frac{N_o A_o e^2 Z^2}{a_o} \left(1 - \frac{1}{n}\right) \quad (2.7)$$

where $N_o$ is the Avogadro number, $A_o$ is the Madelung constant, $e$ is the electronic charge, $Z$ is the highest common factor of the ionic charges, $a_o$ is the equilibrium
distance and \( n \) is the repulsion exponent. Since \( a_o \) is given as \( r_+ + r_o \), where \( r_+ \) is the ionic radius of cation and \( r_o \) is the ionic radius of the anion, an atom with larger cation would have larger equilibrium position and so lower lattice energy (Dey et al., 2011). Lower lattice energy helps the salts to dissociate in polymer because a lower energy is required to break the ionic bond between the cation and anion leading to higher charge carrier concentration and improvement of conductivity (Bamford et al., 2001; Scrosati, 1993). The conductive properties have led polymer electrolytes to be intensively studied for potential application in electrochemical devices such as lithium batteries (Sun et al., 2014; Wong et al., 2014), proton batteries (Deraman et al., 2013; Rudhziah et al., 2011; Shukur et al., 2013) and DSSCs (Dzulkurnain et al., 2015; Khanmirzaei & Ramesh, 2014; Seo et al., 2012).

From the perspective of the electrochemical device application of the solid polymer electrolytes such as in DSSCs, the used of iodide salts as doping salt and redox mediator have been reported. It is well known that the iodide salts play important role in the ionic conductivity for polymer electrolytes and DSSCs performance. Moreover, the electrolytes based iodide/iodine have been the most efficient and commonly used as redox mediators due to the fact that \( \Gamma^- \) allows for a fast regeneration of the oxidized dye whereas the reduction of \( \text{I}_2 \) and \( \text{I}_3^- \) for a high carrier collection efficiencies (Wang et al., 2012; Wu et al., 2007).

There has been great interest on polymer host doped with LiI, NaI, for NH\(_4\)I, KI for DSSCs application (Bella et al., 2014; Bhattacharya et al., 2009; Khanmirzaei & Ramesh, 2014; Singh et al., 2013; Singh et al., 2014). However, the role of the cation size of salt (in view of their ionic radii) in governing ionic conductivity in polymer electrolyte and DSSCs performance is still poorly understood. Therefore, in the present
work, different cation iodide salts, the cation being, \( \text{Li}^+ \), \( \text{Na}^+ \), \( \text{NH}_4^+ \) and \( \text{DNH}_4^+ \), with wide variation in their ionic radii were used as doping salt. The \( \text{Li}^+ \) was chosen as the smallest ion and the \( \text{DNH}_4^+ \) as the largest ion. Some characteristics of the iodide salts are tabulated in Table 2.6.

### Table 2.6: Some characteristics of iodide salts used in this study

<table>
<thead>
<tr>
<th>Iodide Salt</th>
<th>Structure</th>
<th>Cation radius (in Å)</th>
<th>Solubility</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiI</td>
<td>( \text{Li}^+ \text{I}^- )</td>
<td>0.76</td>
<td>soluble in ethanol, propanol, ethanediol, ammonia</td>
<td>Bhattacharya et al., 2009</td>
</tr>
<tr>
<td>NaI</td>
<td>( \text{Na}^+ \text{I}^- )</td>
<td>1.02</td>
<td>Water, Acetone, Ethanol</td>
<td>Bhattacharya et al., 2009</td>
</tr>
<tr>
<td>NH\textsubscript{4}I</td>
<td>( \text{N}^+\text{H}\text{H}\text{H}\text{I}^- )</td>
<td>1.5</td>
<td>water, alcohol, glycerol, methanol</td>
<td>Bhattacharya et al., 2009</td>
</tr>
<tr>
<td>DNH\textsubscript{4}I molten salts</td>
<td>( \text{CH}_3\text{CH}_3\text{H}_3\text{CSN}^+\text{I}^- )</td>
<td>Bulkym and asymmetric organic cation</td>
<td>water, alcohol, glycerol, methanol</td>
<td>Bechara, 2012</td>
</tr>
</tbody>
</table>

#### 2.12 Biopolymer electrolytes

In order to develop environmentally friendly polymer electrolytes, biodegradable polymer has been widely investigated as alternative to conventional nondegradable or incompletely degrading synthetic biopolymers. Recently, the development of polymer
electrolytes based on biodegradable polymers such as starch (Kumar et al., 2012; Sudhakar & Selvakumar, 2012; Tiwari et al., 2014; Tiwari et al., 2011), cellulose (Samsudin & Isa, 2014), agar (Nwanya et al., 2015; Wang et al., 2011) and carrageenan (Jumaah et al., 2014; Mobarak et al., 2012) have been impressively recommended.

Samsudin and co-workers (2012) has developed new biopolymer electrolytes based on CMCE by incorporating dodecyltrimethyl ammonium bromide, DTAB via solution casting technique. The polymer–salt complex has been analyzed using FTIR spectroscopy, XRD analysis, impedance measurement and TNM measurement. They reported that the CMCE containing 35 wt % DTAB exhibited the highest conductivity at room temperature of $7.72 \times 10^{-4}$ S cm$^{-1}$. They also reported that temperature dependence of all the biopolymer electrolytes system exhibited Arrhenius behavior. They found that the conductivity of the samples is depends on the number of mobile ions and the mobility of the ions.

Similar observation has been reported by Khanmirzai and Ramesh (2014). They prepared biodegradable polymer electrolytes by incorporating lithium iodide salt into rice starch. They found that the RS-7 sample with 35 % wt of LiI salt with the highest ionic conductivity has the lowest glass transition temperature. The results revealed that the addition of LiI salt resulted in an increase mobility of charge carriers, ionic conductivity, amorphous behaviour and a decrease in glass transition temperature due to increased flexibility of polymeric chains. Some solid biopolymer based electrolytes reported in literature are listed in Table 2.7.
Table 2.7: Ionic conductivities of some solid biopolymer electrolytes

<table>
<thead>
<tr>
<th>Solid biopolymer electrolyte system</th>
<th>Conductivity, $\sigma$ (S cm$^{-1}$)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chitosan acetate + Adipic acid</td>
<td>$1.40 \times 10^{-9}$</td>
<td>Idris et al., 2009</td>
</tr>
<tr>
<td>Chitosan + NH$_4$Cl</td>
<td>$3.3 \times 10^{-5}$</td>
<td>Du et al., 2010</td>
</tr>
<tr>
<td>Potato starch + NH$_4$I</td>
<td>$2.40 \times 10^{-4}$</td>
<td>Kumar et al., 2012</td>
</tr>
<tr>
<td>Cellulose acetate + NH$_4$BF$_4$</td>
<td>$2.18 \times 10^{-7}$</td>
<td>Harun et al., 2012</td>
</tr>
<tr>
<td>CMCE + DTAB</td>
<td>$7.72 \times 10^{-4}$</td>
<td>Samsudin et al., 2012</td>
</tr>
<tr>
<td>HPMC + NaI</td>
<td>$1.13 \times 10^{-6}$</td>
<td>Rani et al., 2014</td>
</tr>
<tr>
<td>RS + LiI</td>
<td>$4.68 \times 10^{-5}$</td>
<td>Khanmirzaei &amp; Ramesh, 2014</td>
</tr>
<tr>
<td>Arrowroot + KI</td>
<td>$1.04 \times 10^{-4}$</td>
<td>Singh et al., 2014</td>
</tr>
<tr>
<td>Arrowroot starch + NaI</td>
<td>$6.70 \times 10^{-4}$</td>
<td>Tiwari et al., 2014</td>
</tr>
<tr>
<td>Corn starch + LiOAc</td>
<td>$2.07 \times 10^{-5}$</td>
<td>Shukur et al., 2014</td>
</tr>
<tr>
<td>Chitosan + LiTFSI</td>
<td>$5.86 \times 10^{-4}$</td>
<td>Taib &amp; Idris, 2014</td>
</tr>
<tr>
<td>CMCE + NH$_4$F</td>
<td>$2.68 \times 10^{-7}$</td>
<td>Ramlli et al., 2015</td>
</tr>
</tbody>
</table>

2.13 Biopolymer blend electrolytes

In order to enhance the properties of single biopolymer based electrolytes such as conductivity and mechanical properties, polymer blending is used. Blending of a polymer is an economical technique to develop new polymeric materials with properties that are superior compared to the individual component polymer (Lee & Park, 2001). The properties of materials produced by this technique depend on the properties of the
component polymers, their composition and mainly on the degree of miscibility of the polymers (da Silva Neiro et al., 2000).

The miscibility of blends and their morphology have significant impact on the ionic conductivity of the polymer blend electrolytes. In fact, miscible blends present only one phase, that is, no phase separation and there are often specific interactions between groups or polymer segments. The miscibility of the polymer blend is an important factor for obtaining desired properties. There are several factors which contribute to the miscibility of polymer blends. These include polarity, specific group attraction, molecular weight, blend ratio and crystallinity of polymer (Deanin & Manion, 1999). The miscibility of polymer blend can also be described using specific interaction like hydrogen bonding, dipole-dipole interaction, ionic interaction metal coordination and other strong interactions between the electron donor and electron acceptor. The experimental methods that can be used to study the miscibility of polymer blends are DSC, DMA, SEM and FTIR.

Wu et al., (2012) have studied structural characterization and properties of konjac glucomannan (KGM)/curdlan blend films. They prepared a series of novel edible blend films of KGM and curdlan by solvent-casting technique with different blending ratios of the two polymers. They used FTIR, XRD, DSC, SEM, etc. to characterize the change of structure and properties of the blend films. The results showed that strong intermolecular hydrogen bonds took place between KGM and curdlan and the interaction of the blend film was much greater than that of the others when the KGM content in the blend films was around 70 wt % (KC7), resulting in excellent miscibility (Wu et al., 2012).
Another group of authors who reported on the miscibility study of polymer blend is Wang and coworkers (2014). These authors studied interactions between carboxymethyl konjac glucomannan (CMKGM) and soy protein isolate in blended film. They used $T_g$ to determine the compatibility and miscibility of the blending polymer using DSC analysis. The DSC analysis showed that all the blends have an endothermic peak from 0 to 250 °C. The results indicated that the CMKGM and SPI have good compatibility/miscibility. They also reported that the CMKGM/SPI blend films possessed enhanced tensile strength and elongation at break as compared to pure CMKGM and SPI films (Wang et al., 2014).

For polymer blend based electrolytes, addition of salt can influence the miscibility of the polymer blend via the formation of multi polymer or cation coordination (Wang, 2007). Rocco et al. (2001) initially studied the miscibility of polymer electrolyte based on blend of polyethylene oxide (PEO)/poly(methyl vinyl ether-maleic acid (PMVE-Mac). The DSC result showed a single $T_g$ in all compositions of PEO/PMVE-Mac blend. They also reported that the presence of PMVE-MAc in the blends hindered the crystallization of PEO, thus decreasing the calculated degree of crystallinity and size of the PEO spherullites and depressing the melting point of the system. The results clearly showed that PEO/PMVE-MAc blends are miscible due to intramolecular hydrogen bonds. They then further their investigation on the PEO/PMVE-Mac blend based electrolytes. They doped PEO/PMVE-Mac blend with LiClO$_4$. They found only one $T_g$ for all blend compositions after the addition of LiClO$_4$. This indicated that the miscibility of the blend components in all salt composition.

Biopolymer electrolytes developed using polymer blends have also been reported to exhibit good conductive and mechanical properties (Buraidah & Arof, 2011;
El-Hefian et al., 2011). Buraidah and Arof (2011) reported that the conductivity of $3.73 \times 10^{-7} \text{ S cm}^{-1}$ for the system containing 55 wt % chitosan-45 wt % NH$_4$I increased to $1.77 \times 10^{-6} \text{ S cm}^{-1}$ upon blending with 27.5 wt % of PVA. This result was attributed to the additional complexation sites and amorphous nature of PVA. El-Hefian and friends (2011) investigated mechanical, thermal and surface properties of chitosan/PVA blend film. They found that blending chitosan with PVA improved the tensile strength up to 40% PVA content. Some of the reported biopolymer blend based electrolytes are listed in Table 2.8.

**Table 2.8: Ionic conductivities of some biopolymer blend electrolytes**

<table>
<thead>
<tr>
<th>Biopolymer blend electrolyte system</th>
<th>Conductivity, $\sigma$ (S cm$^{-1}$)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chitosan/I–carrageenan + H$_3$PO$_4$ + PEG</td>
<td>$6.29 \times 10^{-4}$</td>
<td>Arof et al., 2010</td>
</tr>
<tr>
<td>PVA/chitosan + NH$_4$I</td>
<td>$1.77 \times 10^{-6}$</td>
<td>Buraidah &amp; Arof, 2011</td>
</tr>
<tr>
<td>Starch/chitosan + NH$_4$NO$_3$</td>
<td>$3.89 \times 10^{-5}$</td>
<td>Khiar &amp; Arof, 2011</td>
</tr>
<tr>
<td>Starch/chitosan + LiClO$_4$</td>
<td>$1.20 \times 10^{-7}$</td>
<td>Sudhakar &amp; Selvakumar, 2012</td>
</tr>
<tr>
<td>Chitosan/PEG + LiClO$_4$</td>
<td>$1.1 \times 10^{-4}$</td>
<td>Sudhakar et al., 2013</td>
</tr>
<tr>
<td>Starch/chitosan + NH$_4$Cl</td>
<td>$6.47 \times 10^{-7}$</td>
<td>Shukur et al., 2014</td>
</tr>
<tr>
<td>Starch/chitosan + NH$_4$I</td>
<td>$3.04 \times 10^{-4}$</td>
<td>Yusof et al., 2014</td>
</tr>
<tr>
<td>CMCE/chitosan + DTAB</td>
<td>$1.85 \times 10^{-6}$</td>
<td>Bakar &amp; Isa, 2014</td>
</tr>
<tr>
<td>CMCE/chitosan + NH$_4$NO$_3$</td>
<td>$1.03 \times 10^{-5}$</td>
<td>Kamarudin et al., 2015</td>
</tr>
<tr>
<td>Starch/chitosan + LiCF$_3$SO$_3$</td>
<td>$7.11 \times 10^{-7}$</td>
<td>Navaratnam et al., 2015</td>
</tr>
</tbody>
</table>
2.14 CMKC and CMCE blend based electrolytes

Blending of polymers has been considered in order to enhance the conductivity as well as to improve mechanical strength and thermal stability of biopolymer electrolytes. Blending can be useful because of the ease of preparation and control of the properties of polymer electrolytes. Polymer blends often exhibit properties that are superior compared to the individual component polymers (Lee & Park, 2001). In this study, biopolymer blend electrolytes based on CMKC has been investigated. A second polymer, CMCE was blended with CMKC to improve conductivity and mechanical stability.

Bakar and Isa (2014) studied solid biopolymer electrolyte systems based on CMCE/chitosan–DTAB. They found that the increment of composition of DTAB can influence the conductivity of the systems. The maximum ionic conductivity value of $1.86 \times 10^{-6}$ S cm$^{-1}$ has been obtained from the systems containing 5 wt % of DTAB. Similar result has been reported by Kamarudin et al. (2015). This group of researchers reported that the ionic conductivity of CMCE/chitosan was influenced by the addition of ammonium NH$_4$NO$_3$ concentration. The maximum ionic conductivity was achieved at 40 wt % NH$_4$NO$_3$ of $1.03 \times 10^{-3}$ Scm$^{-1}$. The ionic conductivity also was affected by temperature and obeyed the Arrhenius law.

To the best of the author’s knowledge, studies on CMKC/CMCE blend for use as host in polymer electrolytes have never been reported in the literature. It is therefore very interesting to investigate the properties of the CMKC/CMCE electrolytes and their performance as electrolyte in DSSCs. The modified cellulose and carrageenan synthesized in this work are expected to show a good conducting property due to the
higher in oxygen number and weaker in hydrogen bonding in their structure leading to greater amorphicity.

2.15 Summary

In this chapter, an overview of DSSC such as its background and its operating mechanism as well as the function of all its components has been presented. Some general properties of materials used such as $k$-carrageenan, cellulose, CMKC, CMCE and doping salts have also been described. This chapter also includes some previous studies on biopolymer blend electrolytes.
CHAPTER 3: EXPERIMENTAL METHOD

3.1 Introduction

This chapter describes the method of sample preparation and characterization. In this work, electrolytes based on the blend of modified natural polymer (host polymers) namely, carboxymethyl k-carrageenan and carboxymethyl cellulose were successfully developed for potential used in solid state DSSCs. For preliminary study, the CMKC and CMCE were synthesized from k-carrageenan and cellulose. The cellulose was initially extracted from kenaf fiber. Next, CMKC/CMCE blend films were prepared followed by doping iodide salt to optimum blend ratio. Four electrolyte systems, CMKC/CMCE-LiI and CMKC/CMCE-NaI, CMKC/CMCE-NH$_4$I and CMKC/CMCE-DNH$_4$I were prepared. All the biopolymer electrolytes that have been prepared are using solution casting method. The investigation of the electrolytes were done using FTIR, DMA, EIS, TNM and LSV in order to study the interaction between polymer and salt, thermal, electrical and electrochemical characteristics of CMKC/CMCE blend electrolyte films. Then, selected CMKC/CMCE blend based electrolytes were used to fabricate DSSC. Figure 3.1 shows the flow chart that explain all the work carried out in this thesis.
Figure 3.1: Flow chart of experimental work
3.2 Materials

*k*-carrageenan was supplied by Takarra Sdn. Bhd., Sabah, Malaysia. Meanwhile, kenaf fibers were obtained from KFI Sdn. Bhd., Kelantan, Malaysia. Sulfuric acid (98%), NaOH (99%), sodium chlorite (80%), acetic acid (99.5%), distilled water (1–0.1 \( \mu \text{S} \cdot \text{cm}^{-1} \)), isopropanol, ethanol, monochloroacetic acid, LiI, NaI, NH\(_4\)I, DNH\(_4\)I, iodine (I\(_2\)), N719 and platinum (Pt) were purchased from SYSTERM-chemAR and Sigma-Aldrich (St. Louis, MO, USA). Meanwhile, the TiO\(_2\) paste DSL 18 NR-AO was supplied from Dyesol (New South Wales, Australia). All materials were used as received.

3.3 Sample preparation

3.3.1 Extraction of cellulose from kenaf fiber

In this work, cellulose was extracted from kenaf fiber (Figure 3.2 (a)) by the following steps. The kenaf fiber was cut into small pieces, and then treated by an alkali treatment and bleaching process to remove the remaining hemicellulose, lignin as well as other impurities. For an alkali treatment, the small pieces of kenaf fiber was first treated with 4 wt % NaOH solution in a round bottom flask under mechanical stirring at 80 °C for 3 hours. The process was repeated three times and refluxing was conducted throughout the process. The solution was then filtered three times using distilled water. Following alkali treatment, the bleaching process was performed by adding aqueous chlorite (1.7 w/v %), acetic buffer solution (5 < pH < 6) and distilled water at reflux for 4 hour. The mixture was allowed to cool and filtered using distilled water. The process was repeated twice.
3.3.2 Preparation of k-carrageenan and cellulose derivatives

CMKC and CMCE were synthesized according to the method proposed by Sun et al., (2008). 5 g of k-carrageenan (Figure 3.2 (b)) (or 50 g of cellulose from kenaf fiber, sodium hydroxide, isopropanol and water were mixed together and alkalinized at 50 °C for 1 hour. Monochloroacetic acid dissolved in isopropanol was later added to the mixture. This solution mixture was then stirred for 4 hours at 50 °C and then terminated by adding ethanol. The solid was filtered and rinsed with 70 %, 80 % and 90 % ethanol solution and then vacuum dried at room temperature to form powder. The degree of substitution (DS) of the carboxymethyl for each sample was estimated using potentiometric titration (Fan et al., 2011).

Figure 3.2: Photo of (a) kenaf fiber and (b) k-carrageenan
3.3.3 *CMKC/CMCE blend film preparation*

Polymer blend films in this study were prepared by solution casting method. For the preparation of CMKC/CMCE blend with wt % ratio of 50:50, 0.5 g of CMKC powder was dissolved in 50 ml of 1 % acetic acid at 40 °C. After 2 hours, 0.5 g of CMCE was added and stirred for a few hours to form homogenous solution. The solution was then poured into Petri dishes and allowed to dry at room temperature for 2 weeks to obtain free standing films. The free standing films obtained were kept in a desiccator for further drying. The procedure was repeated to obtain other blends with CMKC:CMCE ratios of 60:40, 70:30, 80:20 and 90:10. The weight percentage of CMCE added to CMKC was calculated using the following equation:

$$\text{wt}_{\text{CMCE}}\% = \frac{\text{wt}_{\text{CMCE}}}{\text{wt}_{\text{CMKC}} + \text{wt}_{\text{CMCE}}} \times 100\%$$  \hspace{1cm} (3.1)

where $w_{t\text{CMKC}}$ and $w_{t\text{CMCE}}$ are the weights of CMKC and CMCE respectively. The compositions of the samples and their designations are listed in Table 3.1.

**Table 3.1: The designation of the CMKC:CMCE (wt/wt%) blend samples**

<table>
<thead>
<tr>
<th>CMKC: CMCE blend</th>
<th>Sample designation</th>
</tr>
</thead>
<tbody>
<tr>
<td>100:0</td>
<td>B0</td>
</tr>
<tr>
<td>90:10</td>
<td>B1</td>
</tr>
<tr>
<td>80:20</td>
<td>B2</td>
</tr>
<tr>
<td>70:30</td>
<td>B3</td>
</tr>
<tr>
<td>60:40</td>
<td>B4</td>
</tr>
<tr>
<td>50:50</td>
<td>B5</td>
</tr>
</tbody>
</table>
3.3.4 CMKC/CMCE blend electrolytes film

The biopolymer blend based on CMKC/CMCE electrolyte films were prepared by adding different weight percentages of iodide-salt (10 wt % - 50 wt %) to solutions containing 1 g of CMKC/CMCE of optimum mass ratio. 50 ml of 1 % of acetic acid was used as the solvent. The weight percentage of salt was calculated using the equation:

\[
wt_{salt} \% = \frac{wt_{salt}}{wt_{CMKC} + wt_{CMCE}} \times 100 \%
\]  

(3.2)

where \( wt_{salt} \), \( wt_{CMKC} \), and \( wt_{CMCE} \) are the weights of salt, CMKC and CMCE respectively. The solutions were stirred at room temperature for a few hours and poured into Petri dishes and left to evaporate slowly to form films. The prepared films with thickness between 0.20 to 0.30 mm were then kept in a vacuum desiccator to ensure that the films were completely dried before measurement. The block diagram of the preparation of the electrolytes is shown in the Figure 3.3.
Figure 3.3: Flow chart for the preparation of biopolymer electrolytes based on CMKC/CMCE blend
3.4 Characterization of samples

In this study, the potential of \(k\)-carrageenan and kenaf-cellulose derivatives as biopolymer electrolyte was explored. CMCE and CMCE powder which were synthesized have been characterized using FTIR, X-ray diffraction (XRD) and elemental analysis. Furthermore, in order to identify the best blend ratio for potential use as host in polymer electrolytes, the investigation was done using FTIR, tensile measurement, SEM, DMA, EIS and LSV to obtain information of their structural, mechanical, viscoelastic and electrical properties.

Meanwhile, the investigation of the CMKC/CMCE biopolymer blend electrolytes were done using FTIR, DMA, EIS, TNM and LSV in order to study the interaction between polymer and salt, thermal, electrical and electrochemical characteristics of CMKC/CMCE blend electrolyte films. The selected electrolytes for each system were used to fabricate DSSCs in order to investigate the electrochemical performance of the electrolytes in DSSC.

3.4.1 Fourier transform infrared spectroscopy

FTIR spectroscopy was performed using PerkinElmer Frontier spectrophotometer. The spectrophotometer was equipped with an Attenuated Total Reflection accessory with a germanium crystal. The studied sample was put on the germanium crystal and infrared light was passed through the sample in the frequency range from 550 to 4000 cm\(^{-1}\) with spectra resolution of 1 cm\(^{-1}\). The FTIR data were recorded in the transmittance mode. This analysis was conducted to observe the changes of the functional group before and after modification of \(k\)-carrageenan and kenaf-
cellulose. This FTIR method can also be used to investigate the interactions among various constituents in the polymer blend system and polymer electrolyte systems.

### 3.4.2 Scanning electron microscopy and energy dispersive X-ray spectroscopy

Scanning electron microscopy is an instrument which can be used for examining the morphology of the sample. In this study, SEM technique is used in order to examine the surface morphology change of natural polymers when the functional group was modified. SEM technique is also used to study the morphology changes of CMKC blended with CMCE.

In this work, the ZEISS EVO MA10 scanning electron microscope with an accelerating voltage of 10 kV was used to examine the cross sectional morphology of the CMKC:CMCE films. The blend films were sputter-coated with a thin gold layer before measurement. Meanwhile, elemental analysis of $k$-carrageenan, cellulose and derivatives were examined with the energy dispersive X-ray using Oxford Aztec X-Act EDX spectrometer.

### 3.4.3 X-ray diffraction

X-ray diffraction is a versatile, non-destructive technique that can be used to study the crystalline nature of materials. Crystalline materials are characterized by sharp and distinct peaks while amorphous materials show broad peaks commonly known as amorphous humps.
In this study, X-ray diffraction was performed to study the crystalline nature of \( k \)-carrageenan, cellulose and its derivatives. The XRD spectra of the polymer electrolyte films studied in this work were recorded using a PANalytical in the \( 2\theta \) range from 5° to 60°. The films were scanned with a beam of monochromatic Cu-K\( \alpha \)-X radiation of wavelength 1.5406 Å.

### 3.4.4 Dynamic mechanical analysis

Dynamic mechanical analysis is a useful technique to investigate the viscoelastic or thermal behaviour of polymers. In this study, the viscoelastic properties of CMKC/CMCE blend and CMKC/CMCE electrolyte films were determined using Perkin Elmer DMA 8000 in tension mode. Rectangular strip specimens (width 10 mm, length 20 mm, thickness between 0.20 mm and 0.30 mm) were used. The dual cantilever mode of deformation was used at the test temperatures ranging from -40 °C to 100 °C with a heating rate of 2 °C min\(^{-1}\) at the frequency of 1 Hz under liquid nitrogen flow. Glass transition temperatures of films were determined from the peak of the tan \( \delta \)-\( T \) curves.

### 3.4.5 Electrochemical impedance spectroscopy

The conducting capability of the sample were studied using a high frequency response analyzer, (Solartron 1260) in the frequency range of 10 Hz – 4 MHz with 10 mV voltage amplitude at room temperature and at various temperatures ranging from 303 K to 333 K. The sample for the measurement was sandwiched between the stainless
steel blocking electrodes with a contact surface area of 3.142 cm$^2$ and placed in a dry chamber. The conductivity of the sample was calculated using equation,

$$\sigma = \frac{l}{R_b A}$$  \hspace{1cm} (3.3)

where $l$ is the thickness of the sample, $A$ is the area of blocking electrode and $R_b$ is the bulk resistance of the material which can be obtained from the intersection of complex impedance plot with the real impedance axis. For each electrolytes system, six samples were used and the average conductivity was determined. Analysis of the impedance experimental data can be carried out by plotting the impedance imaginary part ($Z''$) against the real part ($Z'$) in a graph called impedance plot.

In order to investigate dielectric properties of the polymer blend based electrolytes prepared in this study, the impedance data have been analyzed in other parameter, namely dielectric constants $\varepsilon_r$. The dielectric constant, $\varepsilon_r$ was determined from the equation,

$$\varepsilon = \frac{Z_l}{\omega C_0 (Z_r^2 + Z_i^2)}$$  \hspace{1cm} (3.4)

where $C_0$ is vacuum capacitance.

3.4.6 Transference number and linear sweep voltammetry

The electrochemical stability window and transference number measurement of the CMKC/CMCE blend and electrolytes films were determined using Wonatech Zive
MP2 multichannel electrochemical instrument. For electrochemical stability window measurement, the sample was sandwiched between two stainless steel electrodes and data were recorded at 1 mV s\(^{-1}\) scan rate. The voltage was applied in the range of 0 to 5 V. Meanwhile, ionic transference number was measured by Wagner’s polarization method. In this technique, polymer electrolyte is sandwiched between standard steel. The value of ionic transference number \((t_{\text{ion}})\), was evaluated from the polarization current versus time plot using equation,

\[
I_{\text{ion}} = \frac{I_{\text{initial}} - I_{\text{final}}}{I_{\text{initial}}} \quad (3.5)
\]

\[
t_e = \frac{I_{\text{final}}}{I_{\text{initial}}} \quad (3.6)
\]

where \(t_e\) is electronic transference number, \(I_{\text{initial}}\) is the initial current due to the movement of ions and electrons in the applied electric field whereas \(I_{\text{final}}\) is steady state electron current.

### 3.4.7 Mechanical properties

The tensile strength and elongation at break of the CMKC/CMCE films were tested using INSTRON 3366 universal testing machine. Six rectangular strips (width 5 mm, length 60 mm) were cut from blend films. The samples were clamped with initial grip length of 3 cm and deformed under tensile loading using a 10 N load cell with the cross head speed of 30 mm min\(^{-1}\) until the sample was broken.
3.5 Fabrication and characterization of dye sensitized solar cell

Solid-state dye sensitized solar cell with active area about 1 cm$^2$ was fabricated using selected electrolytes from each systems. In order to prepare the DSSC photoelectrode, the TiO$_2$ paste was spread on FTO conducting glass using doctor blade technique followed by sintering process at 450 °C for 30 min. This electrode was then immersed into the solution of the dye N719 for 24 hours. Meanwhile, the platinum FTO glass counter electrode was prepared by brush painting technique and heating at 450 °C for 30 min. For redox couple formation in DSSC, iodine was added into prepared electrolyte solution. This electrolyte solution was cast onto TiO$_2$/dye photoelectrode and heated at 50 °C to form film. Next, the TiO$_2$/dye photoelectrode with electrolyte film was then assembled with a platinum counter electrode. The schematic diagram for DSSC is depicted in Figure 3.4.

![Figure 3.4: Schematic diagram of DSSC](image-url)
The photocurrent density-voltage characteristics of the solid state DSSC were obtained under white light illumination (100 mW cm\(^{-2}\)) using Wonatech Zive MP2 multichannel electrochemical workstation. The fill factor, \(ff\) was determined using the following equation:

\[
ff = \frac{V_{\text{max}} \times J_{\text{max}}}{V_{\text{oc}} \times J_{\text{sc}}}
\]

(3.7)

where \(J_{\text{sc}}\) is the short-circuit current density (mA cm\(^{-2}\)), \(V_{\text{oc}}\) is the open-circuit voltage (V), and \(J_{\text{max}}\) (mA cm\(^{-2}\)) and \(V_{\text{max}}\) (V) are the current density and voltage in the \(J-V\) curves, respectively at the maximum power output. The external light to energy conversion efficiency, \(\eta\) % was obtained from the following equation:

\[
\eta\% = \frac{V_{\text{oc}} \times J_{\text{sc}} \times ff}{P_{\text{in}}} \times 100\%
\]

(3.8)

where \(P_{\text{in}}\) is the incident light power (W). Figure 3.5 shows the fabricating procedure of FTO-TiO\(_2\)-dye/CMKC/CMCE-electrolytes+I\(_2\)/Pt-FTO and typical cell devices.
Figure 3.5: The fabricating procedure of FTO-TiO₂-dye/CMKC/CMCE-electrolytes+I₂/Pt-FTO
CHAPTER 4: K-CARRAGEENAN AND CELLULOSE DERIVATIVES

4.1 Introduction

In this chapter, the results of the synthesized of CMKC and CMCE are presented and compared with the pristine polymers. This work was undertaken to extent the used of pristine polymers, k-carrageenan and kenaf-cellulose. The chemical modification or introduction of new functional group to pristine polymer is considered as one of the most important methods to enhance the properties of these natural biopolymers and it leads in producing promising properties.

4.2 Characterization of carboxymethyl k-carrageenan and carboxymethyl cellulose powder

4.2.1 Result of FTIR analysis

Figure 4.1 presents the infrared spectra of k-carrageenan and the synthesized CMKC. Figure 4.1 shows the basic k-carrageenan bands at 1237 cm\(^{-1}\) and 841 cm\(^{-1}\) which are assigned respectively to O=S=O symmetric vibration and -O-SO\(_3\) stretching vibration while the band at 1374 cm\(^{-1}\) and 926 cm\(^{-1}\) are attributed to the -CH\(_2\) scissoring and C-O-C of 3,6-anyhydro-D-galactose respectively (Fan et al., 2011; Silva et al., 2010; Tranquilan-Aranilla et al., 2012). The bands at 3385, 2919 and 1033 cm\(^{-1}\) are assigned to O-H stretching, C-H stretching and C-O stretching respectively. After the substitution of carboxymethyl group in the k-carrageenan, obvious changes in FTIR spectrum (Figure 4.1) are observed. New peaks are observed at 1583 and 1410 cm\(^{-1}\) due to COO\(^-\) asymmetrical anion and COO\(^-\) symmetrical stretching of carboxylate group
The appearance of the new peaks confirm that carboxymethylation of \(k\)-carrageenan has been successfully done.

![FTIR spectra of \(k\)-carrageenan and CMKC](image)

**Figure 4.1: FTIR spectra of \(k\)-carrageenan and CMKC**

Shown in Figure 4.2 are FTIR spectra of the synthesized cellulose and CMCE. In comparison to the spectrum of cellulose, the FTIR spectrum of the CMCE has all the characteristic absorbance signals of cellulose (3344 cm\(^{-1}\) (O-H stretching), 2892 cm\(^{-1}\) (C-H stretching), 1407 cm\(^{-1}\) (CH\(_2\) symmetric bending), 1322 cm\(^{-1}\) (C-H bending), 1045 cm\(^{-1}\) (CHO-CH\(_2\) stretching), 894 cm\(^{-1}\) (-CH\(_2\) stretching vibration) and also signature peak at 1586 cm\(^{-1}\) attributed to the COO\(^{-}\) asymmetrical of carboxylate anion (Hebeish et al., 2010; Mohkami & Talaeipour, 2011). The appearance of a new peak at 1586 cm\(^{-1}\) confirms the introduction of the carboxymethyl side chain into the cellulose backbone (dos Santos et al., 2015).
4.2.2 SEM-EDX studies

The modification onto \(k\)-carrageenan and kenaf-cellulose fiber is expected to induce morphological changes. The structure of Figure 4.3 and Figure 4.4 show surface morphology while Table 4.1 illustrates element contents of \(k\)-carrageenan, cellulose, CMKC and CMCE. Table 4.1 also shows the degree of substitution of CMKC and CMCE. Figure 4.3 shows the surface morphology of \(k\)-carrageenan and its derivative. \(k\)-carrageenan exhibits uneven and roughs surface. In contrast, surface morphology for the CMKC is smoother and continuous. Figure 4.4 presents the surface morphology of kenaf-cellulose fiber and its derivative. It is observed that the fibril structure of CMCE
decreased and separated into individual fiber. The surface morphology changes indicate that the modified functional group induced changes on the morphology of the polymers.

Table 4.1 shows that the amount of oxygen content in CMKC and CMCE is higher compared to the pristine k-carrageenan and cellulose. This means that monochloroacetic acid moiety has reacted with the k-carrageenan and cellulose forming CMKC and CMCE. The degree of substitution of CMKC and CMCE were 0.85 and 1.93. This result agrees with that reported by Mobarak et al. (2012). The increase in amount of oxygen is favourable because oxygen atoms carry one pair electrons that can coordinate with cations of doping salt leading to enhanced ionic conductivity (Noor et al., 2010).
Figure 4.3: Cross-sectional SEM images of *k*-carrageenan and CMKC at 100× magnification
Figure 4.4: Cross-sectional SEM images of cellulose and CMCE at 100× magnification
Table 4.1: Elemental data of \( k \)-carrageenan, cellulose and their derivatives

<table>
<thead>
<tr>
<th>Sample</th>
<th>Carbon (%)</th>
<th>Oxygen (%)</th>
<th>Sulphur (%)</th>
<th>DS</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k )-carrageenan</td>
<td>40</td>
<td>47</td>
<td>23</td>
<td>-</td>
</tr>
<tr>
<td>CMKC</td>
<td>33</td>
<td>59</td>
<td>8</td>
<td>0.85</td>
</tr>
<tr>
<td>Cellulose</td>
<td>56</td>
<td>44</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CMCE</td>
<td>46</td>
<td>54</td>
<td>-</td>
<td>1.93</td>
</tr>
</tbody>
</table>

4.2.3 XRD study

The XRD study was carried out in order to determine the nature of the new derivative samples whether amorphous or semi-crystalline. The diffractogram of \( k \)-carrageenan, cellulose and their derivatives are depicted in Figure 4.5 and 4.6. Meanwhile, the crystallinity index \( (X_c) \) of \( k \)-carrageenan, cellulose and their derivatives are listed in Table 4.2. In this study, the \( X_c \) was calculated using the equation as follows:

\[
X_c = \frac{A_c}{A_T} \times 100
\]  

(4.1)

where \( A_c \) is the crystalline area and \( A_T \) is the total area under the diffraction curve between \( 2\theta = 5^\circ - 80^\circ \). The spectra show that the \( k \)-carrageenan and kenaf-cellulose are semicrystalline in nature. The peaks of kenaf-cellulose at \( 2\theta = 15.7^\circ \) and \( 22.9^\circ \) represent the (110) and (002) planes respectively (Kaco et al., 2014; Kargarzadeh et al., 2012; Sosiati & Harsojo, 2014). Upon modifications, their crystalline properties decrease due to the presence of carboxymethyl residue, which hindered the formation of inter- and extra-molecular hydrogen bonds (Ma et al., 2008). Similar result was reported by
Mohkami and Talaeipur (2011). The reduction of crystallinity is much more visible in the case of cellulose. The crystallinity index of the cellulose of 23.9 % decreased when treated with NaOH due to breakage of hydrogen bonds in the crystalline part of cellulose chain. This is due to the cleavage of hydrogen bonding. The crystallinity of the cellulose was associated with inter- and extra-molecular hydrogen bonds of cellulose. In addition, the CMCE is water soluble due to the loss of the crystalline structure in the cellulose granules (Adinugraha & Marseno, 2005).

![Figure 4.5: XRD spectra of κ-carrageenan and CMKC powder](image-url)
Figure 4.6: XRD spectra of kenaf-cellulose and CMCE powder

Table 4.2: Crystallinity index of \(k\)-carrageenan, kenaf-cellulose and their derivatives

<table>
<thead>
<tr>
<th>Sample name</th>
<th>(X_c) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k)-carrageenan</td>
<td>14.6</td>
</tr>
<tr>
<td>CMKC</td>
<td>11.5</td>
</tr>
<tr>
<td>Kenaf-cellulose</td>
<td>23.9</td>
</tr>
<tr>
<td>CMCE</td>
<td>-</td>
</tr>
</tbody>
</table>
4.3 Summary

New derivatives, CMKC and CMCE were successfully synthesized from the initial polymers. FTIR analysis confirmed the introduction of carboxymethyl groups into \( k \)-carrageenan and kenaf-cellulose fiber. The result of XRD analysis showed that the new derivatives have lower crystallinity as compared to the pristine polymers. The morphology of the new derivatives was changed indicating that the modified functional group induced morphological changes. The degree of substitution of CMKC and CMCE was 0.85 and 1.93. The characteristics of CMKC, CMCE, and CMCK/CMCE blend films are investigated in Chapter 5.
CHAPTER 5: STUDIES ON CMKC/CMCE BLEND SYSTEM

5.1 Introduction

In this study, the synthesized CMKC and CMCE were blended in different compositions with the aims to identify the best blend ratio for potential use as host in polymer electrolytes. The properties of the prepared CMKC and CMKC/CMCE blend films were subjected to FTIR, SEM, DMA, EIS, LSV and tensile measurement to obtain information of their structural, viscoelastic, electrical and mechanical properties.

5.2 Characterization of CMKC/CMCE films

5.2.1 FTIR analysis

FTIR analysis was carried out on the CMKC/CMCE blend films to detect peak shifts due to interaction like ionic interaction and hydrogen bonding between the two polymers. The characteristic absorption peaks of ether group, carbonyl group and amine group etc. associated with the interaction in the blend films are expected to be shifted or broadened and their intensity are expected to be depressed or enhanced. Figure 5.1 presents the FTIR spectra of CMKC (B0) and CMKC/CMCE (B1, B2, B3 and B4) films in the spectral region from 800 to 4000 cm\(^{-1}\). For comparison purposes, the spectrum of CMKC film (B0) is also included in the figure. The characteristic bands of hydroxyl stretching (3365 cm\(^{-1}\)), O=S=O symmetric vibration (1228 cm\(^{-1}\)) and C-O-C stretching (926 cm\(^{-1}\)) in the CMKC are the main focus in the detection of ionic interaction (Mobarak et al., 2012). The bands at 3365, 1583, 1228 and 923 cm\(^{-1}\) of the CMKC (Figure 4.1) have undergone of small shift to higher wavenumbers of 3377, 1587, 1230 and 925 cm\(^{-1}\), respectively. The shifts of the CMKC bands are attributed to
interactions between the acetic acid solvent and the oxygen donors of CMKC powder (Kadir et al., 2011). A new peak at 1041 cm\(^{-1}\) in the IR spectrum of CMKC film indicates the presence of H\(^+\) in the samples due to the dissociation of CH\(_3\)COOH (Çelik et al., 2008). By blending CMKC with CMCE, the O-H stretching (3377 cm\(^{-1}\)) of the CMKC (B0) shifted to lower wavenumbers of 3366 cm\(^{-1}\) (B1), 3364 cm\(^{-1}\) (B2), 3361 cm\(^{-1}\) (B3) and 3358 cm\(^{-1}\) (B4). This indicates an increase of intermolecular hydrogen bond between CMKC and CMCE (Wu et al., 2012). Meanwhile, the bands at 1413 cm\(^{-1}\) that corresponds to COO\(^-\) symmetric stretching and asymmetric stretching of CMKC/CMCE are detected at a lower wavenumbers of 1410 cm\(^{-1}\) (B1), 1409 cm\(^{-1}\) (B2 and B3) and 1408 cm\(^{-1}\) (B4).

Figure 5.1 also shows the band at 1230 cm\(^{-1}\) due to O=S=O symmetric stretching of CMKC is shifted to a lower wavenumber of 1228 cm\(^{-1}\) in the system containing 10 wt % of CMCE (B1) but to higher wavenumbers in the system with 20 wt % (B2), 30 wt % (B3) and 40 wt % (B4) of CMCE. The intensity of C-O-C band at 925 cm\(^{-1}\) of CMKC/CMCE film is observed to decrease with addition of CMCE from 10 wt % to 40 wt %. The peak shifts are seen for all the blends suggest that the intermolecular interaction has occurred between the two component polymers (Wu et al., 2012).
Figure 5.1: FTIR spectra of BO, B1, B2, B3 and B4 films
5.2.2 SEM study

Cross-sectional SEM images of CMKC and the CMKC/CMCE blend films are shown in Figure 5.2. The SEM images of CMKC (B0 sample), with different magnifications, show clearly that the surface of CMKC improved from a rough and brighter surface to a smooth and dark surface. According to Su’ait et al. (2011) and Monikowska et al. (2007), the presence of the dark and bright regions in the SEM micrograph represents an amorphous and crystalline phase, respectively. Therefore, the increase of the smooth and dark region in the CMKC/CMCE blend suggests an increase of amorphous region in the polymer blend.

Cracks could also be observed and are testified of the brittle character of the CMKC at liquid nitrogen temperature (while fracturing samples for SEM analyses). No phase separation in the blend of CMKC/CME also could be observed. This could be explained by a good miscibility between the CMKC and CMCE owing to their interactions as detected by FTIR analysis.

![Figure 5.2: Cross-sectional SEM images of CMKC and CMKC/CMCE blend films](image)

<table>
<thead>
<tr>
<th>Film</th>
<th>500×</th>
<th>1000×</th>
<th>2000×</th>
</tr>
</thead>
<tbody>
<tr>
<td>B0</td>
<td><img src="image" alt="Image" /></td>
<td><img src="image" alt="Image" /></td>
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</tbody>
</table>

20 µm 10 µm 2 µm
<table>
<thead>
<tr>
<th>Film</th>
<th>500×</th>
<th>1000×</th>
<th>2000×</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td><img src="image1" alt="Image" /></td>
<td><img src="image2" alt="Image" /></td>
<td><img src="image3" alt="Image" /></td>
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<td><img src="image4" alt="Image" /></td>
<td><img src="image5" alt="Image" /></td>
<td><img src="image6" alt="Image" /></td>
</tr>
<tr>
<td>B3</td>
<td><img src="image7" alt="Image" /></td>
<td><img src="image8" alt="Image" /></td>
<td><img src="image9" alt="Image" /></td>
</tr>
<tr>
<td>B4</td>
<td><img src="image10" alt="Image" /></td>
<td><img src="image11" alt="Image" /></td>
<td><img src="image12" alt="Image" /></td>
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<tr>
<td>B5</td>
<td><img src="image13" alt="Image" /></td>
<td><img src="image14" alt="Image" /></td>
<td><img src="image15" alt="Image" /></td>
</tr>
</tbody>
</table>

‘Figure 5.2, continued’
5.2.3 DMA study

Viscoelastic properties of CMKC/CMCE blend films were analyzed using DMA analysis. Figure 5.3 depicts the damping curves (tan δ) for the neat CMKC and CMKC/CMCE blend films with different concentrations of CMCE. For the neat CMKC, as the temperature increases, damping curve increases and goes through a maximum at $T_g$ before decreasing with further increase in temperature. The damping curve of the neat CMKC shows one relaxation process with a maximum of tan δ at -7.5 °C. This relaxation becomes larger when the wt % of CMCE in the blend increase indicates the good interaction between CMKC and CMCE chain. This observation is in good agreement with the SEM observation.

It’s worthy noticing that the value of $T_g$ (temperature at the peak of tan δ curve) of CMKC/CMCE blend film decreases with increase in CMCE concentration up to 40 wt % as tabulated in Table 5.1. The decrease in $T_g$ values suggest that the mobility of CMKC segment increases and generates free volume with addition of CMCE. The ions can easily migrate via the free volume helping in ionic conductivity increment (Ninan et al., 2013; Su'ait et al., 2014). However, $T_g$ value increases at CMCE content of 50 wt %. This might be due to the host polymer (CMKC) becomes more crowded with CMCE that leads to an increase in the CMKC/CMCE network. Moreover, all the blend compositions show a single peak showing that the blend components are miscible (Wang et al., 2014). Among the blend films, the film containing 40 wt % of CMCE shows the lowest glass transition temperature (-13.5 °C).
Figure 5.3: Tan δ versus temperature curves for B0, B2, B4 and B5

Table 5.1: Glass transition temperatures for CMKC and CMKC/CMCE blend films

<table>
<thead>
<tr>
<th>Blend film</th>
<th>Glass transition temperature, $T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100:0</td>
<td>-7.5</td>
</tr>
<tr>
<td>90:10</td>
<td>-9.2</td>
</tr>
<tr>
<td>80:20</td>
<td>-10.0</td>
</tr>
<tr>
<td>70:30</td>
<td>-10.9</td>
</tr>
<tr>
<td>60:40</td>
<td>-13.5</td>
</tr>
<tr>
<td>50:50</td>
<td>-12.2</td>
</tr>
</tbody>
</table>
### 5.2.4 Impedance study at room temperature

Figure 5.4 presents the impedance plot for the highest conducting film, B4 (0 wt % salt) at room temperature. The plot depicts a titled spike indicating that there was a good contact between the electrolyte and the electrode. The experimental data can be fitted well with an equivalent circuit containing $R_b$ and CPE for which $R_b$ is bulk electrolytes resistance and CPE is constant phase element. The model of the equivalent circuit to determine the bulk resistance for the ionic conductivity calculation is shown in Figure 5.5. The existence of CPE could be due to a capacitor that changes with frequency and arise if there is air present in between the electrode-electrolyte surface (Ali et al., 2008; Noor et al., 2010)

![Figure 5.4: Typical impedance plot for B4 (0 wt % salt) blend film](image)
The room temperature conductivity of the CMKC/CMCE blend films investigated in this study is depicted in Figure 5.6. The conductivity of the CMCKC/CMCE blend is observed to gradually increase with addition of CMCE up to a maximum at 40 wt % of CMCE (corresponding to B4 sample) after which the conductivity decreases with higher concentration of CMCE. The increase in conductivity can be attributed to the increase in segmental motion and fraction of amorphous region as shown by DMA and XRD studies. Meanwhile, the decrease in the conductivity at 50 wt % of CMCE is ascribed to the increase in CMKC/CMCE network stiffness as indicated by the increase in $T_g$ value discussed earlier. The blend film with 60:40 wt % ratio (B4 sample) possesses the highest conductivity of $3.25 \times 10^{-4}$ cm$^{-1}$.

The conductivity for CMKC/CMCE blend films obtained in this study is also higher compared to conductivity obtained for CMKC film reported by Mobarak et al. (2012). This shows that the blending of CMKC and CMCE is a feasible approach to enhance conductivity to a reasonable value for application in power sources. The proposed ion conductivity mechanism in the CMKC/CMCE films is shown in Figure 5.7.
Figure 5.6: Variation of log conductivity of CMKC/CMCE blend as a function of CMCE concentration
Figure 5.7: H⁺ conduction mechanism and intermolecular interaction in CMKC/CMCE blend
5.2.5 LSV study

LSV was carried out on the highest conducting CMKC/CMCE blend film in order to determine the electrochemical stability window of the film. Figure 5.8 shows the linear sweep voltammogram of the CMKC/CMCE (B4) blend films as a function of voltage. There is no obvious current flow in the electrolyte up to ~2.0 V. The current related to the decomposition of the polymer electrolyte increases gradually when the electrode potential is higher than 2.0 V. From Figure 5.8, it is determined that the electrochemical stability window for the blend film is up to 2.75 V. This indicates that this blend films is suitable to be applied in energy storage devices such as DSSC.

Figure 5.8: Linear sweep voltammetry curve
5.2.6 Mechanical studies

The dependence of the tensile strength (TS) and the breaking elongation (EAB) on the CMCE content for the CMKC/CMCE blend films are summarized in Table 5.2. TS and EAB values for CMKC film are 5.67 MPa and 45.68 % respectively. For the blend films, the tensile strength of the blend films improved with the increase of CMCE contents and reaches a maximum point of 15.15 MPa at 40 wt % of CMCE content. The enhancement of TS of the blend films might be attributed to the hydrogen bonding interaction between CMKC and CMCE and improvement of intermolecular interaction between the two polymers (Wu et al., 2012).

Besides, the flexibility of the films was also affected by the blending composition. As tabulated in Table 5.2, the EAB of the film increases as the CMCE content in the CMKC film increases. This result could be related to structural modification of the CMKC and CMCE content, which causes a greater flexibility in polymer structure.

Table 5.2: Mechanical properties of CMKC and CMKC/CMCE blend films

<table>
<thead>
<tr>
<th>Blend film</th>
<th>TS (MPa)</th>
<th>EAB (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100:0</td>
<td>5.67</td>
<td>45.68</td>
</tr>
<tr>
<td>90:10</td>
<td>6.33</td>
<td>52.62</td>
</tr>
<tr>
<td>80:20</td>
<td>6.67</td>
<td>66.92</td>
</tr>
<tr>
<td>70:30</td>
<td>10.78</td>
<td>68.67</td>
</tr>
<tr>
<td>60:40</td>
<td>15.15</td>
<td>76.36</td>
</tr>
<tr>
<td>50:50</td>
<td>12.40</td>
<td>65.12</td>
</tr>
</tbody>
</table>
5.3 Summary

The properties of CMKC/CMCE blends were investigated in order to identify the best blend composition for use as host of green polymer electrolytes. DMA result showed depression of glass transition of CMKC/CMCE blend indicating enhancement of segmental motion of polymer chains. The film containing 40 wt % of CMCE had the lowest glass transition of -13.5 °C. DMA result also showed single damping for all blend compositions which suggested that the two polymers are miscible. This was further supported by the result of FTIR study. The interactions between the two polymers were expected to occur between hydroxyl groups of the polymers. EIS results showed that the conductivity of CMKC/CMCE blend films increased with increasing CMCE content. The polymer blend system containing 40 wt % of CMCE was found to be the highest conducting among all the polymer blend films. Tensile measurement exhibited that this blend films were less brittle and more flexible compared to the unblended film. Based on the results, it can be concluded that the blend containing 40 wt % of CMCE is the best CMKC/CMCE blend ratio to be used for further investigation as host biopolymer. Therefore this composition was chosen to prepare solid biopolymer electrolyte systems by the incorporation of LiI, NaI, NH₄I and DNH₄I. The characteristics of the biopolymer electrolytes based CMKC/CMCE blend are presented and discussed in Chapter 6.
CHAPTER 6: STUDIES ON CMKC/CMCE BLEND ELECTROLYTE SYSTEMS AND THEIR PERFORMANCE IN SOLID STATE DSSC

6.1 Introduction

This chapter describes the effect of salts containing various size of cations such as Li\(^+\), Na\(^+\), NH\(_4\)\(^+\) and DNH\(_4\)\(^+\) to the optimum CMKC/CMCE blend system. The effects of cations have been investigated using FTIR, DMA, EIS, TNM and LSV. The selected electrolytes in all four systems were then used to fabricate solid state DSSC and their performances were investigated.

6.2 Characterization of CMKC/CMCE-electrolyte films

6.2.1 Result of FTIR Analysis

FTIR spectra were taken and analyzed in order to study the interactions of polymer host-salt complexes. The recorded FTIR spectra of CMKC/CMCE with various concentrations of LiI in the spectral region 600 to 4000 cm\(^{-1}\) are presented in Figure 6.1.

The bands at 3358, 1581, 1408, 1320, 1232 and 924 cm\(^{-1}\) correspond to O-H stretching, COO\(^-\) asymmetrical of carboxylate anion, COO\(^-\) symmetric stretching, -CH\(_2\) scissoring, O=S=O symmetric vibration and C-O-C stretching of CMKC/CMCE (0 wt % Li) (Le-Tien et al., 2004; Tranquilan-Aranilla et al., 2012). The peaks in CMKC/CMCE blend (0 wt %) are shifted to higher wavenumbers after addition of LiI salt. The OH band (3363 cm\(^{-1}\)) of the CMKC/CMCE blend is shifted to higher wavenumbers of 3373 cm\(^{-1}\) (10 wt %), 3409 cm\(^{-1}\) (20 wt %) and 3407 cm\(^{-1}\) (30 wt %) with the addition of LiI salt. The bands of CMKC/CMCE blend at 1582, 1408, 1321 and 1225 cm\(^{-1}\) are also detected at higher wavenumbers. These bands become less intense upon salt addition. This
maybe due to the interactions of Li$^+$ ions with carboxyl and hydroxyl group of polymer blend. The above mentioned changes confirm the biopolymers-salt interaction in the CMKC/CMCE electrolytes.

Similar observation have been reported by Wang (2007). He has developed solid polymer electrolytes of polyurethane and polyether-modified polysiloxane blends with lithium salts. They discovered that the intensity of the ether group absorption peak at 1110 cm$^{-1}$ in the FTIR spectra decreased as the lithium salt concentration increased, and the -OH peak around 3300 cm$^{-1}$ of their host polymers became much broader and shifted to lower frequency wavenumber. This indicates that Li$^+$ can interact with both the ether oxygen and hydroxyl oxygen sites on PTMG (Wang, 2007).

The FTIR spectra for system NaI, NH$_4$I and DNH$_4$I are illustrated in Figure 6.2, 6.3 and 6.4 respectively. Similarly, the peaks of CMKC/CMCE blend at wavenumbers of 3358, 1581, 1408, 1320, 1232 and 924 cm$^{-1}$ are also shifted to higher wavenumbers. The FTIR spectra of all four systems prove occurrence of complexation between the host polymer and the iodide salts. The possible interaction between the host polymer and the iodide iodide salt is depicted in Figure 6.5
Figure 6.1: FTIR spectra for (a) LiI and CMKC/CMCE-LiI films containing (b) 0, (c) 10, (d) 20 and (e) 30 wt% of LiI.
Figure 6.2: FTIR spectra for (a) NaI and CMKC/CMCE-NaI films containing (b) 0, (c) 10, (d) 20 and (e) 30 wt % of NaI
Figure 6.3: FTIR spectra of (a) NH₄I and CMKC/CMCE containing (b) 0, (c) 10, (d) 20 and (e) 30 wt % of NH₄I
Figure 6.4: FTIR spectrum of (a) DNH₄I and CMKC/CMCE containing (b) 0, (c) 10, (d) 20, (e) 30 and (f) 40 wt % of DNH₄I
Figure 6.5: Possible interactions between CMKC and CMCE with iodide salts.

6.2.2 Result of DMA

The effect of iodide salts to the thermal properties of CMKC/CMCE blend was investigated using DMA analysis. Figure 6.6 displays the tan δ-temperature curves
while Table 6.1 presents the $T_g$ variation for CMKC/CMCE-iodide salt complexes as a function of salt concentration. The damping curves presented in Figure 6.6 show the main relaxation process in the amorphous region of the CMKC/CMCE-iodide salt complexes. The damping peak corresponds to $T_g$ of B4 film (CMKC/CMKC-0 wt % salt) is observed at -13.5 °C. The value of $T_g$ decreases gradually with incorporation of salt. In the system of CMKC/CMCE-LiI (Figure 6.6 (a)), $T_g$ value decreases from -13.5 °C to -14.5 °C, -16.7.0 °C and -43.0 °C with with incorporation of 10, 20 and 30 wt % salt respectively. In the system of CMKC/CMCE-Nal (Figure 6.6 (b)), $T_g$ value decreases from -13.5 °C to -14.1 °C, -48.1 °C and -64.3 °C. Similarly, in system of CMKC/CMCE-DNH$_4$I (Figure 6.6 (d)), $T_g$ value decreases from -13.5 °C to -28.6 °C, -30.0 °C, -35.9 °C and -50.7 °C. The decrease of the $T_g$ value with the addition of salt could be due to the plasticizing effect of the salt which results in a weakening of the dipole-dipole interactions between the polymer chains. This plasticizing effect softens the polymer backbone and thus produces a flexible polymer backbone. The flexible polymer backbone increases the segmental motion of the polymer matrix, hence producing free volume. The existence of the free volume is expected to facilitate ions migration (Ali et al., 2008).

However, the value of $T_g$ of CMKC/CMCE blend film is increased with increase in NH$_4$I content as presented in Figure 6.6 (c) and tabulated in Table 6.1. The increase in $T_g$ with addition of the salt is due to an increase in formation of transient cross-linking between the CMKC/CMCE chains and salt. The increase in the formation of transient cross-linking leads to an increase in the CMKC/CMCE network stiffness which in turns increases $T_g$ (Kim et al., 2003; Zainal et al., 2013). Similar results were reported by Zainal et al. (2013) and Kim et al. (2003).
(a) 

(b)
Figure 6.6: Tan δ versus temperature for CMKC/CMCE films containing (a) LiI, (b) NaI, (c) NH₄I and (d) DNH₄I salt
Table 6.1: Glass transition temperatures for CMKC/CMCE blend electrolytes

<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration of salt (wt %)</th>
<th>Glass transition temperature, $T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMKC/CMCE-LiI</td>
<td>0</td>
<td>-13.5</td>
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<tr>
<td></td>
<td>10</td>
<td>-14.5</td>
</tr>
<tr>
<td></td>
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<td>-16.7</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>-43.0</td>
</tr>
<tr>
<td>CMKC/CMCE-NaI</td>
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<td>-13.5</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>-14.1</td>
</tr>
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<td></td>
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<td></td>
<td>30</td>
<td>-64.3</td>
</tr>
<tr>
<td>CMKC/CMCE-NH₄I</td>
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<td>-13.5</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>-11.3</td>
</tr>
<tr>
<td></td>
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<td></td>
<td>30</td>
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<td>CMKC/CMCHE-DN₄I</td>
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<td>-13.5</td>
</tr>
<tr>
<td></td>
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<td>-28.6</td>
</tr>
<tr>
<td></td>
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<td></td>
<td>30</td>
<td>-35.9</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>-50.7</td>
</tr>
</tbody>
</table>
6.2.3 Result of ionic conductivity at room temperature

The biopolymer electrolytes for all four studied systems were analyzed using impedance spectroscopy. Figure 6.7 presents the impedance plots for CMKC/CMCE films containing 0, 10, 20, 30 wt % of LiI, NaI, NH₄I and DNH₄I at room temperature. All the plots depict a titled spike indicating the prevailing of the resistive component of the polymer electrolytes (Hema et al., 2008; Ramesh & Arof, 2001; Ramya et al., 2008). The data can be well fitted with the equivalent circuit consisting of a $R_b$ and CPE for which $R_b$ is bulk electrolytes resistance and CPE is constant phase element. The model of the equivalent circuit is presented in Figure 6.8. The existence of CPE could be due to a capacitive behaviour that changes with frequency and arises due to the presence of air between the electrode-electrolyte surface (Ali et al., 2008; Noor et al., 2010). The $R_b$ of the films was determined from the intercept of the tilted spike at real impedance axis. Table 6.2 shows the parameters of equivalent circuit for the CMKC/CMCE electrolyte films. It can be observed that for all systems the values of $R_b$ decreases with increasing salt concentration.
(a) Impedance plots for the films of CMKC/CMCE-LiI
(b) Impedance plots for the films of CMKC/CMCE-NaI
(c) Impedance plots for the films of CMKC/CMCE-NH₄I
Figure 6.7: Impedance plots for the films of CMKC/CMCE containing (a) LiI, (b) NaI, (c) NH₄I and (d) DNH₄I
Figure 6.8: Model of equivalent circuit for CMKC/CMCE electrolytes

Table 6.2: The parameters of the equivalent circuit

<table>
<thead>
<tr>
<th>System</th>
<th>CMKC/CMCE:salt (wt %)</th>
<th>$R_b$</th>
<th>CPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>B4</td>
<td>100:0</td>
<td>11.08</td>
<td>$2.84 \times 10^{-5}$</td>
</tr>
<tr>
<td></td>
<td>90:10</td>
<td>6.76</td>
<td>$1.39 \times 10^{-5}$</td>
</tr>
<tr>
<td>CMKC/CMCE-LiI</td>
<td>80:20</td>
<td>1.97</td>
<td>$2.77 \times 10^{-5}$</td>
</tr>
<tr>
<td></td>
<td>70:30</td>
<td>1.21</td>
<td>$2.59 \times 10^{-5}$</td>
</tr>
<tr>
<td>CMKC/CMCE-NaI</td>
<td>90:10</td>
<td>4.59</td>
<td>$2.39 \times 10^{-5}$</td>
</tr>
<tr>
<td></td>
<td>80:20</td>
<td>1.56</td>
<td>$2.16 \times 10^{-5}$</td>
</tr>
<tr>
<td></td>
<td>70:30</td>
<td>1.18</td>
<td>$1.16 \times 10^{-4}$</td>
</tr>
<tr>
<td>CMKC/CMCE-NH₄I</td>
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<td>8.90</td>
<td>$7.09 \times 10^{-5}$</td>
</tr>
<tr>
<td></td>
<td>80:20</td>
<td>2.27</td>
<td>$2.64 \times 10^{-5}$</td>
</tr>
<tr>
<td></td>
<td>70:30</td>
<td>1.46</td>
<td>$2.38 \times 10^{-7}$</td>
</tr>
<tr>
<td>CMKC/CMCE-DNH₄I</td>
<td>90:10</td>
<td>4.80</td>
<td>$1.20 \times 10^{-5}$</td>
</tr>
<tr>
<td></td>
<td>80:20</td>
<td>2.11</td>
<td>$2.15 \times 10^{-5}$</td>
</tr>
<tr>
<td></td>
<td>70:30</td>
<td>1.82</td>
<td>$7.39 \times 10^{-7}$</td>
</tr>
<tr>
<td></td>
<td>60:40</td>
<td>0.76</td>
<td>$3.63 \times 10^{-5}$</td>
</tr>
</tbody>
</table>
Meanwhile, Table 6.3 lists the average room temperature conductivity of the biopolymer electrolytes with different iodide salt content. The table shows that the ionic conductivity value increases gradually after addition of iodide salts. However, the CMKC/CMCE films containing more than 30 wt % of salt (LiI, NaI and NH₄I) and 40 wt % of DNH₄I salt were not free standing and therefore impedance measurement was not done on them. The highest ionic conductivities achieved for CMKC/CMCE system containing LiI (30 wt %), NaI (30 wt %), NH₄I (30 wt %) and (40 wt %) are $3.89 \times 10^{-3}$ S cm⁻¹, $4.55 \times 10^{-3}$ S cm⁻¹, $2.41 \times 10^{-3}$ S cm⁻¹ and $6.68 \times 10^{-3}$ S cm⁻¹ respectively. The highest ionic conductivity among the four systems is obtained for the CMKC/CMCE-40 wt % of DNH₄I.

The CMKC/CMCE containing DNH₄I salt shows greater ionic conductivity enhancement as compared to those containing LiI, NaI and NH₄ salts. This result may be related to low lattice energy of DNH₄I. The lattice energy, in principal, is proportional to the reciprocal of the ionic radius. Hence, an atom with larger cation would have lower lattice energy. The lower lattice energy of the doping salt is generally expected to promote greater dissociation of salts and thus provides higher concentration of ions to mobile (Su’ait et al., 2011).

The size of cation of salts increases in the order of LiI < NaI < NH₄I < DNH₄I respectively. Therefore, the ionic conducting is expected to enhance in order of LiI < NaI < NH₄I < DNH₄I. However in this study, the ionic conductivity of CMKC/CMCE-NH₄I is the lowest among all of the other system. Based on DMA result for CMKC/CMCE-NH₄I system, the $\sigma$-salt content trend opposes the $T_g$–salt content trend. In general, the conductivity decreases when the $T_g$ increases since there is less segmental motion. This apparent inconsistency can be described in terms of cross-
linking between the CMKC/CMCE chains and NH₄I salt as mentioned earlier. In this system, the cross-links are well separated in space and can move with respect to each other to a certain extent thereby contributing to ionic conductivity (Zainal et al., 2013). The ionic conductivity may also be contributed by the anions which interact weakly with the polymers (Johansson et al., 1996). Therefore, the ionic conductivity of CMKC/CMCE blend significantly enhanced by addition of NH₄I.

The increase in ionic conductivity with increasing salt concentration can also be attributed to the increase in the number of charge carrier concentration (Aravindan & Vickraman, 2007; Singh et al., 2013). The ionic conductivity of electrolytes is given as

\[
\sigma = nq\mu
\]  

(6.1)

where \(n\) is the mobile charge carriers density, \(q\) is the charge of ion and \(\mu\) is mobility of the charge carriers. Therefore any increase in either \(n\) or \(\mu\) leads to increase in the conductivity. According to electrolyte dissociation theory of Barker (Barker Jr & Thomas, 1964),

\[
n = n_o \exp \left( - \frac{U_o}{2\kappa_B e T} \right)
\]  

(6.2)

where \(U_o\) is dissociation energy of the salt, \(\kappa_B\) is the Boltzmann constant, \(e\) is dielectric constant of electrolyte system at selected frequency and \(T\) is the temperature of sample. In this study, the dissociation energy values for the each salts was taken from the book entitled The Strengths of Chemical Bonds, 1958. Using equation 6.2, the relative number of charge carriers \((n/n_o)\) for each film prepared in this study was calculated and the values are tabulated in Table 6.3. The \(n/n_o\) increases with salt concentration. The CMKC/CMCE film with the highest ionic conductivity in each system exhibited the
highest \( n/n_0 \). This confirms the conductivity of the CMKC/CMCE film is governed by the number of charge carriers. Similar observations have been reported by Singh et al. (2013) and Singh et al. (2014) who investigated the PVP-KI and Arrowroot-KI electrolyte systems.

The conductivity for CMKC/CMCE blend electrolyte films obtained in this study is higher compared to the conductivity obtained using a single biopolymer reported by Kumar et al. (2012) and Khanmirzaei and Ramesh (2013). Kumar and friends (2012) reported that the potato starch film with 20 wt % of NH\textsubscript{4}I gives the best conductivity value of \( 2.40 \times 10^{-4} \) cm\textsuperscript{-1} (Kumar et al., 2012). Meanwhile, Khanmirzaei and Ramesh (2013) reported that the potato starch film with 35 wt % of LiI exhibited maximum conductivity value of \( 4.68 \times 10^{-4} \) cm\textsuperscript{-1} (Khanmirzaei & Ramesh, 2013). The observed higher conductivity in this study is attributed to the additional complexation sites upon blending two polymers. Thus, there are more sites for ion migration which lead to higher conductivity.

The conductivity obtained from this study also higher than biopolymer blend electrolytes reported in the literature (Buraidah & Arof, 2011; Kamarudin et al., 2015; Yusof et al., 2014). This is due to the type of natural polymers used and also some modification on pristine polymers. It is well known that both \( k \)-carrageenan and cellulose have excellent functionality, which both natural polymers rich of coordination sites in their chain.

The plots of dielectric constant variation with salt concentration for all four systems at selected frequencies from 10 Hz to 40 kHz at room temperature are shown in Figure 6.9. The highest dielectric constant is observed at low frequency. At low
frequency, the period of the applied electric field is long and the ions accumulate at the electrode/electrolyte interface. The dielectric constant for every frequency is observed to increase with the increase in salt concentration. The increase in dielectric constant with salt concentration gives a reflection of an increase in the number of charge carriers (Hema et al., 2008). This observation is consistent with the results of $n/n_o$ listed in Table 6.2.

Table 6.2: Conductivity and relative number of charge carriers for the CMKC/CMCE blend electrolyte films at room temperature

<table>
<thead>
<tr>
<th>System</th>
<th>CMKC/CMCE:Salt</th>
<th>Conductivity, $(\sigma \pm \Delta \sigma)$ (S cm$^{-1}$)</th>
<th>$n/n_o$</th>
</tr>
</thead>
<tbody>
<tr>
<td>B4</td>
<td>100:0</td>
<td>$(3.25 \pm 0.25) \times 10^{-4}$</td>
<td>-</td>
</tr>
<tr>
<td>CMKC/CMCE-LiI</td>
<td>90:10</td>
<td>$(1.66 \pm 0.16) \times 10^{-3}$</td>
<td>0.973</td>
</tr>
<tr>
<td></td>
<td>80:20</td>
<td>$(2.73 \pm 0.09) \times 10^{-3}$</td>
<td>0.985</td>
</tr>
<tr>
<td></td>
<td>70:30</td>
<td>$(3.89 \pm 0.27) \times 10^{-3}$</td>
<td>0.989</td>
</tr>
<tr>
<td>CMKC/CMCE-NaI</td>
<td>90:10</td>
<td>$(1.59 \pm 0.05) \times 10^{-3}$</td>
<td>0.984</td>
</tr>
<tr>
<td></td>
<td>80:20</td>
<td>$(2.94 \pm 0.15) \times 10^{-3}$</td>
<td>0.993</td>
</tr>
<tr>
<td></td>
<td>70:30</td>
<td>$(4.55 \pm 0.08) \times 10^{-3}$</td>
<td>0.997</td>
</tr>
<tr>
<td>CMKC/CMCE-NH$_4$I</td>
<td>90:10</td>
<td>$(6.36 \pm 0.25) \times 10^{-4}$</td>
<td>0.933</td>
</tr>
<tr>
<td></td>
<td>80:20</td>
<td>$(1.41 \pm 0.30) \times 10^{-3}$</td>
<td>0.987</td>
</tr>
<tr>
<td></td>
<td>70:30</td>
<td>$(2.41 \pm 0.07) \times 10^{-3}$</td>
<td>0.994</td>
</tr>
<tr>
<td>CMKC/CMCE-DNH$_4$I</td>
<td>90:10</td>
<td>$(2.04 \pm 0.19) \times 10^{-3}$</td>
<td>0.987</td>
</tr>
<tr>
<td></td>
<td>80:20</td>
<td>$(3.37 \pm 0.10) \times 10^{-3}$</td>
<td>0.992</td>
</tr>
<tr>
<td></td>
<td>70:30</td>
<td>$(4.65 \pm 0.19) \times 10^{-3}$</td>
<td>0.993</td>
</tr>
<tr>
<td></td>
<td>60:40</td>
<td>$(6.68 \pm 0.20) \times 10^{-3}$</td>
<td>0.997</td>
</tr>
</tbody>
</table>
(a) The plots of real part of dielectric constant versus temperature at various frequencies for CMKC/CMCE-LiI films

(b) The plots of real part of dielectric constant versus temperature at various frequencies for CMKC/CMCE-NaI films
(c) The plots of real part of dielectric constant versus temperature at various frequencies for CMKC/CMCE-NH$_4$I films

(d) The plots of real part of dielectric constant versus temperature at various frequencies for CMKC/CMCE-DNH$_4$I films

Figure 6.9: The plots of real part of dielectric constant versus temperature at various frequencies for CMKC/CMCE blend films containing (a) LiI, (b) NaI, (c) NH$_4$I and (d) DNH$_4$I films
6.2.4 Result of ionic conductivity study at various temperatures

The temperature dependence of ionic conductivity of the CMKC/CMCE blend electrolytes was investigated in the temperature range from 303 to 333 K in order to understand the conductivity-temperature behaviour of the biopolymer blend-salt films. The electrochemical impedance data at various temperatures were collected and analyzed. Figure 6.10 demonstrates the temperature dependent conductivity of CMKC/CMCE blend electrolyte films. The ionic conductivity is observed to increase with temperature. This illustrates that the ionic conduction in the biopolymer electrolytes follows Vogel-Tammann-Fulcher (VTF) relationship which is expressed as,

$$
\sigma = \sigma_0 T^{-\frac{1}{2}} \exp \left( \frac{-E_a}{k_B (T - T_o)} \right)
$$

(6.3)

where $\sigma_0$ is the pre-exponential factor which is proportional to the number of charge carriers, $E_a$ is the activation energy for conduction which is related to polymer segmental motion, $k_B$ is the Boltzmann constant, $T$ is the absolute temperature and $T_o$ is the ideal vitreous transition temperature at which the polymer segments start to move. $T_o$ is also the reference temperature taken as the glass transition temperature, $T_g$. In this study, experimental $T_g$ was determined using DMA analysis.

The rise in temperature enhances the flexibility of polymer chains as a result of increasing in thermal oscillation mode. The movement of polymer segments is thus improved. Fast segmental mobility could promote the breaking down of the weak interaction between cation and polar group in the polymer. The detachment of the cation
creates more free voids for the ions to jump from an interstitial site to another adjacent equivalent site and eventually generate ionic transportation (Liew et al., 2014).
(a) VTF plots for CMKC/CMCE-LiI films

(b) VTF plots for CMKC/CMCE-NaI films
Figure 6.10: VTF plots for CMKC/CMCE blend films containing (a) LiI, (b) NaI, (c) NH$_4$I and (d) DNH$_4$I.

(c) VTF plots for CMKC/CMCE-NH$_4$I films

(d) VTF plots for CMKC/CMCE-DNH$_4$I films
Table 6.3: The activation energy of CMKC/CMCE blend films containing LiI, NaI, NH₄I and DNH₄I

<table>
<thead>
<tr>
<th>CMKC/CMCE: wt % salt</th>
<th>$E_a$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LiI</td>
</tr>
<tr>
<td>0</td>
<td>0.015</td>
</tr>
<tr>
<td>10</td>
<td>0.008</td>
</tr>
<tr>
<td>20</td>
<td>0.012</td>
</tr>
<tr>
<td>30</td>
<td>0.019</td>
</tr>
<tr>
<td>40</td>
<td>-</td>
</tr>
</tbody>
</table>

6.2.5 Result of transference number

Ionic transference number is a parameter for electrolytes to indicate fraction of conductivity that is due to movement of ions. The ionic transference number for the highest ionic conducting film for each system has been determined by the DC polarization method. Figure 6.11 illustrates the plots of the polarization current versus time for the highest ionic conductivity for each system. The value of ionic transference numbers of the electrolytes containing iodide salt of LiI, NaI, NH₄I and DNH₄I are found to be ~ 0.99. This suggests that the charge transport in the electrolytes was primarily ionic and only negligible contribution came from electron (Kumar et al., 2012). Kumar et al. (2012) reported that their biopolymer electrolyte system based of potato starch-NH₄I was an ionic conductor. The ionic transference number of their system was ~ 0.95.
(a) Polarization current versus time for the CMKC/CMCE-LiI

(b) Polarization current versus time for the CMKC/CMCE-NaI
Figure 6.11: Polarization current versus time for the CMKC/CMCE-NH$_4$I blend films containing (a) 30 wt % LiI, (b) 30 wt % of NaI, (c) 30 wt % of NH$_4$I and (d) 40 wt % of DNH$_4$I.
6.2.6 Result of LSV

Linear sweep voltammograms for the highest conducting CMKC/CMCE blend electrolyte films as a function of voltage are depicted in Figure 6.12. In the figure, the current onset at room temperature for all systems is detected at the range of ~1.0 V to ~2.0 V which is assumed to be the polymer electrolyte breakdown voltage. The results reveal that the electrochemical stability window of the blend electrolyte films is up to 1.0 V. This indicates that the CMKC/CMCE blend film is electrochemically stable for application in DSSC.

(a) LSV curve for CMKC/CMCE- (30 wt %) LiI film
(b) LSV curve for CMKC/CMCE-(30 wt %) NaI film

(c) LSV curve for CMKC/CMCE-(30 wt %) NH₄I film
Figure 6.12: Linear sweep voltammograms for the highest conducting CMKC/CMCE electrolyte films

6.2.7 Performance of solid state DSSCs employing CMKC/CMCE based electrolytes

Solid state DSSCs were fabricated using selected CMKC/CMCE blend electrolytes from all the four systems. All the electrolytes had a 10:1 salt/I_2 molar ratio. In this sub-chapter, the relationship between iodide concentrations, electrolytes conductivity, cation size and energy conversion efficiency, η % of DSSC are discussed.

Figure 6.13 presents the photocurrent density-voltage curves of DSSCs fabricated using CMKC/CMCE added with different iodide salts containing different wt % of salt at light intensity of 100 mW cm\(^{-2}\). Meanwhile, the values of \(V_{oc}, J_{sc}, \eta\) and \(\eta\ %\) are tabulated in Table 6.4. As can be observed from Table 6.4, the effect of increasing the iodide salts (iodide concentration) is positive on both conductivity and \(J_{sc}\) values. It is well known that the regeneration of the dye cation needs I\(^-\), thus the
increase in the energy conversion efficiency while increasing the iodide concentration can be due to the availability of more iodide ions (Bella et al., 2014). For FTO-TiO$_2$/CMKC/CMCE+LiI/I$_2$/Pt-FTO cell, the $\eta$ % of 10LI cell is 0.02 % with $V_{oc}$ of 0.50 V, $J_{sc}$ of 0.05 mA cm$^{-2}$ and $ff$ of 0.90. The energy conversion efficiency, $\eta$ % of 30LI cell is 0.11 % with $V_{oc}$ of 0.44 V, $J_{sc}$ of 0.42 mA cm$^{-2}$ and $ff$ of 0.57. It is observed that 10LI cell shows a lower $J_{sc}$ and higher $V_{oc}$. The lower value of $J_{sc}$ of this cell is ascribed to its lower ionic conductivity. A higher resistance to ion migration reduces the supply of I$_3^-$ to the Pt counter-electrode. This causes depletion of I$_3^-$ and also retards the kinetics of dye regeneration and therefore decreases the $J_{sc}$ value. Meanwhile, the slight increase of $V_{oc}$ for the DSSC, 20LI cell is related to the reduction of the back electron-transfer reaction (Kim et. al, 2005). The values of $J_{sc}$ and the solar cell efficiency increase with addition of LiI salt. The higher value of $J_{sc}$ exhibited by 30LI is attributed to its higher ionic conductivity. The higher conductivity leads to the faster regeneration of the dye sensitizer in the oxidized state to its original state at the interface of the dye-electrolyte (Rahman et al., 2014). Similar observation is obtained for NA, NH and DN cells which indicates that the $J_{sc}$ value is directly related to the iodide salts (iodide concentration) and conductivity values. The highest $\eta$ % achieved for CMKC/CMCE electrolytes system containing LiI (30 wt %), NaI (30 wt %), NH$_4$I (30 wt %) and (40 wt %) are 0.11 %, 0.16 %, 0.13 % and 0.21 % respectively.

In this study, the energy conversion efficiency of the FTO-TiO$_2$/CMKC/CMCE electrolyte/I$_2$/Pt-FTO cell is observed to increase in order of electrolyte LiI < NH$_4$I < NaI < DNH$_4$I. Referring to Table 6.3, the performances of Cell NA and Cell DN increase with conductivity of the electrolytes. Meanwhile, Cell LI shows lower performance than Cell NH although the conductivity of the electrolyte in Cell LI study is slightly higher than that in Cell NH. The lower performance of LI cell may be due to
the formation of Ti$_3^+$ species which trap electrons in localized states upon intercalation of Li$^+$ ions into a TiO$_2$ nanostructured photoelectrode (Bella et al., 2014).

Furthermore, the DSSCs performance does not depend only on the concentration of the iodide salt and conductivity of electrolytes but it also depends on the selected size cation. It is well known that the mobility of small cation is higher than large cation due to the fact that the larger cation is less solvated cation which reduces the ion mobility (Bella et al., 2014). However, in this study the DSSC performance is contradicted. In fact, the energy conversion efficiency in this present work is found to be independent of the cation size but dependent to the iodide concentration and conductivity of electrolytes.

The DSSC utilizing the biggest cation size and the highest conducting electrolyte exhibits the highest energy conversion efficiency of 0.21%. The value is low and may be due to poor contact at the electrode-electrolyte interface. However, this value is comparable and higher to those reported by Su’ait et al. (2013) and Khanmirzaei et al. (2013). Singh et al. (2013) obtained an efficiency of 0.003% for DSSC prepared using PU-LiI system while Khanmirzaei et al. (2013) achieved an efficiency of 0.17% for rice starch/LiI/MPLI/TiO$_2$ system. The observed higher efficiency might be due to higher ionic conductivity (~10$^{-3}$ S cm$^{-1}$) of the CMKC/CMCE electrolyte. The result of this study reveals that the blend biopolymer system based on $k$-carrageenan/cellulose derivatives has potential to be further explored for application in DSSC.
(a) Photocurrent density-voltage for FTO-TiO$_2$/CMKC/CMCE+LiI/I$_2$/Pt-FTO cell

(b) Photocurrent density-voltage for FTO-TiO$_2$/CMKC/CMCE+NaI/I$_2$/Pt-FTO cell
Figure 6.13: Photocurrent density-voltage of DSSCs with different iodide salt in CMKC/CMCE electrolyte.

(c) Photocurrent density-voltage for FTO-TiO$_2$/CMKC/CMCE+$\text{NH}_4I/I_2$/Pt-FTO cell

(d) Photocurrent density-voltage for FTO-TiO$_2$/CMKC/CMCE+$\text{DH}_4I/I_2$/Pt-FTO cell
Table 6.4: $J$-$V$ performance of FTO-$\text{TiO}_2$/Electrolyte+$I_2$/Pt-FTO

<table>
<thead>
<tr>
<th>Electrolyte/I$_2$</th>
<th>wt % salt</th>
<th>Cell designation</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>$ff$</th>
<th>$\eta$ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMKC/CMCE + Li$_2$I (Cell LI)</td>
<td>10</td>
<td>10LI</td>
<td>0.50</td>
<td>0.05</td>
<td>0.90</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>30LI</td>
<td>0.44</td>
<td>0.40</td>
<td>0.57</td>
<td>0.11</td>
</tr>
<tr>
<td>CMKC/CMCE + Na$_2$I (Cell NA)</td>
<td>10</td>
<td>10NA</td>
<td>0.47</td>
<td>0.12</td>
<td>0.57</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>30NA</td>
<td>0.43</td>
<td>0.81</td>
<td>0.44</td>
<td>0.16</td>
</tr>
<tr>
<td>CMKC/CMCE + NH$_4$I (Cell NH)</td>
<td>20</td>
<td>20NH</td>
<td>0.55</td>
<td>0.25</td>
<td>0.45</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>30NH</td>
<td>0.50</td>
<td>0.42</td>
<td>0.57</td>
<td>0.13</td>
</tr>
<tr>
<td>CMKC/CMCE + DNH$_4$I (Cell DN)</td>
<td>30</td>
<td>30DN</td>
<td>0.41</td>
<td>0.48</td>
<td>0.63</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>40DN</td>
<td>0.38</td>
<td>0.85</td>
<td>0.65</td>
<td>0.21</td>
</tr>
</tbody>
</table>

6.3 Summary

The FTIR and thermal analyses confirmed the interaction between polymers and salt. The conductivity of the electrolytes based on CMKC/CMCE blend enhanced with the increase of iodide salts. The increase in conductivity was attributed to the increase in the number and mobility of charge carriers. The highest conductivity of $6.68 \times 10^{-3}$ S cm$^{-1}$ was achieved for CMKC/CMCE containing 40 wt % of DNH$_4$I. The temperature dependence of conductivity study showed that all polymer electrolytes based CMKC/CMCE based polymer electrolytes obeyed VTF model conductivity-temperature behavior. The results of transference number measurements showed that the charge transport in CMKC/CMCE electrolyte films was mainly due to ions. Meanwhile, LSV result demonstrated that these electrolytes were electrochemically stable for DSSC application.
DSSCs based blend derivatives of $k$-carrageenan and kenaf-cellulose fiber with different cations iodide salt were successfully fabricated. The performance of DSSC was observed due to the iodide concentration and conductivity of electrolytes. DSSC employing the highest conducting CMKC/CMCE-DNH$_4$I exhibited the best performance of 0.21 %. The results suggested that this blend biopolymer system has favorable properties for DSSC application.
CHAPTER 7: CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

7.1 Conclusions

The research work for the present thesis was performed with the objectives to develop biopolymer electrolytes based on \( k \)-carrageenan/kenaf-cellulose derivatives for solid state DSSC. In this study, the derivatives, CMKC and CMCE were successfully obtained by using carboxymethylation process. The CMKC and CMCE were obtained from \( k \)-carrageenan and kenaf-cellulose. The obtained CMKC and CMCE were blended and used as the host polymer. The blending of CMCE into CMKC was found to be a promising strategy to improve the material properties such as mechanical and conductive properties. Iodide salts with cations of different sizes (LiI, NaI, NH\(_4\)I and DNH\(_4\)I) were used as the dopant salt to prepare solid polymer electrolytes for DSSC application. The performance of the CMKC and CMCE blend based DSSC was an indicative of the electrolyte promising prospect for practical application.

From the results of the present work, it can be concluded to that:

(a) The introduction of carboxymethyl groups into \( k \)-carrageenan and kenaf-cellulose was confirmed by FTIR analysis. The XRD analysis showed that the new derivatives have lower crystallinity as compared to pristine polymers. The morphology of the new derivatives were gradually changed indicating that the modified functional group improved the amophousity properties of the pristine polymers. The carboxymethyl derivatives also showed the increment of percentage oxygen content. The degree of substitution of CMKC and CMCE was 0.85 and 1.93.
(b) DMA result showed single damping for all blend compositions which suggested that the two polymers are miscible. This was further supported by the result of FTIR study. The interactions between the two polymers were believed to occur between hydroxyl groups of the polymers. The film containing 40 wt % of CMCE had the lowest glass transition of -13.5 °C and had the highest conducting among all the polymer blend films. Tensile measurement exhibited that this blend films were less brittle and more flexible compared to the unblended film. Based on its properties, the blend containing 40 wt % of CMCE was identified to be the most suitable blend to be used as host for further investigation to prepare green polymer electrolytes.

(c) The conductivity of the CMKC/CMCE electrolytes complexed with various iodide salts was found to depend on the size of cation of the salt. The highest conductivity of $6.68 \times 10^{-3}$ S cm$^{-1}$ was achieved for CMKC/CMCE containing large cation, 40 wt % of DNH$_4$I. The increase in conductivity with salt content was attributed to the increase in the number and mobility of charge carriers. The temperature dependence of conductivity study showed that all polymer electrolytes based CMKC/CMCE obeyed VTF model conductivity-temperature behavior. All electrolytes had low activation energy which indicated that the electrolytes facilitated fast ions motion in the polymer network. Meanwhile, FTIR and thermal analyses confirmed the occurrence of interaction between segmented polymers and salts to form a coordinate bond and subsequently form complexation between polymers and salt. The results of transference number measurements demonstrated that the charge transport in CMKC/CMCE electrolyte films was mainly due to ions. The CMKC/CMCE blend based these
electrolytes were also found to be electrochemically stable for DSSCs application.

(d) The cell efficiency, $\eta$ % and short circuit current, $J_{sc}$, have been found to depend on the iodide concentration and conductivity of electrolytes. The DSSC fabricated using the highest conducting electrolyte system, CMKC/CMCE-(40 wt %) DNH$_4$I exhibited the highest efficiency of 0.21% under light intensity of 100 mW cm$^{-2}$. This showed that the CMKC/CMCE blend electrolytes have favourable properties for solid state DSSCs applications.

7.2 Suggestions for further work

Even though solid state DSSCs employing CMKC/CMCE electrolytes showed response under light intensity of 100 mW cm$^{-2}$ and exhibited promising potentials for DSSCs giving the focus on bio based polymer electrolyte, the performance of DSSCs in this studied is comparatively low compared to liquid electrolytes which commonly used in commercial DSSC systems. Therefore, further work should be carried out to enhance the DSSCs performance. This can be done by several possible approaches listed below:

1. Using mixed cations salt such as the mixed of LiI and KI or LiI and tetrahexylammonium iodide as doping salt in CMKC/CMCE blend system:
   An electrolyte system containing mixed cations gives better solar cell performance compared to a single cation system due to beneficial effects from both types of cations.
2. Using different electrode materials which are more compatible with electrolytes:

The use of electrode materials which are more compatible with electrolytes will improve the DSSC performance. The use of a compatible materials helps in the reduction of the charge transfer resistance at counter electrode.

3. The surface modification approach by doping low cost inorganic material for absorbing layer such as kesterite (Cu₂ZnSnS₄) onto TiO₂ photoelectrode surface:

The doped of absorbing layer is expected to enhance the DSSC performance by reducing the electron recombination in electrode electrolytes interfaces of DSSC.
REFERENCES


LIST OF PUBLICATIONS

