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THE ELECTRICAL, STRUCTURAL AND ELECTROCHEMICAL STUDIES OF MAGNESIUM– AGAROSE BASED GEL POLYMER ELECTROLYTES INCORPORATED WITH DEEP EUTECTIC SOLVENT

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ABSTRACT

Three systems of agarose-based gel polymer electrolyte, which are agarose–$Mg(NO_3)_2$, agarose–$Mg(ClO_4)_2$, agarose–$Mg(ClO_4)_2$–DES are prepared by using the solution casting method and characterized to determine their electrical, structural and electrochemical properties. Effects of lattice energy of the additive salts ($Mg(NO_3)_2$ and $Mg(ClO_4)_2$) on ionic species and conductivity characteristics in the gel polymer electrolyte is studied because the value of lattice energy will affect the degree of salt dissociation in polymer matrix. However, the combination of agarose and Mg salt alone are retained in high crystallinity which limited the performance of agarose-based polymer electrolyte. Thus, an additive known as DES is added to the complexed polymer electrolyte to enhance the electrical, structural dan electrochemical behaviour of agarose-based polymer electrolyte. The ionic conductivity can be calculated where the system with agarose–30 wt% $Mg(ClO_4)_2$ exhibit a better ionic conductivity about 6.247×10^{-4} S·cm^{-1} while the agarose–30 wt% $Mg(NO_3)_2$ defined at 1.48×10^{-5} S·cm^{-1}, indicate the system with low lattice energy contribute the effectiveness dissociation of salt that promotes the production of free ions. The agarose-based polymer electrolyte is further prepared by addition of DES into the agarose–30 wt% $Mg(ClO_4)_2$ and recorded the R_b value at 23.559 Ω and results in enhancement of ionic conductivity from 6.247×10^{-4} S·cm^{-1} (0 wt% addition of DES) to 1.525×10^{-3} S·cm^{-1} after involving 30 wt% of DES. The presence of DES in polymer electrolyte not only increased the dissociation of salt but also introduced new free ion, Cl$^-$ as alternative pathway during the transportation of ions. The ionic conductivity for all three system was also studied at various temperature (323 K, 343 K and 363 K), where are represented in graph of log σ against 1000/T to prove the Arrhenius rule are obeyed in all system. By using the same plot, the activation energy is calculated and recorded lowest at high conducting sample of all system. The structural properties of agarose-based polymer electrolyte is examined by using XRD and reinforced by using FTIR. From XRD pattern, the semicrystalline properties of agarose are observed at 2θ=18.8°, where these peaks are deconvoluted to determine the crystallite size in all three system. The system with the presence of DES recorded the smallest crystallite size about 0.91 nm compared to the system of agarose–$Mg(NO_3)_2$ and agarose–$Mg(ClO_4)_2$ that having crystallite size of 3.02 nm and 1.54 nm, respectively. The behaviour is supported by the FTIR study to observe the molecular interaction between the constituent occur in the systems. The percentage of free and contact ions are also determined by using FTIR deconvolution and result in higher percentage of free ion appear in the high conducting sample of all system. The electrochemical properties are done by using LSV and CV. The LSV curve shows the widest range of potential window obtained in agarose–$Mg(ClO_4)_2$–DES polymer electrolyte, which reveal at 3.75 V and recorded the voltage breakdown at 3.85 V, thus proves the suitability of this electrolyte to be applied in electrochemical application as they are having excellent range (>3 V). While CV is operated to observe the presence of anodic and cathodic peak appear in electrolyte system which prove the presence of Mg^{2+} conduction in the agarose-based polymer electrolyte systems.

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CHAPTER ONE
INTRODUCTION

1.1   Research Background

Polymer electrolyte has been frequently studied as it provides versatility and dimensional stability for all-solid state electrochemical devices such as rechargeable batteries, capacitors and solar cells (Pavani, 2012). Polymer electrolyte possesses several advantages such as high compliance, processability, good electrode-electrolyte contact, compatibility and flexibility, which become the factors of polymer electrolyte to be in great demand (Manjuladevi et al., 2017; Sharma & Hashmi, 2018). According to Rayung et al. (2020), the ionic conductivity and transportation of ions are the main parameter to determine the effectiveness of polymer electrolytes. These properties are affected by the mobility and dielectric constant of polymer host, the concentration and dissociation of salt when dissolving in the polymer matrix. Therefore, the selection of host polymer, inorganic salt, solvent and additive must be accounted as they can contribute to a designation of an excellent polymer electrolyte system.

Solid polymer electrolyte (SPE) is one of the polymer electrolytes that is mostly reported due to its excellent mechanical properties, low flammability and thermal stability. Nevertheless, its unable to form an electrolyte with good ionic conductivity and interfaces with the electrode leads to the limitations for SPE to be commercialized extensively in the industry (Osman et al., 2012; Cheng et al., 2018). Currently, a new system known as gel polymer electrolyte (GPE) exists in the form of a thin film by dissolving salt and solvents in the polymer matrix to form a gelled matrix solution has been introduced. It possesses some advantages over liquid electrolytes including higher safety, shape flexibility, reduced leakage and low reactivity (Tang et al., 2016). The ability of GPE to act as not only an electrolyte but also a separator leads to easy fabrication and the possibility of miniaturized devices (Pandey et al., 2009). This system also offers a comparable ionic conductivity with liquid electrolytes (Kurc, 2014). Liquid electrolyte is well known due to its ability to exhibit higher ionic conductivity ($\sim10^{-3}$–10^{-2} S·cm^{-1}) than most polymer electrolytes. However, it tends to face leaking and corrosion problems during packaging (Cheng, et al., 2018). Some of liquid electrolytes are flammable and contain high toxicity proves that they are not safe to be used and can

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