

UNIVERSITI TEKNOLOGI MARA

**ELECTRICAL, STRUCTURAL AND
ELECTROCHEMICAL STUDIES OF
CALCIUM SALT—AGAROSE BASED
GEL POLYMER ELECTROLYTE
WITH THE ADDITION OF
NATURAL DEEP EUTECTIC
SOLVENT**

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ABSTRACT

Current interest in divalent calcium-based gel polymer electrolyte systems was rapid growth because of their potential in developing high-energy storage devices such as supercapacitors. However, research in calcium-based electrolytes was still poorly understood regarding the poor ionic conductivity, high crystalline structure and low electrochemical potential because of the obstacles in finding suitable electrolytes incorporate with the calcium salts. Therefore, this thesis focuses on the preparation and characterization of calcium thiocyanate (CaSCN) and calcium nitrate (Ca(NO₃)₂) based gel polymer electrolytes. The research included two stages of work where at stage one various salt concentrations from 0 wt.% to 45 wt.% of CaSCN and Ca(NO₃)₂ salts were added with 0.5 g of agarose polymer matrix and dissolved in 20 ml of DMSO, they were stirred for several days until a clear solution formed. Then, to produce a free-standing film, they were cast by solution casting method and heated in the oven at the temperature of ~80 ° C. They were characterized using Electrical Impedance Spectroscopy (EIS) to examine their conductivity studies, structural analysis by X-Ray Diffraction Spectroscopy (XRD), and Fourier Transform Infrared Spectroscopy. Voltage potential characterization by Linear Sweep Voltammetry (LSV) and Cyclic Voltammetry (CV). Both salts produce the optimum conductivity value at 40 wt.% of concentration where CaSCN—agarose resulted in $8.01 \times 10^{-05} \text{ S.cm}^{-1}$ and Ca(NO₃)₂—agarose resulted in $1.52 \times 10^{-4} \text{ S.cm}^{-1}$. The anion size of the salts also influences the ionic conductivity, the size of the nitrate anion (NO₃⁻) is bigger than the thiocyanate anion (SCN⁻). Bigger anion size has a weak attraction force between cation-anion interaction, thus ease to dissociate and promote better ionic conduction of the electrolytes system. By comparing these two systems, the highest conducting sample of Ca(NO₃)₂—agarose had been chosen to undergo stage two where the natural deep eutectic solvent (NADES) was added into its system to improve the electrical, structural and electrochemical properties of the electrolytes. The addition of NADES into the system increased the ionic conductivity until reach the maximum of $1.61 \times 10^{-03} \text{ S.cm}^{-1}$ and improve the structural properties by increasing the amorphicity of the electrolytes due to the increment of the volume of the agarose polymer matrix and encouraging the pathways for ions migration, the highest conducting sample of each system has the lowest percentage of crystallinity and smallest crystallite size. Intermolecular interaction studies support the result of the amorphicity as the addition of NADES increases the coordination site for ion transport mechanism by the presence of hydroxyl and carbonyl group from choline chloride and glycerol. The increment of the sites increases the number of charge carrier transport in the electrolytes system and increases the ionic conductivity of the electrolytes. The percentage of free ions and contact ions had been studied from the intermolecular analysis and resulted in the highest conducting samples having the highest percentage of free ions and the biggest area of calcium ion (Ca²⁺) bonded with C=O. NADES successfully improved the result of electrochemical studies as it increased the electrochemical potential window of electrolytes from 2.90 V to 4.20 V, there is no appearance of anodic and cathodic peaks in the CV profile of NADES indicating high stability of the electrolytes and the occurrence of electrical double layer formation that highly desired for the production of supercapacitor.

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CHAPTER ONE

INTRODUCTION

1.1 Research Background

The rapid development of technologies that prioritize the hyperconnectivity between people, objects and spaces using advanced artificial intelligence and smart cities surge the exhaustive efforts to explore new energy storage devices which can provide high energy density with low cost and longer life such as supercapacitors. Technologies that evolve constantly promote the demand for electrical supply exclusively generated from renewable energy such as solar, wind, geothermal and biomass. The exploration of clean energy promotes positive impacts in reducing environmental issues like global warming due to the overloading emission of carbon dioxide into the atmosphere. Therefore, researchers start extensive work in harnessing the use of biodegradable materials such as agarose, cellulose and starch as the goal of new materials research tendencies in the application of bio-based supercapacitor, storing charge in supercapacitor which is constructed using renewable materials is a very attractive from an environmental point of view (Armelin et al., 2016).

High-energy storage devices such as supercapacitors use electrolytes as the essence of device fabrication. Research in polymer electrolytes are constantly attracted great interest due to ease of synthesis, high ionic conductivity in a solid state, and potential to improve energy density significantly (Deivanayagam et al., 2019). Polymer electrolytes are mainly classified into three types which are liquid electrolytes (LEs), solid electrolytes (SEs), and gel polymer electrolytes (GPEs). These three types of electrolytes will specifically be discussed further in Chapter Two. In the case of GPEs, they are produced by swelling up in the organic solvent such as dimethyl sulphoxide (DMSO), dimethyl carbonate (DMC), diethyl carbonate (DEC), ethylene carbonate (EC) and propylene carbonate (PC), the low molecular weight of organic solvent improves the electrolyte conductivity (Asmara et al., 2011). GPEs possess high advantages over LEs because of their physical properties enhancement for ions transportation, leak-proof, and provide better electrode-electrolyte interface compared to the SEs (Omar et al., 2015).