

**STUDY ON IONIC INTERACTION IN
CARBOXYMETHYL CELLULOSE-KAPPA
CARRAGEENAN DOPED NH₄CL FOR BIO-
ELECTROLYTE MEMBRANES**

LEONG PEI MUN

**BACHELOR OF APPLIED SCIENCE (HONS)
MATERIAL TECHNOLOGY
UNIVERSITI MALAYSIA PAHANG**

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LEONG PEI MUN

(SUPERVISOR: DR AHMAD SALIHIN BIN SAMSUDIN)

Thesis submitted in partial fulfilment of the requirements for the award of the degree of
Bachelor of Applied Science (Hons) Material Technology

**Faculty of Industrial Sciences and Technology
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DECEMBER 2016

SUPERVISOR'S DECLARATION

I hereby declare that I have checked this thesis and in our opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Bachelor of Applied Science (Hons) Material Technology.

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STUDENT'S DECLARATION

I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

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LIST OF SYMBOLS

| | | |
|--------------------|---|----------------------------|
| <i>ml</i> | - | Mililitre |
| $^{\circ}\text{C}$ | - | Degree Celcius |
| <i>g</i> | - | Grams |
| $^{\circ}$ | - | Degree |
| σ | - | Ionic Conductivity |
| $\%$ | - | Percentage |
| π | - | Pi |
| θ | - | Theta |
| <i>A</i> | - | Area |
| <i>cm</i> | - | Centimeter |
| cm^{-1} | - | Per Centimeter |
| cm^2 | - | Square Centimeter |
| <i>F</i> | - | Frequency |
| <i>Hz</i> | - | Hertz |
| <i>MHz</i> | - | Mega Hertz |
| <i>Zi</i> | - | Imaginary Parts of Modulus |
| <i>Zr</i> | - | Real Parts of Modulus |
| \sim | - | Approximately |
| <i>a.u</i> | - | Arbitrary unit |
| η | - | Number of ions |
| <i>D</i> | - | Diffusion coefficient |
| μ | - | Ions mobility |

LIST OF ABBREVIATIONS

| | |
|--------------------|---|
| BEMs | Biopolymer electrolyte membranes |
| CMC | Caboxymethyl cellulose |
| EIS | Electrochemical impedance spectroscopy |
| FTIR | Fourier transform infrared spectroscopy |
| KC | Kappa-carrageenan |
| NH ₄ Cl | Ammonium chloride |
| PEs | Polymer electrolytes system |
| SPEs | Solid polymer electrolytes |
| XRD | X-ray diffractometer |

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ABSTRAK

Peranti elektronik yang menyebabkan isu-isu pembuangan dan bahan-bahan berbahaya membuat sisa elektronik pepejal menarik kebimbangan global kerana bahan-bahan toksik dan berbahaya yang telah digunakan sebagai sistem elektrolit. Disebabkan masalah ini, penyelidik lebih berminat dalam menghasilkan polimer berasaskan sumber semula jadi seperti kanji, chitosan, pektin, asid hyaluronik, getah asli, carrageenan, selulosa dan derivatif selulosa. Kepentingan utama dalam membangunkan polimer sebagai elektrolit terletak pada harapan bahawa sistem tersebut akan mengelakkan banyak masalah yang diambilkira apabila menggunakan bahan-bahan bahaya. Tertunggak kepada fakta yang diberikan, penyelidikan sekarang ini dibentangkan CMC/KC didopkan NH₄Cl sebagai membran biopolimer elektrolit. CMC/KC didopkan telah disediakan dengan teknik pelarutan dan telah dikaji dengan Spektroskopi Inframerah (FTIR), Spektroskopi sinar-X (XRD) dan Spektroskopi Impedans Elektrik (EIS). Berdasarkan analisis FTIR, ia menunjukkan terdapat complexation telah berlaku antara CMC / KC dan NH₄Cl kerana peralihan nombor gelombang. Tambahan pula, ia juga boleh didapati di sana adalah perubahan keamatian dengan memperkenalkan daripada NH₄Cl dalam CMC / KC gabungan dan membuktikan bahawa NH₄Cl memainkan peranan sebagai pendopan di kompleks polimer sistem elektrolit. Analysis XRD menunjukkan semua elektrolit biopolimer adalah bersifat amorfus dengan pendopan NH₄Cl. Kekonduksian ionik untuk CMC/KC telah meningkat and mencapai 1.25×10^{-4} bagi sampel D dengan pendopan 20 wt.% NH₄Cl pada suhu bilik . Kekonduksian ionik dipengaruhi oleh suhu dan ditunjukkan dalam Arrhenius semua sampel haba diaktifkan. Rice dan Roth telah membuktikan bahawa kekonduksian ionik dalam sistem ini diperintah oleh pergerakan ion dan pekali resapan pembawa cas. Kerja ini menunjukkan kemungkinan sistem CMC / KC berpotential digunakan sebagai sistem elektrolit untuk peranti elektrokimia.

ABSTRACT

Energy storage devices that cause disposable and harmful issues make them attracts global concerns due to toxic and hazard materials used as an electrolyte system. Due to this problem, researches are more interested in producing electrolyte based on polymer especially natural resources such as starch, chitosan, pectin, natural rubber, carrageenan derivatives and cellulose derivatives. The main interest in developing polymer as an electrolyte lies in the hope that such system will avoid many of problems accounted when using the hazard materials. In arrears to the fact given, this present research presented CMC/KC doped NH₄Cl as biopolymer electrolyte membranes (BEMs). The CMC/KC BEMs system were successfully prepared by using solution casting method and were characterised by different techniques, which are Fourier Transform Infrared (FTIR) spectroscopy, X-ray Diffractometer (XRD) spectroscopy, and Electrical Impedance Spectroscopy (EIS). Based on FTIR analysis, it showed there is complexation has occurred between CMC/KC and NH₄Cl due to the shifting of wavenumber. In addition, it also can be found there is changes of intensity with the introducing of NH₄Cl in CMC/KC blend and proved that NH₄Cl play a role as dopant in the polymer complexes electrolyte system. XRD analysis revealed that the BEMs system has increased in amorphous phase when NH₄Cl were added. The ionic conductivity of CMC/KC BEMs system were found to increase and achieved to maximum value at 1.25×10^{-4} Scm⁻¹ for sample contain with 20 wt.% NH₄Cl at ambient temperature. The ionic conductivity-temperature for CMC/KC BEMs system shown the Arrhenius behaviour where all the samples are thermally activated. Rice and Roth method showed that the ionic conductivity in this present system was governed by ionic mobility and diffusion coefficient of charge carriers. This work implies the possible application of CMC/KC BEMs system can be used as an electrolyte system for electrochemical devices.

CHAPTER 1

INTRODUCTION

1.1 Background of research

The enormous growth in portable consumer electronic devices such as mobile phones, laptop computers, digital cameras has gave rise to a large interest in compact, high-energy density and lightweight batteries. However, most electrolytes used made of non-biodegradable material and in the form of liquid based (Samsudin et al.2012).

It is important to know that the electrolyte from petro-based can contain materials which harmful to the environmental if not disposed properly. Therefore, commercial using liquid electrolytes are not suitable due to drawbacks such as insufficient of resources,inadequate electrochemical stability, leakage, and harmful to the environment (Ahmad et al., 2011).

Three categories of electrolyte have been identified namely liquid electrolyte, gel electrolyte, and solid electrolyte. Liquid electrolyte has good properties than organic electrolyte and can dissolve large concentrations of various ionic compounds, enabling high electrical conductivity and particularly attractive for high power density applications. However, liquid electrolyte may harm the environment and high in cost. Also, liquid electrolyte are easily turn to corrode condition for devices due to the leakage problem. For example, the using of potassium hydroxide, sulphuric acid and mercury as electrolyte materials (Jeanne, 2008). Most of this materials are toxic and hazard to human and also environment.

Meanwhile, gel electrolyte must be charged at a slower rate, low voltage not more than 14.1volt to prevent excess gas from damaging the cells which is not suitable for auxiliary equipment of manufacturers (Barry, 2014). Gel electrolyte has higher cost of production

than liquid electrolyte. With containing the liquid and solid form, this kind of electrolytes also have a problem with leakage.

Solid electrolyte present as the alternative to deal with the problem of liquid and gel form electrolyte. It can be produced in thin film form, so easily to miniaturize, flexible and prevention of leakage. Besides, it also non-flammable, has a very long shelf life, and can operate at constant parameters in a wide temperature range. Solid electrolyte also compatible with electrodes in providing good mechanical properties, easy to process, light in weight and the cost of production is low (Ou. et al., 2012)

1.2 Problem statement

Electronic devices that cause disposable issues and hazardous materials make solid electronic waste attracts global concerns. Toxic and non-biodegradable materials contain in commercial batteries can be very hazardous to the environment and risk in human. (Chai et al., 2012). It will continue exist in the environment for a long time without being decomposed and break down naturally. In addition, if these same substances are toxic, they may contaminate the soil and source of water. Therefore, researches are more interested in producing polymer based natural resources such as starch, chitosan, pectin, hyaluronic acid, natural rubber, carrageenan, cellulose and cellulose derivatives (Liew et al., 2015). Natural polymer or can be called as bio-polymer electrolytes are grabbing attention due to their easy to access in nature, low in cost, simple production process, and bio-degradable (Samsudin et al. ,2012).

Among all the bio polymer, carboxymethyl cellulose (CMC) and kappa carrageenan shown as good candidate to be explored for this research as host polymers due to their desirable attributes as proton conducting polymers. CMC contain no toxicity, biocompatibility, biodegradability, high hydrophilicity, and able to form film easily (Chai et al., 2011). CMC is widely used in many industrial sectors like food industry, paper industry, adhesives and paints industry, mineral processing and cosmetics (Hebeish et al., 2010). Kappa carrageenan is selected as host polymer as it can form cross-linking networks with other components in polymer electrolytes because of its rich hydroxyl group and also oxygen that can from bond with cations (Yang et al., 2011).

1.3 Objectives

The objectives of the research as follows:

1. To prepare electrolyte membranes based on carboxymethyl cellulose (CMC)/kappa carrageenan (KC) doped ammonium chloride (NH_4Cl).
2. To analyze the complexation between CMC/KC and NH_4Cl biopolymer electrolytes membranes (BEMs).
3. To determine the ionic conductivity and transport properties of CMC/KC doped ammonium chloride BEMs system.

1.4 Thesis outline

Chapter 2 covered the literature review based on work done by previous researchers which focusing this present research.

In Chapter 3, materials and methodology of this research were presented and can be divided into two sections. Section 1: the preparation of membranes based CMC/KC doped NH_4Cl biopolymer electrolyte meanwhile in section 2: the characterization of prepared CMC/KC doped NH_4Cl BEMs system using Fourier Transform Infrared Spectroscopy (FTIR), X-rays Diffraction (XRD) and Electrical impedance Spectroscopy (EIS).

Chapter 4 covered all the experimental analysis discussion based on the characterization and divided into two sections, namely structural and electrical analysis. Finally, Chapter 5 presented the conclusion for illustrate overall results of the research. In addition, recommendations also provided for further work to enable the research updated and developed according to the current trend

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