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PREPARATION AND CHARACTERIZATION OF CHITOSAN-BASED SOLID POLYMER ELECTROLYTE FILMS WITH ZINC ACETATE

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Abstract

Solid polymer electrolytes based on chitosan with different weight percent ratios of zinc acetate have been prepared by the solution cast technique and then the flexible polymer electrolyte film were made. The conductivity and dielectric response of the solid polymer electrolyte systems were studied within the frequency range of 120Hz and 1kHz at room temperature. The conductivity of an electrolyte depends on the ability of the polymer host to solvate the zinc acetate. Polymers with higher dielectric constant will serve the purpose better. The dielectric constant and ionic conductivity follow the same trend with zinc acetate concentration. The dielectric constant is frequency dependent, so that the values of dielectric constant were decreased with increasing frequency. The sample containing 30 wt.% exhibited the highest room temperature conductivity of 2.44×10^{-9} S cm^{-1} , dielectric constant of 2.87×10^{-6} at 120Hz and 4.84×10^{-7} at 1kHz. Structural changes and complex formations of the polymer-salt systems were ascertained from x-ray diffraction (XRD). In order to check the suitability of the solid polymer electrolyte for its application in energy storage devices, polymer capacitor has been fabricated by sandwiching a separator sheet containing the electrolyte between two electrodes. The overall capacitance has been found to be of the order of 19.8 mF at the operating voltage 0.63 V.

Keywords: Chitosan, Zinc acetate, Polymer electrolytes, Polymer capacitor.

Introduction

Ion conducting polymers are an active area of study in materials research. They are prepared by complexing polymers containing polar groups with alkali metal salts . Being light weight and flexible, attempts have been made to use solid polymer electrolytes in solid-state electrochemical devices such as batteries, fuel cells, electrochromic displays, and smart windows . Polymer electrolytes usually contain both crystalline and amorphous phases. It has been reported that the ion conduction takes place primarily in the

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amorphous phase .Chitosan is a derivative of chitin which can be obtained from crab and shrimp shells. Chitosan is produced from deacetylation of chitin to overcome the solubility limitation of chitin in common solvents . Due to the NH2 and OH functional groups that can serve as conjunction sites, chitosan is a good sorbent with high affinity for transition metal ions. Chitosan has good film forming ability, porous scaffolds, and hydrogels. Ion-conducting polymer electrolytes based on chitosan have also been reported. From the fundamental point of view, ionic conduction in polymer electrolysis still poorly understood. Ion transport is complex and depends on factors such as salt concentration, dielectric constant of host polymer, degree of salt dissociation and ion aggregation, and mobility of polymer chains. Dielectric analysis of ion conducting polymer electrolytes can provide information on ion transport behavior and ionic/molecular interaction in solid polymer electrolytes. This is due to the fact that dielectric constant is both frequency and temperature dependent. Recently Petrowsky and Frech hypothesized that the DC conductivity is not only a function of temperature, but also is dependent on the dielectric constant in organic liquid electrolytes. The main objective of the present work is to investigate the Petrowsky and Frech postulate for solid polymer electrolyte based onchitosan:CH3COONa, as well as to investigate the physics behind the relationship between ionic conductivity and dielectric constant. The X-ray diffraction (XRD) has been used to characterize the chitosan-based solid electrolytes prepared in this study. This paper offers a concise review on the renaissance of a conventional capacitor to electrochemical double layer capacitor or polymer capacitor. Capacitors are fundamental electrical circuit elements that store electrical energy in the order of microfarads and assist in filtering. Capacitors have two main applications; one of which is a function to charge or discharge electricity. This function is applied to smoothing circuits of power supplies, backup circuits of microcomputers, and timer circuits that make use of the periods to charge or discharge electricity. The other is a function to block the flow of DC. This function is applied to filters that extract or eliminate particular frequencies. This is indispensable to circuits where excellent frequency characteristics are required. Electrolytic capacitors are next generation capacitors which are commercialized in full scale. They are similar to batteries in cell construction but the anode and cathode materials remain the same. They are aluminum, tantalum and ceramic capacitors where they use solid/liquid electrolytes with a separator between two symmetrical electrodes. The third generation evolution is the electric double layer capacitor, where the electrical charge stored at a metal/electrolyte interface is exploited to construct a storage device. The interface can store electrical charge in the order of ~106 Farad. The main component in the electrode construction is activated carbon. Though this concept was initialized and industrialized some 40 years ago, there was a stagnancy in research until recent times; the need for this revival of interest arises due to the increasing demands for electrical energy storage in certain current applications like digital electronic devices, implantable medical devices and stop/start operation in vehicle traction which need very short high power pulses that could be fulfilled by electric double layer capacitors (EDLCs). They are complementary to batteries as they deliver high power density and low energy density. They also have longer cycle life than batteries and possess higher energy density as compared to conventional capacitors. This has led to new concepts of the so-called hybrid charge storage devices in which electrochemical capacitor is interfaced with a fuel cell or a battery. These capacitors using carbon as the main electrode material for both anode and cathode with organic and aqueous electrolytes are commercialized and used in day to-day applications.

Experimental

Materials and Methods

Preparation of Samples

Solid polymer electrolyte films were used as host polymer electrolytes and were prepared by standard solution casting techniques. All samples were prepared at room temperature and stored under dry conditions. A 6 g of prepared chitosan flake was dissolved in 600 mL of 1 % (w/v) acetic acid solution. The solution was stirred by hotplate stirrer, for 90 hours at an ambient temperature and then the chitosan acetate host polymer solution was kept on overnight. The solution was maintained at 80 °C in water bath for one hour. The degassed and well-mixed solutions (30 mL) were casted onto petri dish, and dried in air for 3 days at room temperature until constant weight. The dried transparent chitosan films (0% doping salt) were detached from the petri dish. A 1 g of zinc acetate was dissolved in 100 mL with distill water to make 1 % (w/v) doping salt solution by using magnetic stirrer. A 3 mL of 1 % (w/v) doping salt solution was mixed with 27 mL of 1 % (w/v) chitosan acetate solution by using hotplate stirrer. The 30 mL of polymer salt solution was obtained as 10wt % doping salt solution. It was prepared to more 10wt % in each still to still 50wt% dopant . The degassed and well-mixed solution was cast onto petri dish, and dried in air for 3 days at room temperature until constant weight.

The dried transparent chitosan films (10wt% doping salt) were detached from the petri dish. Finally, chitosan film compound of 10 wt% was obtained. The same procedure were carried out for the preparation of chitosan films compound of 20, 30, 40 and 50wt% were prepared. The various compositions of zinc acetate used in preparing the polymer electrolytes are depicted in Table 1.

Characterization of Samples

The ionic conductivities of the samples were measured at within at room temperature using EXTECH 380193 LCR meter with a frequency range of 120 Hz and 1 kHz. The conductivity (σ) was determined using the equation below:

$$\sigma = \frac{1}{\rho(0)/2S/W*\log(e)2} \qquad (1)$$

From equation 1, ρ (0) = $2\pi SR$, 'S' represents the distance between the two contact probe, 'W' represents the thickness of sample and R is the resistance of the sample. The dielectric constant ε_r can be defined as:

$$\varepsilon_r = C_p t / \varepsilon_o A \qquad (2)$$

From equation 2, 't' represents the thickness of sample, 'A' is the area of the surface of the sample, C_p is the capacitance of the specimen in Farad and ε_o is the permittivity of free space.

X-ray diffraction (XRD): In this work, X-ray diffraction were carried out using a Rigaku x-ray powder diffractometer which employs Cu-K_α

x- radiation of wavelength $\lambda = 1.54056\dot{A}$ between a 2θ angle of 5° to 70°. X-ray diffraction was carried out to determine the nature of the materials whether a material is amorphous or crystalline.

Results and Discussion

The structural, conductivity and dielectric properties of the polymer electrolytes based on zinc acetate were investigated. The samples were prepared by solution cast method by taking different concentration of different ratio (i.e., Cs0%, 10%, 20%, 30%, 40% and 50%). The compatibility between the polymer matrix and the inorganic dopants has great influence on the properties ionic conductivity of the polymer electrolytes.

X-ray Diffraction Studies

In order to investigate the effect of zinc acetate on the structure of chitosan-based polymer electrolyte, x-ray diffraction of pure chitosan film, and their complexes have been performed. These crystalline structures contribute to the peaks in the XRD pattern of Cs0%, 10%, 20%, 30%, 40% and 50% are shown in Fig. 1. As seen in the XRD pattern of the pure chitosan Cs0%, the high intensity peak at around $2\theta = 27^\circ$, $2\theta = 40^\circ$ and $2\theta=56^\circ$.However, upon the addition of the zinc acetate liquid as seen in Cs30% , the intensity of the peak at $2\theta = 27^\circ$ was found to be decreased and the peak at $2\theta = 40^\circ$ and $2\theta = 56^\circ$ was found to be disappeared from the XRD pattern. This shows that the addition of the zinc acetate liquid decreased the crystallinity of the backbone of the chitosan and increased the amorphous region of the Cs30wt% sample. This is in agreement with what has been found that in ionic conductivity studies. Furthermore, the changes in the intensity and the disappearance of peaks show that there is some complexation occurring in the polymer matrix of the Cs30 wt% sample.

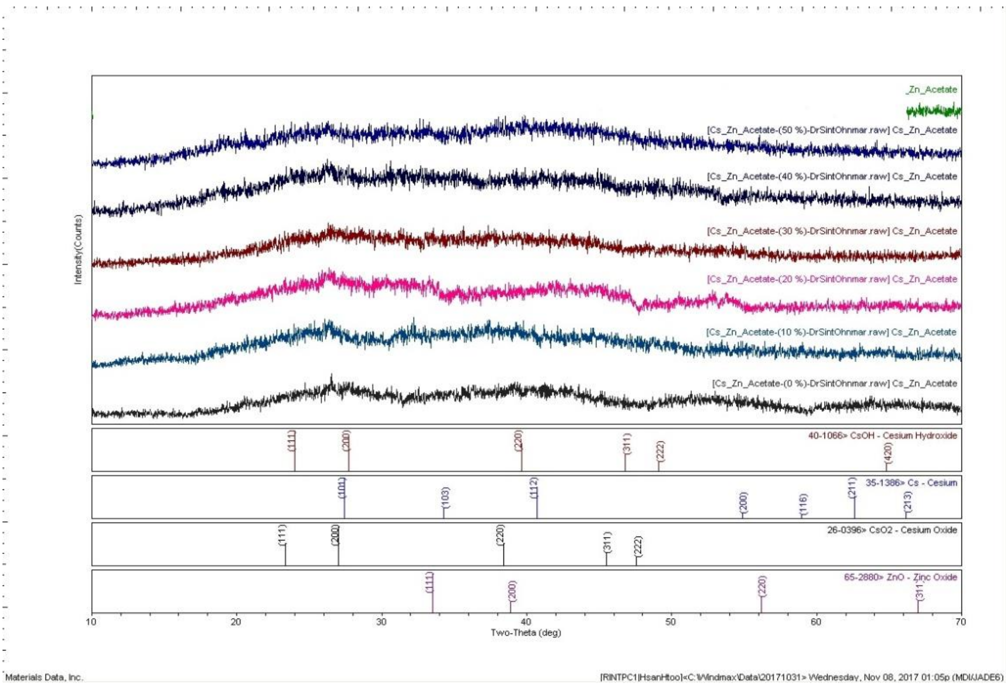

Figure 1: XRD spectra of Zn acetate-chitosan polymer electrolyte films

Electrical Conductivity Studies of Solid Polymer Electrolytes

Table.1 shows the various composition of zinc acetate and chitosan solution. The value of ionic conductivity for solid polymer electrolytes samples with different weight percentages of zinc acetate is plotted in Fig.2 and shown in Table.2. The highest value of conductivity was observed 2.44×10^{-11} Sm^{-1} from 30 wt % at room temperature. The increase of the ionic conductivity up to 30wt % of the zinc acetate added is due to increasing number of mobile ions. However, there is a decrease in ionic conductivity that could be observed when 40 wt % and 50 wt % of zinc acetate added into the system. This is due to the agglomeration of the excess ions from the zinc acetate which causes the mobile ions to form neutral pairs, and this could lead to a decrease in ionic mobility of the solid polymer electrolytes.

Table 1: Various composition of zinc acetate and chitosan solution.

Sample	Volume of 1 % (w/v) Zinc Acetate (mL)	Volume of 1 % (w/v) Chitosan (mL)	Weight percent of Zinc Acetate (%)
Cs0	0	30	0
Cs1	3	27	10
Cs2	6	24	20
Cs3	9	21	30
Cs4	12	18	40
Cs5	15	15	50

Table 2: Conductivity measurement for various composition of zinc acetate solid polymer electrolyte film at room temperature.

Name of Sample	Weight percent of Salt (%)	Conductivity(Sm^{-1})
Cs0	0	1.32E-11
Cs1	10	1.56E-11
Cs2	20	1.91E-11
Cs3	30	2.44E-11
Cs4	40	1.67E-11
Cs5	50	1.41E-11

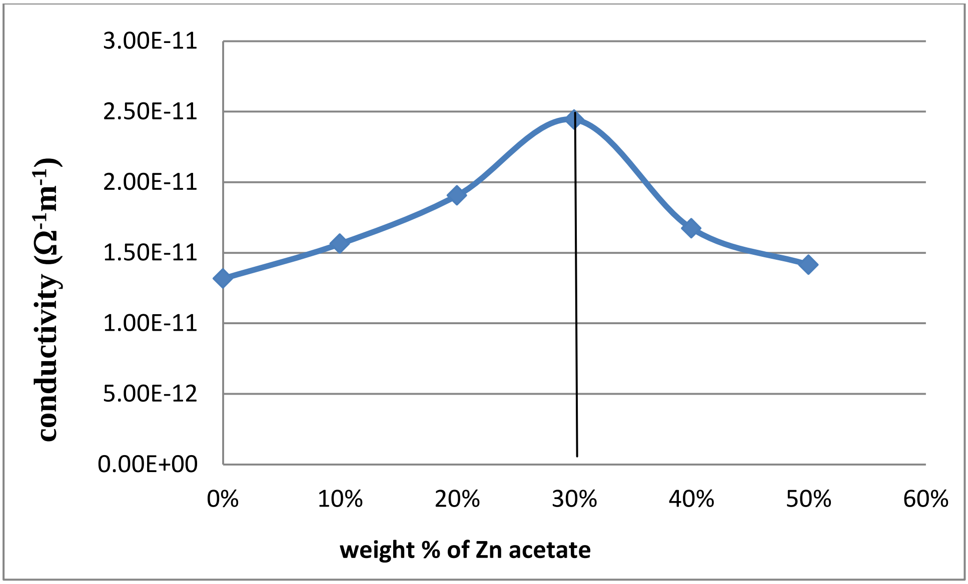

Figure 2: Conductivity measurement for various weight ratio zinc acetate polymer electrolyte films

Dielectric Studies of Solid Polymer Electrolytes

The value of dielectric value for solid polymer electrolytes samples with different weight percentages of zinc acetate is plotted in Fig.3 and shown in Table.3. The dielectric constant was found to increase upon the addition of zinc acetate and these parameters are significantly influenced by the frequency. Higher values of the dielectric constant observed at 30 wt % with frequencies 120 Hz have been also explained on the basis of interfacial/space polarization due to nonhomogeneous dielectric structure.

Table 3: Dielectric measurement for various composition of zinc acetate solid polymer electrolyte film at room temperature.

Name of Sample	Weight percent of Salt (%)	Dielectric (Farad) (120Hz)	Dielectric (Farad) (1kHz)
Cs0	0	6.24E-08	2.30E-08
Cs1	10	8.89E-08	4.48E-08
Cs2	20	9.66E-07	2.76E-07
Cs3	30	2.87E-06	4.84E-07
Cs4	40	1.58E-08	3.79E-09
Cs5	50	9.85E-09	3.09E-09

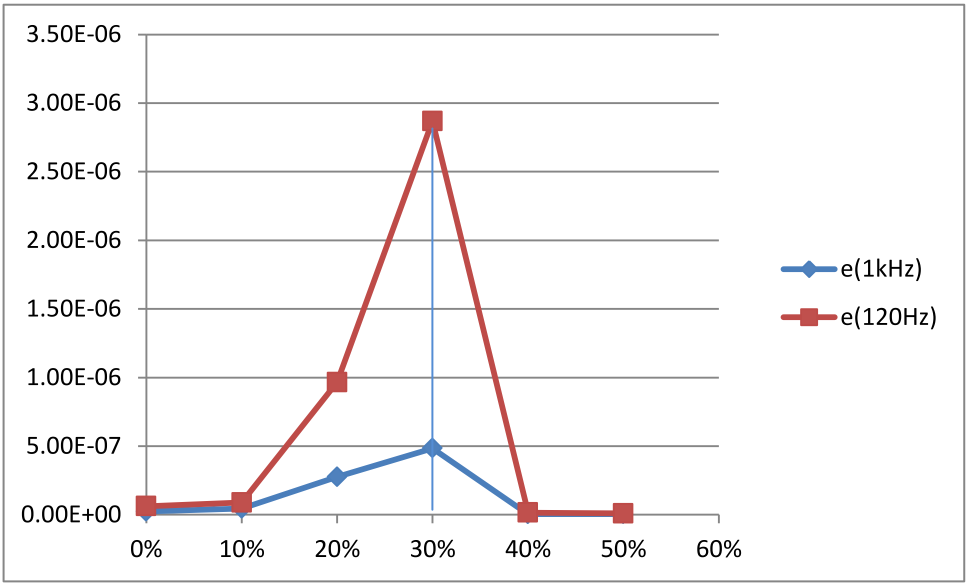

Figure 3: Dielectric measurement for various weight ratio zinc acetate polymer electrolyte films at 120Hz and 1kHz

Capacitance Studies of Double Layer Polymer Capacitor

The primary test platform was a electronics project board, and additional multimeter, variable DC power supply and EXTECH 380193 LCR meter. It is further notable that the capacitance of different weight ratio of double polymer capacitors were measured by silver electrode using the above described instruments and protocol as shown in Table.4. In order to check the suitability of the solid polymer electrolyte for its application in energy storage devices, polymer capacitor has been fabricated by sandwiching a separator sheet containing the electrolyte between two electrodes. The overall capacitance has been found to be of the order of 19.8 mF at the operating voltage 0.63 V. The increasing capacitance with decreasing the sample thickness, but the maximum effective operating voltage of about 0.64 V.

Table 4: Capacitance measurement with silver electrode for various composition of zinc acetate solid polymer electrolyte film.

Sample (wt %)	Sample Thickness (mm)	Operating Voltage (V)	Capacitance Value (mF)
0 %	1.1	0.64	11.7
10%	1.08	0.64	12.6
20%	1	0.64	16.0
30%	0.88	0.63	19.8
40%	1.04	0.64	15.8
50%	0.91	0.64	16.3

Conclusion

The ionic conducting solid polymer electrolytes based on zinc acetate and various concentrations of sodium acetate were prepared using the solution casting method. XRD analyses reveal increase in amorphous nature of the polymer-salt electrolyte films and confirm interaction and complexation between the polymer and the salt. An increase in conductivity is observed with the increase in zinc acetate concentration up to a certain salt content. The ionic conductivity is found to be 2.44×10^{-11} Sm^{-1} at 30 wt.% and also the dielectric constant was found to increase upon the addition of zinc acetate and these parameters are significantly influenced by the frequency. Higher values of the dielectric constant observed 2.87×10^{-6} at 30 wt %. The capacitance of different weight ratio of double polymer capacitors employed zinc acetate based solid polymer electrolyte is 19.8 mF at 30 wt %. Thus, these present the sold polymer electrolyte has potential in energy storage for flexible and lightweight devices.

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