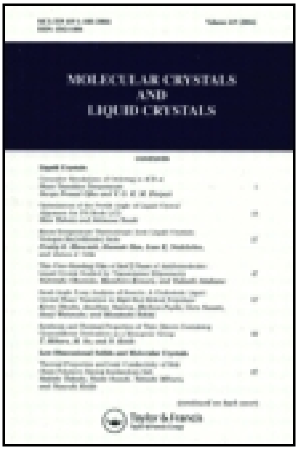

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Electrical Studies on Chitosan Based Proton Conductors and Application in Capacitors

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Ionic conductivity of four chitosan based electrolyte systems viz., chitosan–H_3PO_4, chitosan–H_3PO_4–Al_2SiO_5, chitosan–H_3PO_4–NH_4NO_3 and chitosan–H_3PO_4–NH_4NO_3–Al_2SiO_5 were studied by impedance spectroscopy in the frequency range from 50 Hz to 1 MHz and varying temperatures from 293 K to 373 K. The sample 0.62 chitosan – 0.38 H_3PO_4 has the highest room temperature conductivity of $(5.36 \pm 1.32) \times 10^{-5}$ S cm^{-1}. The sample 0.615 chitosan-0.377 H_3PO_4-0.008 Al_2SiO_5 exhibits the highest ambient conductivity of $(1.12 \pm 0.18) \times 10^{-4}$ S cm^{-1} in the ternary system with filler. In the ternary system with salt but without filler, 0.56 chitosan-0.34 H_3PO_4–0.10 NH_4NO_3 has the highest ambient conductivity of $(1.16 \pm 0.35) \times 10^{-4}$ S cm^{-1}. The quarternary sample 0.5572 chitosan-0.3383 H_3PO_4–0.0995 NH_4NO_3–0.0005 Al_2SiO_5 has the highest conductivity of $(1.82 \pm 0.10) \times 10^{-4}$ S cm^{-1}. All compositions are in weight fraction. The conductivity-temperature relationship is Arrhenian. Results were analyzed using the Rice and Roth model, Joncher's universal power law, $\sigma = \sigma_{DC} + A\omega^s$ and models based on polarons. The frequency dependence conductivity plot shows a frequency independent plateau at low frequency and a high frequency dispersive region, which is dominant at lower temperatures. From the plot of s versus T, it has been shown that the conductivity for Al_2SiO_5 containing chitosan-based electrolyte occurs by way of the overlapping large polaron tunneling model (OLPT) and for the binary chitosan-phosphoric acid system, conduction mechanism may be explained by the quantum mechanical tunneling (QMT) model. The best conducting sample in each system was used as electrolyte in an electric double layer capacitor. From the charge-discharge profile, a small ohmic voltage drop was observed for each 1 mA constant current discharge curve. The specific discharge capacitance of the best EDLC was found to be ~220 mF g^{-1} for 100 cycles.

Keywords: chitosan; conductivity; electrolyte; polarons

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INTRODUCTION

Polymer based proton conductors have received a lot of attention due to their potential application in electrochemical devices. Polyethylene oxide (PEO)-tungstosilicic acid with [EO]/[H^+] mole ratio of 40 exhibits the highest room temperature conductivity of 6.3×10^{-2} S cm^{-1} [1]. PEO-ammonium perchlorate prepared from methanol solution exhibits room temperature conductivity as high as $\approx 10^{-5}$ S cm^{-1} [2]. Under dry conditions, linear and branched poly(ethylenimine) complexed with H_3PO_4 behaves as a solid proton conductor [3]. Anhydrous mixtures of polyacrylamide with H_3PO_4 exhibits a conductivity of the order 10^{-3} S cm^{-1} at 300 K for 1.5 to 2 moles of acid per polymer repeat unit [4]. Zukowska *et al.* [5] have prepared thermally stable proton conducting gel electrolytes from poly(vinylidene fluoride)-dimethylformamide-H_3PO_4 system that exhibits conductivity as high as 5×10^{-4} S cm^{-1} at 20°C. Adebahr *et al.* [6] have shown that the addition of ceramic particles to polymer electrolytes can improve mechanical properties and enhance ionic conductivity.

In this work, chitosan has been chosen as the host polymer for ionic conduction. Chitosan has a considerably high mechanical strength, easy to form thin films and have lone pair electrons in its heteroatoms that can chelate with cations of the doping salt. Chitosan has been doped with orthophosphoric acid in various concentrations to form the chitosan-phosphoric acid system. To the concentration exhibiting the highest room temperature conductivity, different amounts of aluminium silicate filler and ammonium nitrate salt were added to form the chitosan-phosphoric acid-aluminium silicate and chitosan-phosphoric acid-ammonium nitrate system, respectively. Finally, different amounts of aluminium silicate filler were added to the chitosan-phosphoric acid-ammonium nitrate to form the quarternary system. Electrical conductivity was measured at ambient and elevated temperatures. Results were analyzed using the Rice and Roth model [7], Johnscher's universal power law [8] and some models involving polarons, such as overlapping large polaron model [9], small polaron model [10], correlated barrier height model [11] and quantum mechanical tunneling model [12].

EXPERIMENTAL

Preparation of Polymer Electrolytes

Highly viscous chitosan (Fluka), orthophosphoric acid (Ajax), ammonium nitrate (Ajax) and aluminosilicate were used as received.

The chitosan based polymer electrolytes were prepared by solution casting. 1 g of chitosan was dissolved in 100 ml 1% acetic acid solution. After complete dissolution of the chitosan powder, different volume percent (vol.%) of 1% phosphoric acid solution between 9 to 47 vol.% were added to the chitosan-acetic acid solution. The mixtures were then stirred continuously and cast into different petri dish to allow slow evaporation. Different amounts of ammonium nitrate (NH_4NO_3) between 2.5 wt.% to 20 wt.% were added to the chitosan-H_3PO_4 solutions. To prepare the composite samples, different amounts of Al_2SiO_5 between 0.3 wt.% to 2 wt.% were added separately to the highest conducting composition in the CA–H_3PO_4–NH_4NO_3 system.

Impedance Measurement

A HIOKI 3531-01 bridge was used to measure the impedance (from 50 Hz to 1 MHz) at room and elevated temperatures (293 K to 373 K). The sample was sandwiched between two stainless steel electrodes under spring pressure. On determining the bulk resistance R_B from the complex impedance plot, the conductivity, σ was calculated from the equation:

$$\sigma = \frac{t}{R_B A} \tag{1}$$

Here t is thickness of the sample and A is the contact area. AC conductivity was calculated using the equation

$$\sigma_{\mathrm{AC}} = \varepsilon_0 \varepsilon_{\mathrm{i}} \omega \tag{2}$$

where $\omega = 2\pi \mathrm{f}$, ε_0 = permittivity of free space and ε_{i} is the dielectric loss.

Cell Assembly

Figure 1 shows the configuration of the EDLC assembled in this study. The highest proton conducting polymer from each system was placed in between the two electrodes.

RESULTS AND DISCUSSION

Figure 2 shows the changes of conductivity with reciprocal temperature for all the samples given in Table 1.

Listed in Table 2 is the conductivity value for the prepared chitosan based polymer electrolyte in the present study.

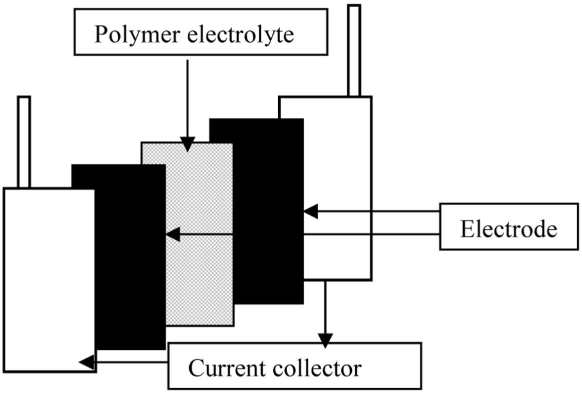

FIGURE 1 Configuration of EDLC with chitosan polymer electrolyte.

In the temperature range studied, the conductivity is found to increase quite linearly with temperature. It also can be seen that there is no abrupt changes in conductivity and shows an Arrhenius-like behavior in the temperature range studied. For all samples, the activation energies, E_a can be calculated from the following equation:

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{kT}\right) \tag{3}$$

and were tabulated in Table 3.

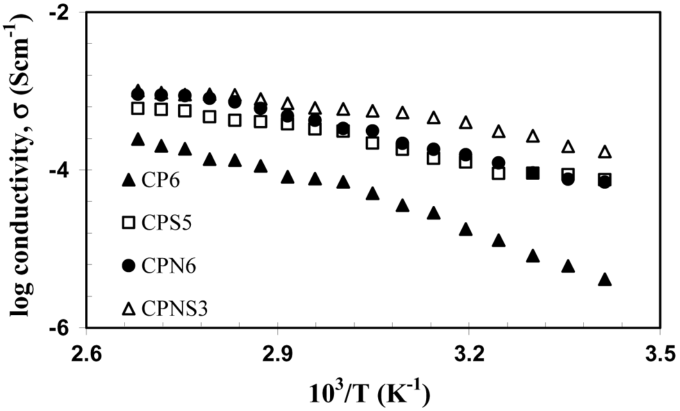

FIGURE 2 Conductivity versus 10^3/T for the highest conducting sample in all systems prepared.

TABLE 1 Electrolyte Used in the Fabrication of EDLC

Designation	Electrolyte
EDLC-1	0.62 chitosan-0.38 H_3PO_4
EDLC-2	0.56 chitosan-0.34 H_3PO_4-0.10 NH_4NO_3
EDLC-3	0.5572 chitosan-0.3383 H_3PO_4-0.0995 NH_4NO_3-0.005 Al_2SiO_5
EDLC-4	0.615 chitosan-0.377 H_3PO_4-0.008 Al_2SiO_5

Note: Composition given in weight fraction.

In order to investigate the enhancement in conductivity in more detail, the number of density of mobile ions was calculated using the Rice and Roth model [7]. This is shown in Figure 3. The Rice and Roth model states that when an ion that is in a localized state gains energy such that it is able to free itself from that state and become a free ion, the ionic conductivity can be represented as

$$\sigma = [2(Ze)^2/3kTm]nE_A\tau\exp(-E_A/kT) \tag{4}$$

Here $Ze =$ charge of the conducting species, $k =$ the Boltzmann constant, $T =$ temperature, $m =$ mass of proton, $E_A =$ activation energy and $\tau =$ the time taken to travel between two complexed sites.

The number density of mobile ions seems to fluctuate about a constant value for all samples that were analyzed. This could imply that the processes of ion dissociation and association took place at almost the same rate. Another possibility is that the complexed protons at the various complexed sites may have been removed and replaced at almost the same time that the number of mobile ions from the acid and salt remains almost the same in the temperature range

TABLE 2 Conductivity Values of Chitosan Based Polymer Electrolyte

Designation	Electrolyte	Average conductivity (Scm^{-1})
C1	0.62 chitosan-0.38 H_3PO_4	$(5.36 \pm 1.32) \times 10^{-5}$
C2	0.56 chitosan-0.34 H_3PO_4-0.10 NH_4NO_3	$(1.16 \pm 0.35) \times 10^{-4}$
C3	0.5572 chitosan-0.3383 H_3PO_4-0.0995 NH_4NO_3-0.005 Al_2SiO_5	$(1.82 \pm 0.10) \times 10^{-4}$
C4	0.615 chitosan-0.377 H_3PO_4-0.008 Al_2SiO_5	$(1.12 \pm 0.18) \times 10^{-4}$

TABLE 3 Activation Energy and Regression Values for Log σ versus $10^3/T$ Graph for the Highest Conducting Sample in All Systems Prepared in the Present Study

Designation	E_a (eV)	Regression, R^2
C1	0.47	0.97
C2	0.33	0.98
C3	0.24	0.97
C4	0.28	0.99

studied. The mobility was calculated using the equation,

$$\mu = \sigma/ne \tag{5}$$

and the variation of mobility, μ with reciprocal temperature is as shown in Figure 4.

Unlike, the number density of mobile ions, the mobility increases with reciprocal temperature by at most one order of magnitude in the temperature range considered. The energy of migration, E_m decreases for the sample with the highest conductivity. All graphs in Figure 4 can be represented by the Arrhenius equation

$$\mu = \mu_0 \exp(-E_m/KT) \tag{6}$$

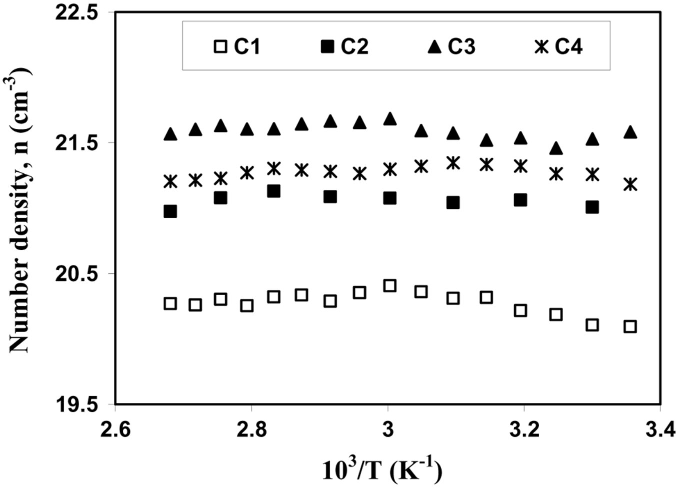

FIGURE 3 Plot of log number density of mobile ion versus $10^3/T$ for the highest conducting sample in all systems prepared in this study.

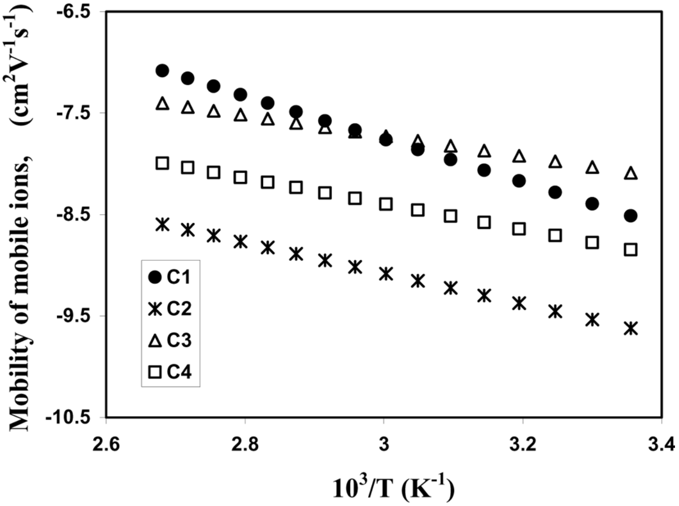

FIGURE 4 Plot of log mobility versus 10^3/T for the highest conducting sample in all systems prepared in this study.

with E_m for C1 > C2 > C4 > C3 i.e. 0.42, 0.30, 0.25 and 0.20 eV respectively.

Figure 5 shows the plot of $\sigma_{AC}(\omega)$ versus ω for the highest conducting sample, C3 in the quarternary system at different temperatures.

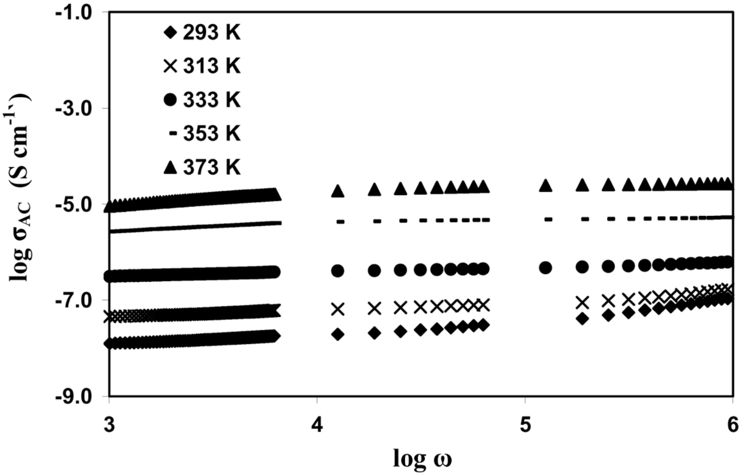

FIGURE 5 Plot of log σ_{AC} versus log ω at different temperatures for C3.

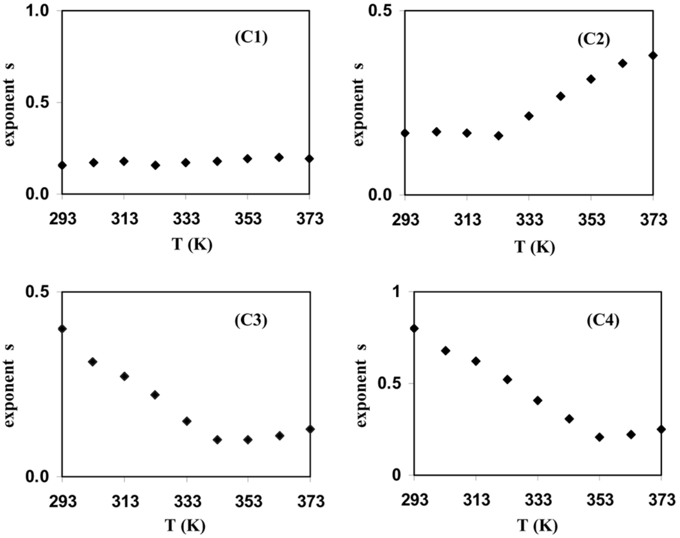

FIGURE 6 Variation of s with temperatures for C1, C2, C3 and C4.

From the slope of the log σ_{AC} versus log ω, the exponent s is obtained for every temperature. The plot of s versus T is as shown in Figure 6 for the highest conducting samples in all systems studied.

The conduction mechanism in the binary system, chitosan-phosphoric acid is by quantum mechanical tunneling and for the other systems, the conduction mechanism may be explained by the OLPT model.

Figure 7 (a)–(d) depicts the charge-discharge curves for the fabricated EDLC in the present work. From the figure, the internal resistance of the EDLC-3 cell is between 31 to 34 Ω. The low internal resistance could be attributed to the high ionic conductivity and good contact with the activated carbon electrode [13]. The capacitance of the EDLCs are not that high, but it is quite constant for 100 cycles. These are shown in Figure 8.

CONCLUSION

The highest conducting samples from four chitosan based electrolyte systems have been analyzed using the Rice and Roth model, Joncher's power law and some polaron models. In the temperature range studied, the number density of mobile ions can be considered

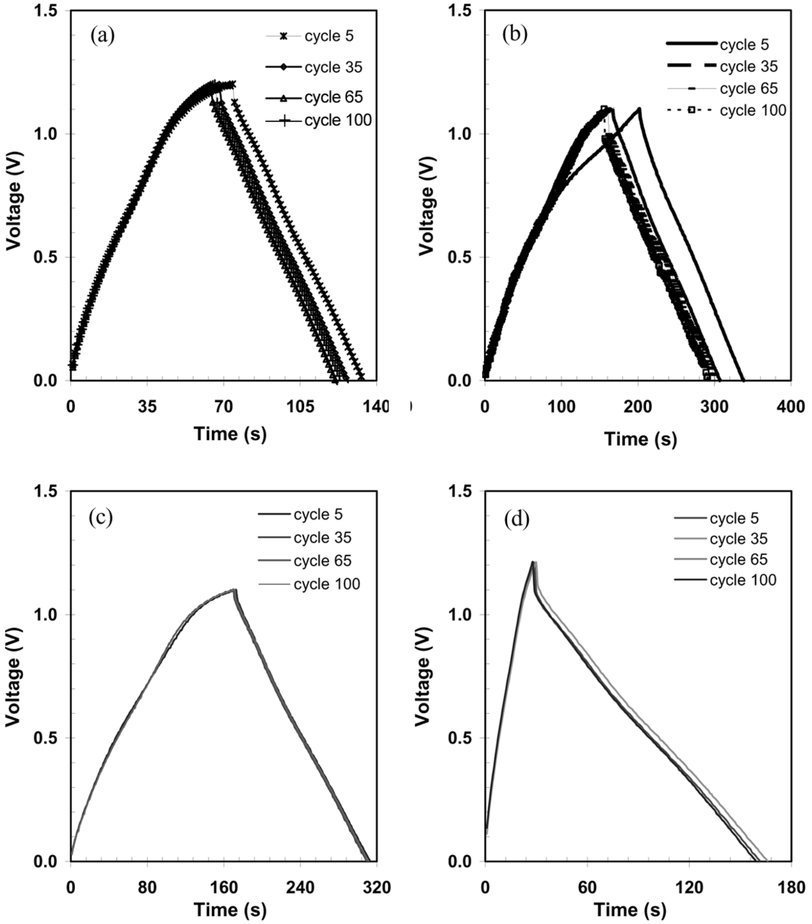

FIGURE 7 The charge-discharge curves for EDLC-3 at room temperature for cycle 5 to 100 for (a) EDLC-1 (b) EDLC-2 (c) EDLC-3 and (d) EDLC-4.

constant. This is explained in terms of the almost equal rate of ion dissociation and association and to the almost equal rate of removal and replacement of protons at the complexation sites. Mobility of the charge carriers increases with temperature in an exponential manner. The conduction mechanism for the binary chitosan-phosphoric system is by quantum mechanical tunneling whereas the conduction mechanism for the other systems can be explained using the OLPT model. The EDLCs fabricated show constant capacitance

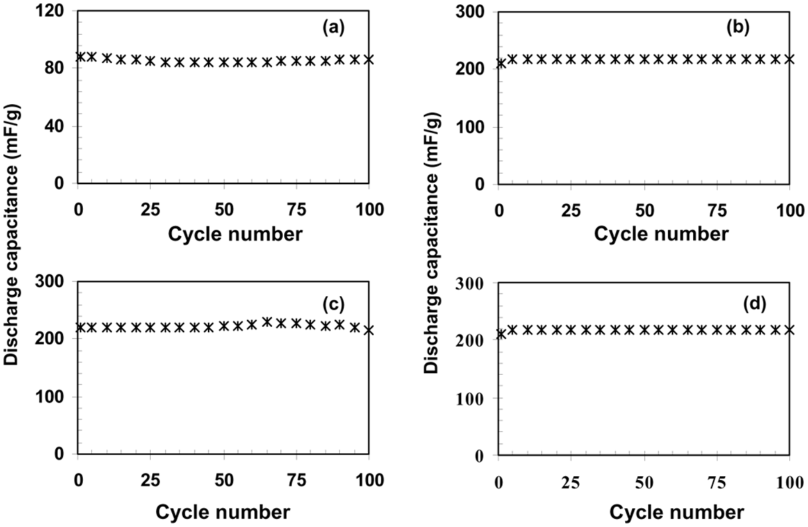

FIGURE 8 Variation of the discharge capacitance as a function of number of cycle for (a) EDLC-1 (b) EDLC-2 (c) EDLC-3 and (d) EDLC-4.

for 100 cycles except for that fabricated from the binary chitosan-phosphoric acid electrolyte which has the lowest conductivity and highest energy of migration of the conducting ions.

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