STUDY ON THE IONIC CONDUCTION PROPERTIES OF ALGINATE BASED BIOPOLYMER ELECTROLYTES AND ITS POTENTIAL APPLICATION IN ELECTRICAL DOUBLE-LAYER CAPACITOR

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SUPERVISOR'S DECLARATION

I hereby declare that I have checked this thesis and, in my opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Doctor of Philosophy

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I hereby declare that the work in this thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at Universiti Malaysia Pahang or any other institutions.

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ABSTRAK

Peranti storan tenaga menghadapi beberapa cabaran asas pada masa kini dan akan datang, termasuk keperluan untuk penanda aras prestasi dan keselamatan yang lebih baik yang mengambil kira pengenalan bahan mesra alam dan penciptaan produk yang boleh dinaik taraf dan mudah dikitar semula. Untuk mengelakkan masalah pencemaran alam sekitar, biopolimer dipercayai menjadi komponen utama dalam cara baharu untuk mengatasi elektrolit polimer sintetik terkini. Oleh itu, polimer alginat mempunyai potensi besar untuk pembangunan menjadi elektrolit biopolimer pepejal (SBE). Matlamat penyelidikan ini adalah untuk membangunkan dan mencirikan kebolehlaksanaan sistem SBE berasaskan alginat yang didopkan dengan pelbagai komposisi asid glikolik (GA) (Sistem I) dan diplastiskan dengan pelbagai komposisi etilena karbonat (EC) (Sistem II) untuk digunakan. dalam kapasitor lapisan dua elektrik (EDLC). Teknik tuangan larutan digunakan untuk menyediakan kedua-dua sistem yang mempunyai filem nipis yang fleksibel, telus dan berdiri bebas. Oksigen pasangan tunggal daripada polimer perumah (alginat) berinteraksi dengan ion H^+ daripada kumpulan karboksilat (COO----H^+) pembawa cas, yang ditunjukkan oleh peralihan dan kehilangan puncak dalam analisis spektroskopi inframerah fourier transformasi (FTIR). Keamatan puncak belauan sinar-x (XRD) menurun secara beransur-ansur untuk kedua-dua sistem apabila sifat amorf SBE bertambah baik, menunjukkan bahawa pergerakan ion H+ melalui matriks polimer, menurunkan tahap kehabluran (X_c) apabila diperkenalkan dengan GA dan EC. SBE yang paling amorfus ditemui untuk Sistem I dan Sistem II terdiri daripada 20 wt. % GA (X_c = 26.99 %) dan 5 wt. % EC (X_c = 18.85 %), masing-masing dengan morfologi licin dan homogen tanpa pemisahan fasa. Menambah EC ke dalam alginat-GA SBEs meningkatkan nilai T_g disebabkan oleh sebatian kitaran struktur EC, yang menjerat rantai polimer yang membawa kepada mengurangkan fleksibiliti dalam kompleks. Kestabilan terma ditentukan menggunakan thermogravemetri analyzer (TGA) manakala suhu penguraian maksimum dinaikkan kepada 300 °C. Penemuan ini membayangkan bahawa sistem SBE adalah stabil dari segi haba dan mampu memenuhi keperluan peranti. Dalam Sistem I, kekonduksian ionik optimum (σ) 5.32 x 10^{-4} S cm^{-1} pada suhu semasa dicapai dengan menambah 20 wt. % GA (GA-4). Sementara itu, kekonduksian ionik optimum (σ) untuk Sistem II (9.06 x 10^{-4} S cm^{-1}) pada suhu semasa dicapai dengan menambah 6 wt. % EC (EC-3). Kedua-dua sistem SBE mematuhi tingkah laku Arrhenius sepenuhnya, dengan nilai regresi yang boleh diterima (R^2 ~ 1). Pendekatan dekonvolusi FTIR digunakan untuk mengira parameter pengangkutan ionik untuk kedua-dua sistem. σ kedua-dua sistem kebanyakannya dipengaruhi oleh mobiliti ionik (μ) dan nombor pekali resapan (D) ion H^+. Pengukuran nombor pemindahan (TNM) digunakan untuk menentukan nombor pemindahan kation (t_{H^+}), yang dinaikkan daripada 0.22 (GA-4) kepada 0.45 (EC-3). Ini membuktikan bahawa kesan pemplastikan berjaya menggalakkan pemisahan H^+ yang lebih besar daripada garam berasid yang digunakan dalam kajian ini. Analisis voltammetri sapuan lelurus (LSV) menunjukkan bahawa Sistem I dan II agak stabil pada suhu bilik. Untuk fabrikasi sel EDLC, sampel pengalir ionik tertinggi daripada setiap SBE telah digunakan. SBE yang diplastiskan, yang diwakili oleh Sistem II Sel, mengatasi sel yang tidak diplastiskan (Sel Sistem I) dari segi ketumpatan kuasa, ketumpatan tenaga, kemuatan spesifik (C_{sp}) dan rintangan siri setara (ESR), yang telah dipertingkatkan dengan ketumpatan arus yang lebih tinggi yang boleh menahan 10,000 kitaran. Penemuan ini mencadangkan bahawa sistem SBE berasaskan alginat menawarkan potensi yang besar untuk aplikasi EDLC.

ABSTRACT

Energy storage device face several fundamental challenges in the present and the future, including the need for improved performance and safety benchmarks that take into account the introduction of environmentally friendly materials and creation of upgradable and easily recyclable products. To prevent environmental contamination problems, biopolymers are believed to be a key component on emerging new ways to overcome recent synthetic polymer electrolytes. Thus, alginate polymers have a great potential for development into solid biopolymer electrolytes (SBEs). The aims of this research are to develop and characterize the feasibility of alginate-based SBE systems doped with varying compositions of glycolic acid (GA) (System I) and plasticized with varying compositions of ethylene carbonate (EC) (System II) to be applied in an electrical double layer capacitor (EDLC). The solution casting technique was used to prepare both systems that possess flexible, transparent, and free-standing films. The lone pair oxygen from the host polymer (alginate) interacted with the H^+ ion from the carboxylate group (COO^----H^+) of the charge carrier, which was shown by the shifting and disappearance of the peak in the Fourier-transform infrared spectroscopy (FTIR) analysis. The x-ray diffraction (XRD) peak intensity decreased gradually for both systems as the amorphous nature of the SBEs improved, demonstrating that movement of H^+ ion through polymer matrix, lowered the degree of crystallinity (X_c) when introduced with GA and EC. The most amorphous SBEs discovered for System I and System II were composed of 20 wt. % GA (X_c = 26.99 %) and 5 wt. % EC (X_c = 18.85 %), respectively with smooth and homogeneous morphology without phase separation. Adding EC into the alginate-GA SBEs increased the T_g value due to the EC structure's cyclic compound, which entangled the polymer chain leading to reduced flexibility in the complexes. Thermal stability was determined using thermogravimetric analysis (TGA) while the maximum decomposition temperature was elevated to 300 °C. These findings imply that the SBEs system is thermally stable and capable of meeting the device requirements. In System I, the optimum ionic conductivity (σ) of 5.32 x 10^{-4} S cm^{-1} at ambient temperature was achieved by adding 20 wt. % GA (GA-4). Meanwhile, the optimum ionic conductivity (σ) for System II (9.06 x 10^{-4} S cm^{-1}) at ambient temperature was achieved by adding 6 wt. % EC (EC-3). Both SBEs systems obeyed the Arrhenius behaviour completely, with acceptable regression values ($R^2 \sim 1$). The FTIR deconvolution approach was used to compute ionic transport parameters for both systems. The σ of both systems were predominantly influenced by ionic mobility (μ) and diffusion coefficient number (D) of H^+ ion. Transference number measurement (TNM) was used to determine cation transference number (t_{H^+}), which was raised from 0.22 (GA-4) to 0.45 (EC-3). This proved that the plasticization effect successfully promoted greater H^+ dissociation from the acidic salt which was utilized in this study. The linear sweep voltammetry (LSV) analysis demonstrated that Systems I and II were relatively stable at room temperature. For the EDLC cell fabrication, the highest ionic conducting sample from each SBEs was used. The plasticized SBEs, represented by System II Cell, outperformed the un-plasticized cell (System I Cell) in terms of power density (P_d), energy density (E_d), specific capacitance (C_{sp}) and equivalent series resistance (ESR), which were improved by a higher current density that can withstand 10,000 cycles. These findings suggest that alginate-based SBE systems offer a significant potential for EDLC applications.

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