CHARACTERISTICS OF IMPURITY DOPED CHITOSAN BASED ELECTROLYTES

by

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DECLARATION

I hereby declare that the work reported in this dissertation is my own unless specified and duly acknowledged by quotation.

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ABSTRACT

Chitosan with a molecular weight of 6 x 10^5 g/mol was used in this present study. Chitosan is doped with silver triflate ($AgCF_3SO_3$) to produce an ion-conducting polymer that can be used as an electrolyte in solid state electrochemical cell. Ethylene carbonate (EC) was added to enhance the electrical conductivity. The polymer film was prepared in 1% acetic acid solution by the solution cast technique. The electrical conductivity of these complexes calculated using the bulk resistance value obtained from the complex impedance plot in the frequency range between 1 kHz to 1 MHz have been studied as a function of temperature. The film containing 0.2 g of doping salt exhibits the highest electrical conductivity, σ (10.2 ± 0.1) x 10^{-6} S/cm. The plot of ln σT versus 10^3/T (303 K ≤ T ≤ 363 K) for each sample seems to obey Arrhenius rule. The value of the square of regression R^2 is between 99.2% to 99.6% indicating a good straight line fitting of the points. The activation energy, E_A was obtained and the increase in electrical conductivity σ can be explained in terms of the decrease in E_A and vice versa. The modulus formalism M(f) indicates that the samples are ionic conductors. Transference number measurement confirms that the major mobile species in the sample are due to Ag^+ cation and $CF_3SO_3^-$ anion. X-ray diffraction confirms the disruption of the crystalline order of plasticized chitosan upon complexation and their conversion to the amorphous state for samples that exhibit increasing electrical conductivity. Infrared spectroscopy (IR) shows the occurrence of chitosan-salt complexation. This is confirmed by X-ray photoelectron spectroscopy (XPS) whereby the signal peak ranging from 375.9 to 376.6 eV is attributable to Ag-N interaction. In this study fractals were found in the films containing more than 0.5 g of silver triflate. When viewed under an optical microscope the fractals appear as dendrites and the edge of these dendrites are never contact with each other. This implies that the fractals must be charged and the charges are similar. The fractals are due to the diffusion of silver ion aggregates since silver metal colloids can be observed at the end of the fractals. The conductivity of the film before fractal growth is lower than after fractal growth due to the electronic conductivity and this was

confirmed by the transference number measurement. X-ray diffractogram, XRD shows that after fractal growth the film is more polycrystalline. The film with the highest electrical conductivity value was used to fabricate the electrochemical cells. The configuration of the cell is Ag | AC + 0.4 g EC + 0.2 g $AgCF_3SO_3$ | AgI. The average open circuit voltage is 0.557 V. The internal resistance of the cell fabricated is 1.2 kΩ while the bulk resistance of electrolyte used is around 900 Ω. This difference is attributed to the interfacial contact between the electrode and the electrolyte. It is also observed that when two cells are connected in series the current density is higher (8.33 $\mu A/cm^2$) than when two cells are connected in parallel (6.17 $\mu A/cm^2$).

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