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Prepared From Chitosan Acetate  
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# Studies of Biodegradable Polymers Electrolytes prepared from Chitosan Acetate with $\text{NH}_4\text{CF}_3\text{SO}_3$ Doping Salt

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**Abstract.** Biodegradable polymer electrolytes materials consisting salt dissolved in high molecular weight chitosan acetate was studied. Mobility and number density of mobile ions of chitosan acetate doped with  $\text{NH}_4\text{CF}_3\text{SO}_3$  and chitosan acetate- $\text{NH}_4\text{CF}_3\text{SO}_3$ -DMC system has been calculated using the Rice and Roth model. The conductivity improved by as much as two orders of magnitude with added salt concentration but the correlation was not apparent. The addition of plasticizer further improved the conductivity. The polymer electrolytes developed were then used in batteries and fuel cells and their performance were evaluated.

## 1.0 Introduction

The interest for polymer electrolytes has been steadily increasing [2]. Polymer electrolytes differ from ceramics, glass and crystal based solid ionic materials with respect to the charge transport mode and ionic conductivity value, which are several orders of magnitude lower than for the latter materials [3]. The conductivity of a polymer complex increases when a salt is dissolved in a polymer matrix as a result of the increase in charge carriers. However the conductivity reaches a maximum as the salt concentration is increased above a certain concentration level. The value of conductivity decreases when the concentration level is further increased. According to Gray [3], solvations of salt in a polymer increasingly introduce a number of transient cross-links in the system, thus making the polymer complex more rigid. The decrease in conductivity has been ascribed to the formation of immobile aggregated species at high salt concentrations. The addition of sufficient entry of high salt concentration can also induce the complex to become crystalline leading to a decrease in conductivity.

In order to obtain a high ionic conductivity,  $\sigma$ , in a material: the concentration of charge carriers and their mobilities have to be high according to:

$$\sigma = \sum \eta_m q_m \mu_m$$

Here  $\eta_m$ ,  $q_m$  and  $\mu_m$  are the concentration, charge and mobility of charge carriers of type  $m$ , respectively. By virtue of this equation and

assuming  $q$  is constant, the increase in conductivity can be attributed to the increase in the number of free mobile ions due to dissociation of the salt.

In the present work, chitosan acetate was doped with  $\text{NH}_4\text{CF}_3\text{SO}_3$ . Chitosan is the product of N-deacetylation of chitin [4]. The transport parameters such as mobility, coefficient diffusion and number of mobile ions have been calculated using the Rice and Roth model [5]. This was done by using the value of activation energy of conduction obtained from the  $\log \sigma$  versus  $1000/T$  plot of the appropriate sample. Conductivity of the system was further enhanced using dimethyl carbonate as plasticizer and the transport parameters of the latter system were also evaluated. The transport parameter of the present work was also compared to the previous work of Chintapalli and co-workers [6] that uses polyethylene oxide (PEO) as host polymer and  $\text{NH}_4\text{CF}_3\text{SO}_3$  as the doping salt. The highest conducting samples in the salted and salted-plasticized samples were used in the fabrication of several electrochemical devices.

## 1. Experimental

### 1.1. Sample Preparation

The polymer electrolytes were prepared by the solution cast technique. 1.00 g of the chitosan powder was dissolved in 100 ml 1% acetic acid solution (Ajax Chemicals). The mixture was stirred continuously with a magnetic stirrer for several hours at room temperature until the chitosan has completely dissolved. Different amounts of  $\text{NH}_4\text{CF}_3\text{SO}_3$  were then added to the

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chitosan solutions and stirred until the salt has completely dissolved. The solutions were then poured into different plastic petri dish and were left to dry at room temperature for the film to form. The plasticized system was prepared by mixing different amounts of dimethyl carbonate to the highest conducting sample of the salted system. The mixtures went through the same process as preparing the chitosan-salt samples and in all these samples the amounts of chitosan and salt were kept constant.

### 1.2. Impedance Measurements

For the impedance measurements, the polymer electrolyte film was sandwiched between two stainless steel electrodes with a diameter of 1 cm. Data was recorded using the HIOKI 3531 Z LCR Hi-tester impedance spectroscopy in the temperature range between 298 K to 373 K.

### 1.3. Electrochemical Cell Studies

#### 3.1. Solid State Battery

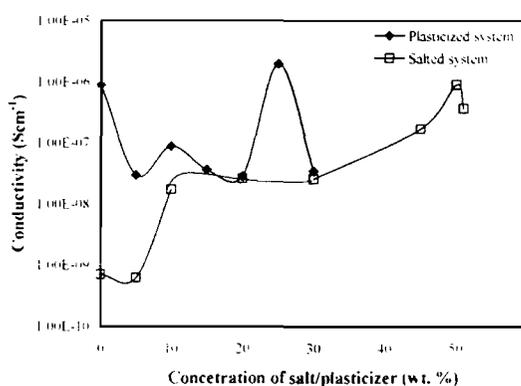
The highest conducting sample was used to fabricate of the batteries. The anode of the battery was made up of a mixture of Zinc, Zinc Sulphate ( $ZnSO_4 \cdot 7H_2O$ ), activated carbon and PVDF with a weight ratio of 60:20:10:10, while the cathode consists of a metal oxide which is  $MnO_2$  (battery grade, Aldrich), activated carbon and PVDF in the weight ratio of 80:10:10. PVDF acts as a binder. The battery was assembled by successively pressing the anode, electrolyte and cathode composition in the same palletizing die to obtain a pellet. The fabricated cell was loaded in a Teflon casing and a good mechanical contact was established by screwing the casing tight.

## 2. Results and Discussion

### 2.1. Conductivity Studies

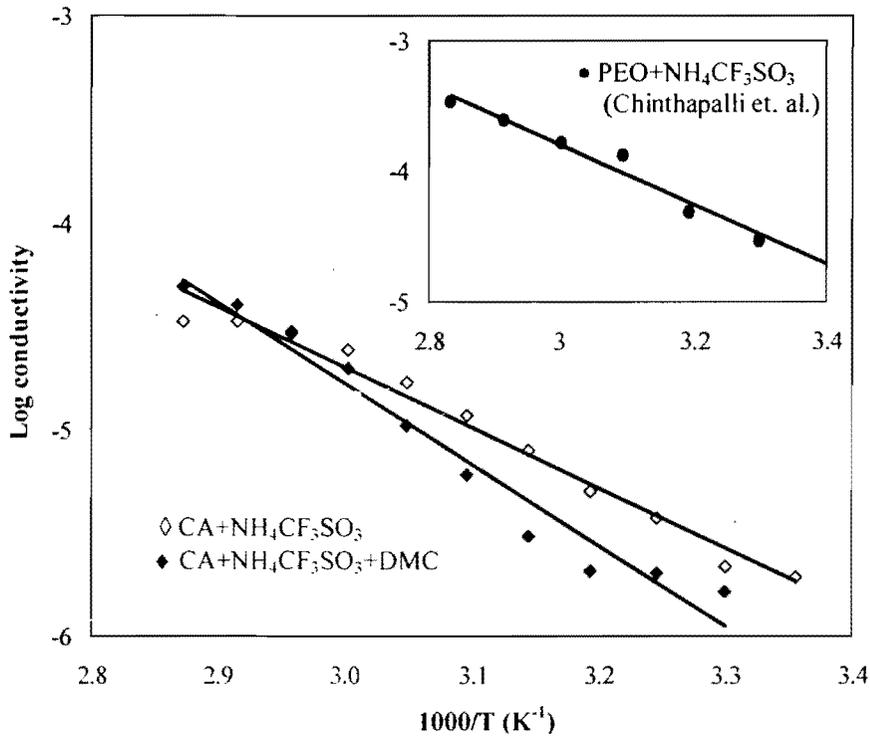
The variation of room temperature conductivity of the system prepared in the present work is shown in Fig. 1. Initially upon addition of 5 wt. % of  $NH_4CF_3SO_3$ , the ionic conductivity decreases. The conductivity then increases by about two orders of magnitude when 10 wt. % of salt was added. The conductivity do not show

any significant change when 20 and 30 wt. % of salt was added. Only after the addition of 45 wt. % of salt, then the conductivity starts to increase again until 50 wt. % of salt was added. When the amount of salt exceeded 50 wt. %, the conductivity decreases. This means that the conductivity of the system was optimized for a salt concentration of 50 wt. %. The conductivity of the salted system was further enhanced with the help of plasticizer. It can be observed that the values of conductivity decreases when 5 wt. % of DMC was added to the system. The conductivity then increases up to 10 wt. % of DMC and then gradually decreases with further addition of plasticizers. The conductivity was optimized at 25 wt. % of DMC. Further increase of DMC leads to a decrease in conductivity. The decrease in conductivity could be attributed to ion association and the increase in conductivity could be attributed to ion dissociation.



**Figure 1** The variation of room temperature conductivity with wt % concentration of  $NH_4CF_3SO_3$

The temperature dependence of the conductivity for the system prepared in the present work and also other polymer electrolyte from previous work which uses the same doping salt is shown in Fig. 2. The plot shows that as temperature increases, the conductivity



**Figure 2** The temperature dependence of the conductivity

increases. Regression values are close to unity (0.97-0.98) suggesting that all the points lie on an almost straight line. This indicates that the plots obey Arrhenius rule given by:

$$\sigma = \sigma_0 \exp(-E_a / kT)$$

Here  $\sigma_0$  is the pre-exponential factor.  $E_a$  is the activation energy,  $k$  is Boltzmann constant and  $T$  is the absolute temperature. Since the conductivity-temperature data obeys Arrhenius

relationship, the nature of cation transport is quite similar to that occurring in ionic crystals, where ions jump into neighboring vacant sites [13]. The activation energy has been calculated from the slope of the line and the values are tabulated in Table 1.

## 2.2. Transport Studies

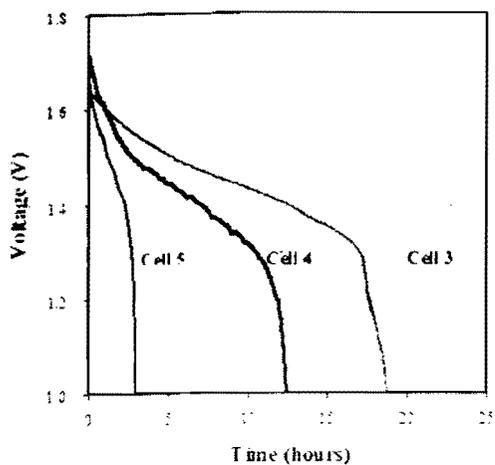
Using the Rice and Roth model, the transport parameters for the samples have been calculated and the values are tabulated in Table 1.

**Table 1**

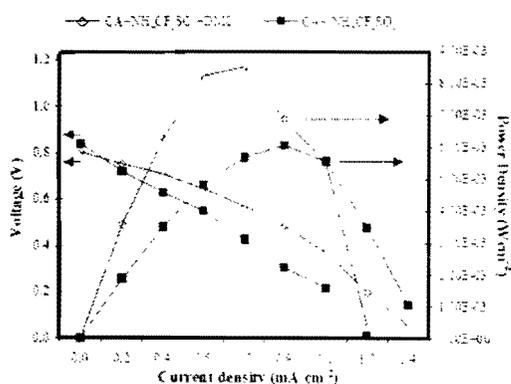
Sample	Temperature (K)	$E_a$ (eV)	$\tau$ (s)	$\mu$ ( $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ )	$D$ ( $\text{cm}^2 \text{s}^{-1}$ )	$n$ ( $\text{cm}^{-3}$ )
CA:AT (1:1)	298	0.78	$8.02 \times 10^{-14}$	$1.61 \times 10^{-8}$	$4.14 \times 10^{-10}$	$3.45 \times 10^{20}$
CA:AT:DMC (1:1:0.5)	298	0.60	$9.11 \times 10^{-14}$	$1.42 \times 10^{-8}$	$3.65 \times 10^{-10}$	$6.96 \times 10^{20}$
PEO:AT (2:1)	293	0.49	$5.07 \times 10^{-14}$	$0.65 \times 10^{-8}$	$1.64 \times 10^{-10}$	$1.90 \times 10^{22}$

It can be observed that the plasticized samples of the present work have a higher number density of mobile ions when compared to the salted system. This shows that the plasticizer has helped in dissociating more free ions which in turn enhanced the conductivity as shown in Fig.

1. When compared to the work of Chintapalli et al [6] using PEO- $\text{NH}_4\text{CF}_3\text{SO}_3$ , the number density of ions of this system is higher by one order of magnitude from the present work. This is reflected by the higher conductivity of the sample at 293 K which is one order of magnitude



**Figure 4** Discharge curves using sample CA:  $\text{NH}_4\text{CF}_3\text{SO}_3:\text{DMC}$  (1:1:0.5) at different current rates of 0.4 mA, 0.5mA and 1mA



**Figure 5** The voltage and power density versus current density plots of both cells operating at ambient temperature

### 3. Conclusions

Polymer electrolyte which uses chitosan as host polymers and  $\text{NH}_4\text{CF}_3\text{SO}_3$  as the doping salt has been developed. Conductivity was enhanced using DMC as plasticizer. The transport parameters of the samples were calculated using

the Rice and Roth model. It was found that conductivity could be attributed to the increase in the number of mobile ions. The transport parameters of the present study were also compared to previous system which uses the same salt but with different polymer which was PEO. Electrochemical cells were fabricated and the performances were evaluated. The polymer electrolytes prepared in the present study was able to drive a battery capacity of ~6 mAh.

### References

- [1] Y.G. Andreev, P.G. Bruce, *Electrochim. Acta* 45 (2000) 1417-1423
- [2] M. Armand, *Solid State Ionics* 69 (1994) 309-319
- [3] F.M. Gray, *Solid Polymer Electrolytes: Fundamentals and Technological Applications*, VCH Publishers, Inc., 1991
- [4] R.A.A. Muzzarelli, *Native, Industrial and Fossil Chitins*, In *Chitin and Chitinases* Edited By P.Joles and R.A.A. Muzzarelli. Birkhäuser Verlag 1999
- [5] M.J. Rice, W.L. Roth, *J. Solid State Chem.* 4 (1972) 29-40
- [6] Sangamithra Chintapalli, Corbin Zea, Roger Frech, *Solid State Ionics* 92 (1996) 205-212
- [7] M. Vijayakumar, S. Selvasekarapandian, D. Jayanthi, R. Kavitha, R., *Solid State Ionics* 154-155 (2002) 773- 777
- [8] S.R. Majid, A.K. Arof, *Physica B* 355 (2005) 78-82
- [9] K. Okuyama, K. Noguchi, M. Kanenari, T. Egawa, K. Osawa, K. Ogawa, *Carbohydrate Polym.* 41 (2000) 237-247
- [10] K.K Maurya, S.A. Hashmi, And S. Chandra. *J. Phys. Soc. Japan* 61 (1992) 1709-1716
- [11] S.A Hashmi, A. Kumar, K.K Maurya. S. Chandra, *J. Phys. D: Appl. Phys.* 23 (1990) 1307-1314
- [12] P. Mukoma, B.R. Jooste, H.C.M. Vosloo. *J. Power Sources* 136 (2004) 16-23
- [13] S. Ramesh, A.K. Arof, *J. Power Sources* 99 (2001) 41-47