IONIC CONDUCTIVITY AND RELATED STUDIES IN METHYL CELLULOSE BASED POLYMER ELECTROLYTES AND APPLICATION IN SUPERCAPACITORS

NOOR ERWANI AZURA BINTI SHUHAIMI

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NOOR ERWANI AZURA SHUHAIMI

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ABSTRACT

Solid polymer electrolytes based on methyl cellulose (MC) were investigated. Two MC based polymer electrolytes systems were prepared using solution cast technique. These are MC-ammonium nitrate (NH_4NO_3) system and MC-NH_4NO_3 system plasticized with poly (ethylene glycol), (PEG). NH_4NO_3 was chosen as the proton source to make MC, a biodegradable polymer conductive. The room temperature conductivity of pure MC is 3.08×10^{-11} S $cm^{-1.}$ The conductivity is increased up to 2.10×10^{-6} S cm^{-1} with addition of 25 wt.% NH_4NO_3. To enhance conductivity of MC-NH_4NO_3 system, PEG was added to 75MC25AN solution in different concentrations (from 5 to 25 wt.%). The optimum conductivity for the plasticized system is 1.10×10^{-4} S cm^{-1} at 15 wt.% PEG concentration. In order to investigate why conductivity increased and decreased in these systems, x-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy and thermogravimetric analysis (TGA) were carried out. XRD studies reveal that, conductivity is higher for samples with low crystalline fraction. The two systems in this work show the same results. The decrease in conductivity at higher salt concentration is due to the recrystallization of NH_4NO_3 out of the unplasticized system and formation of partially crystalline entities in the plasticized system. The formation of ion aggregates at higher salt concentration is also confirmed by FTIR studies. The presence of NH_4NO_3 peaks at 715 and 1754 cm^{-1} in the spectrum of 70MC30AN indicates that salt has recrystallized out of the sample and lowers the number density of charge carriers in the sample. FTIR also shows the interaction between MC-NH_4NO_3, MC-PEG, NH_4NO_3-PEG and MC-NH_4NO_3-PEG. TGA studies exhibit that MC based polymer electrolytes contain some free water in the matrix when samples start to lose mass below 125 °C. The addition of NH_4NO_3 salt reduced the thermal stability of MC based polymer electrolytes because of NH_4NO_3 has lower degradation temperature. PEG did not give any effect on the thermal stability of samples. The plot of σ versus 1000/T for unplasticized system is observed not to obey Arrhernius rule but, for plasticized system, the plot of σ versus 1000/T is thermally assisted and is seen to follow Arrhernius rule. Rice and Roth model implies that the addition of PEG results in the increase in conductivity because PEG helps to dissociate NH_4NO_3 and produce a higher number density of charge carriers. Electrical double layer capacitors (EDLC) have been fabricated using the highest conducting plasticized sample, 63.75MC21.252AN15PEG. The EDLC gives better performance when the electrode was coated with a layer of PEG on the surface. The highest discharge capacitance achieved is 38.45 F g^{-1}.

ABSTRAK

Polimer elekrolit pepejal berasaskan metil selulos (MC) telah dikaji. Dua sistem polimer elektrolit berasaskan MC telah disediakan menggunakan kaedah penuaran larutan. Ia adalah MC-ammonium nitrate (NH_4NO_3) sistem dan MC-NH_4NO_3 sistem diplastikkan dengan poli (etilina glaikol), (PEG). NH_4NO_3 telah dipilih sebagai sumber proton untuk menjadikan MC, polimer yang terbiodegradasikan yang berkoduksi. Nilai kekonduksian MC tulen pada suhu bililk adalah 3.08×10^{-11} S $cm^{-1.}$ Nilai kekonduksian telah meningkat kepada 2.10×10^{-6} S cm^{-1} dengan penambahan 25 wt.% NH_4NO_3. Untuk meningkatkan lagi nilai kekonduksian sistem MC-NH_4NO_3, PEG telah ditambah kepada larutan 75MC25AN dengan kepekatan yang berbeza (dari 5 kepada 25 wt.%). Nilai kekonduksian tertinggi untuk sistem yang diplastikkan adalah 1.10×10^{-4} S cm^{-1} pada kepekatan PEG sebanyak 15 wt.%. Untuk mengkaji mengapa kekonduksian bertambah dan menurun dalam sistem-sistem ini, belauan sinar-x (XRD), spektroskopi inframerah transformasi Fourier (FTIR) dan analisis termogravimetrik (TGA) telah digunakan. Kajian XRD menunjukkan kekonduksian adalah tinggi untuk sampel yang mempunyai pecahan hablur yang rendah. Kedua-dua sistem dalam kajian ini menunjukkan ciri-ciri yang sama. Penurunan nilai kekonduksian pada kepekatan garam yang tinggi adalah berpunca daripada penghabluran keluar NH_4NO_3 daripada sistem yang tidak diplastikkan dan pembentukkan entiti separuh hablur dalam sistem yang diplastikkan. Pembentukan gabungan ion pada kepekatan garam tertinggi telah disahkan dengan kajian FTIR. Kewujudan puncak NH_4NO_3 pada 715 dan 1754 cm^{-1} dalam spektrum 70MC30AN menunjukkan garam telah menghablur kembali keluar dari sampel dan menurunkan bilangan ketumpatan pembawa cas dalam sampel. FTIR juga telah menunjukkan berlakunya interaksi di antara MC-NH_4NO_3, MC-PEG,

NH_4NO_3-PEG and MC-NH_4NO_3-PEG. Kajian TGA menunjukkan bahawa elektrolit polimer berasaskan MC mengandungi air bebas di dalamnya apabila semua sampel didapati mula menunjukkan kehilangan berat pada suhu di bawah 125 °C. Penambahan garam NH_4NO_3 mengurangkan kestabilan terma elektrolit polimer berasaskan MC kerana NH_4NO_3 mempunyai suhu penguraian yang rendah. PEG tidak memberi kesan kepada kestabilan termal sampel. Plot log σ lawan 1000/T bagi sistem yang tidak diplastikkan dilihat tidak mematuhi hukum Arrhernius tetapi, bagi sistem yang diplastikkan plot log σ lawan 1000/T adalah berbantu haba dan dilihat mengikuti hukum Arrhernius. Model Rice dan Roth menyatakan bahawa penambahan PEG menghasilkan peningkatan nilai kekonduksian kerana PEG membantu di dalam penguraian NH_4NO_3 dan menghasilkan bilangan ketumpatan cas pembawa yang tinggi. Kapasitor dwilapisan elektrik (EDLC) telah difabrikatkan menggunakan sampel dengan kekonduksian tertinggi, 63.75MC21.252AN15PEG. EDLC memberi sumbangan terbaik apabila permukaan elektrod disapu dengan PEG. Nilai nyahcas kapasitan yang diperoleh adalah 38.45 F g^{-1}.

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