

**EFFECT OF ANION SIZE AND NANO FUMED SILICA
ON STRUCTURAL, THERMAL AND ELECTRICAL
PROPERTIES OF CHITOSAN POLYMER
ELECTROLYTES**

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Abstract

Chitosan has drawn attention as a potential polymer host for polymer electrolytes due to its promising properties. In the present study, an attempt has been made to determine the role of the different anions, namely, CH_3COO^- and CF_3SO_3^- , on the ionic conductivity of chitosan-based polymer electrolyte. The effect of filler on the sample with the highest conducting anion sample was also investigated. Many research studies on polymer electrolytes have shown that the dielectric values at high frequencies and electric modulus at low frequencies are constant. In this study, it has been further investigated to validate such findings. Chitosan-based polymer electrolytes comprising ethylene carbonate and propylene carbonate (1:1) as a plasticizer and a lithium salt LiX ($\text{X} = \text{CH}_3\text{COO}^-$ and CF_3SO_3^-) were prepared by solvent cast technique. Conductivity studies showed both systems obeyed Arrhenius behaviour and the ionic conductivity values obtained were $6.18 \times 10^{-7} \text{ S cm}^{-1}$ for the system with acetate anion and $5.01 \times 10^{-6} \text{ S cm}^{-1}$ for the system with triflate ion. It could be understood that the type of anion influences the ionic conductivity. Nano size fumed silica was added to the system with triflate ion to enhance the ionic conductivity. The highest room temperature conductivity value $5.41 \times 10^{-5} \text{ S cm}^{-1}$ was obtained by the composite electrolyte system with 2 wt. % silica. The improvement in the conductivity has also been supported by differential scanning calorimetry (DSC), X-ray diffraction (XRD) and Fourier transform infrared-spectroscopy (FTIR) studies. From DSC studies it is observed the glass transition temperature T_g decreased from 197°C to 166°C on addition of 2 wt. % silica. Lower T_g means greater polymer segmental motion and this implies faster ion conduction. XRD studies and FTIR showed the sample had lowest degree of crystallinity and highest number of free ions respectively. Dielectric behaviour of the prepared systems showed strong dependence on frequency and temperature. The prepared materials are ionic conductors.

ABSTRAK

Kitosan telah menarik perhatian sebagai sebuah polimer penerima yang berpotensi untuk elektrolit polimer disebabkan oleh cirri-cirinya yang meyakinkan. Dalam kajian lalu, usaha telah dilakukan untuk menentukan peranan anion berlainan seperti CH_3COO^- dan CF_3SO_3^- , bagi konduktiviti ionik elektrolit polimer berasaskan kitosan. Kesan pengisi terhadap sampel dengan anion berkonduktiviti tertinggi juga telah dikaji. Banyak kajian tentang elektrolit polimer telah menunjukkan bahawa nilai dielektrik pada frekuensi tinggi dan modulus elektrik pada frekuensi rendah adalah tetap. Dalam kajian ini, penyelidikan lebih lanjut dilakukan untuk mengesahkan penemuan tersebut. Elektrolit polimer berasaskan kitosan mengandungi etilin karbanat dan propilin karbonat (1:1) sebagai bahan pemplastik dan garam litium LiX ($\text{X} = \text{CH}_3\text{COO}^-$ dan CF_3SO_3^-) telah disediakan melalui teknik acuan pelarut. Kajian konduktiviti menunjukkan kedua-dua system mengikut kelakuan Arrhenius dan nilai konduktiviti ionik didapati ialah $6.18 \times 10^{-7} \text{ S cm}^{-1}$ bagi system dengan anion asetat dan $5.01 \times 10^{-6} \text{ S cm}^{-1}$ bagi sistem dengan ion triflat. Ia boleh difahami bahawa jenis anion mempengaruhi konduktiviti ionik. Silica berasap bersaiz nano telah ditambah ke dalam sistem dengan ion triflat untuk menambah konduktiviti ionik. Nilai konduktiviti ionik tertinggi pada suhu bilik yang didapati ialah $5.41 \times 10^{-5} \text{ S cm}^{-1}$ bagi system elektrolit komposit dengan 2 berat % silika. Pembaikan dalam konduktiviti juga disokong oleh kajian differential scanning calorimetry (DSC), X-ray diffraction (XRD) dan Fourier transform infrared-spectroscopy (FTIR). Melalui kajian DSC suhu T_g menurun daripada 197°C ke 166°C dengan penambahan 2 berat % silika. T_g rendah bermakna lebih banyak segmen polimer bergerak dan ini mempercepatkan konduksi ion. Kajian XRD dan FTIR menunjukkan sampel mempunyai darjah pegkristalan yang terendah dan nombor ion bebas yang tertinggi masing-masing. Sifat dielektrik

sistem yang disediakan menunjukkan pengantungan yang kuat terhadap frekuensi dan suhu. Dalam kajian ini, nilai dielektrik dan modulus menurun dengan perlahan-lahan pada frekuensi tinggi dan frekuensi rendah masing-masing. Bahan yang disediakan adalah konduktor ionik.

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