

Short communication

# Protonic battery based on a plasticized chitosan-NH<sub>4</sub>NO<sub>3</sub> solid polymer electrolyte

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## Abstract

Plasticized chitosan-proton conductor polymer electrolyte films were prepared by dissolving chitosan powder, ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>) salt and ethylene carbonate (EC) plasticizer in acetic acid solution. The highest conductivity of the chitosan-salt with 40 wt.% NH<sub>4</sub>NO<sub>3</sub> in the film at room temperature was  $8.38 \pm 4.11 \times 10^{-5} \text{ S cm}^{-1}$  and this increased to  $9.93 \pm 1.90 \times 10^{-3} \text{ S cm}^{-1}$  with 70 wt.% EC. Batteries with a configuration of: Zn + ZnSO<sub>4</sub>·7H<sub>2</sub>O/18 wt.% CA-12 wt.% NH<sub>4</sub>NO<sub>3</sub>-70 wt.% EC/MnO<sub>2</sub> provided an open-circuit voltage of  $1.56 \pm 0.06 \text{ V}$ . The discharge characteristics using a 1 mA constant current demonstrated a capacity of  $17.0 \pm 2.6 \text{ mAh}$ . The internal resistance was  $29.8 \pm 5.1 \Omega$ . While the highest power density was  $8.70 \pm 1.91 \text{ mW cm}^{-2}$ .

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## 1. Introduction

Chitosan is a biopolymer and has various usages. It is a unique polysaccharide and attracts much attention in many fields such as manufacturing and medicine [1]. Recently chitosan have been used as a polymer host to study solid polymer electrolytes (SPE) for batteries [2–5] and the proton exchange membranes (PEM) for fuel cells [6,7]. A proton conductor based on chitosan-NH<sub>4</sub>NO<sub>3</sub> has been reported with a conductivity around  $10^{-5} \text{ S cm}^{-1}$  at room temperature [8]. However, this conductivity value is too low for application in a solid-state protonic battery.

To enhance the conductivity, several approaches were suggested in the literature, including the use of blend polymers, the addition of a ceramic filler, plasticizer and even radiation. Compared to other methods, plasticization is the simplest, lowest cost and most effective way to improve the conductivity of a SPE. Among a number of plasticizers, the most used plasticizers are ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC) and diethyl carbonate (DEC) [9].

To the best of our knowledge there are no systematic studies on proton batteries based on a chitosan SPE. In this paper, a study is carried out on chitosan-NH<sub>4</sub>NO<sub>3</sub>-EC systems, and then applied to Zn + ZnSO<sub>4</sub>·7H<sub>2</sub>O/MnO<sub>2</sub> proton batteries.

## 2. Experimental

Chitosan films were prepared from highly viscous powder supplied by Chito-Chem, Malaysia. One gram of chitosan was dissolved in 100 ml of 1% acetic acid solutions. NH<sub>4</sub>NO<sub>3</sub> (Merck) and EC (Aldrich) were added accordingly. The mixture was dispersed and stirred for 24 h. After complete dissolution, the solutions were cast onto petri dishes and left to dry by evaporation at room temperature (25 °C) to form films of pure chitosan acetic (CA), CA-NH<sub>4</sub>NO<sub>3</sub> and CA-NH<sub>4</sub>NO<sub>3</sub>-EC. The films were then transferred into a desiccator for continuous drying.

When the films were formed, they were cut into a suitable size and placed between blocking stainless steel electrodes in a conductivity cell which was connected to a computer. Electrical conductivity measurements were performed using an Autolab PGSTAT 30 Frequency Response Analyzer (Eco Chemie B.V.) in a frequency range of between 1 Hz and 1 MHz. The measurements were carried out at room temperature.

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Batteries were fabricated from the film CA-NH<sub>4</sub>NO<sub>3</sub>-EC that gave the highest electrical conductivity. 4.5 g Zn of powder (Merck) and 1.5 g of ZnSO<sub>4</sub>·7H<sub>2</sub>O (Univar) were mixed with acetylene black (AB, Gunbai) and polytetrafluoroethylene (PTFE, Fluka) to form an anode pellet of the battery, while a mixture of 4.5 g MnO<sub>2</sub> (Aldrich) with AB and PTFE were used to form the cathode pellet. Stainless steel mesh was used as a current collector in the middle of the pellet.

Three batteries were used in order to get an average and standard deviation values. The open-circuit voltage (OCV) was measured for the batteries stored at an open-circuit condition for 24 h. The batteries were discharged using a constant current of 1 mA. Current drains ranging from 2.0 μA to 100.0 mA were used to plot the current–voltage (*I*–*V*) and current density–power density (*I*–*P*) curves. The average of each battery's voltage was monitored for each current drain after 10 s of operation. All the battery characteristics were measured by using the galvanostat of Autolab PGSTAT 30 GPES (Eco Chemie B.V.).

### 3. Results and discussion

#### 3.1. Solid polymer electrolytes characterization: CA-NH<sub>4</sub>NO<sub>3</sub> system

Films with a composition of CA-40 wt.% NH<sub>4</sub>NO<sub>3</sub> had the lowest bulk resistance (*R*<sub>b</sub>) with an average of 55.0 Ω and the calculated surface contact was around 20.1 Ω. From the *R*<sub>b</sub> the specific conductivity of the polymer electrolyte was calculated to be  $8.38 \pm 4.11 \times 10^{-5} \text{ S cm}^{-1}$  at the room temperature. The value was almost similar to the previous research by Majid and Arof [8] which gave an electrical conductivity  $2.53 \times 10^{-5} \text{ S cm}^{-1}$  with 45 wt.% NH<sub>4</sub>NO<sub>3</sub>.

Other electrical conductivity values with different amounts of NH<sub>4</sub>NO<sub>3</sub> are given in Fig. 1. It can be observed that the elec-

trical conductivity increases sharply with addition of 10 wt.% of NH<sub>4</sub>NO<sub>3</sub> and it increases by an order of magnitude when a 10–40 wt.% of NH<sub>4</sub>NO<sub>3</sub> was added to the CA. In the preparation of the films, 100 ml of acetic acid solution was used to dissolve 1 g of chitosan. Different amounts of NH<sub>4</sub>NO<sub>3</sub> were added to each solution. Hence, the volume of the host matrix (the volume of acetylated chitosan) was the same for all the films. As more and more NH<sub>4</sub>NO<sub>3</sub> was added, the host matrix became more crowded with dopant ions. Such overcrowding reduces the number of charge carriers due to the limitation of ionic mobility [2]. Thus, the conductivity decreases after 40 wt.% NH<sub>4</sub>NO<sub>3</sub>.

#### 3.2. Solid polymer electrolytes characterization: CA-NH<sub>4</sub>NO<sub>3</sub>-EC system

Fig. 2 shows the variation of conductivity as a function of plasticizer content in a CA-40 wt.% NH<sub>4</sub>NO<sub>3</sub> system at room temperature. It can be observed that the highest conductivity at room temperature was  $9.93 \pm 1.90 \times 10^{-3} \text{ S cm}^{-1}$ , and achieved for the film with 70 wt.% EC (18 wt.% CA-12 wt.% NH<sub>4</sub>NO<sub>3</sub>-70 wt.% EC). The value of *R*<sub>b</sub> decreases at about 54.5 Ω and the surface resistance was at 19.7 Ω when compared to the highest unplasticized film. An addition of concentration of EC beyond 70 wt.% causes the poor mechanical strength. Therefore, the amount of EC was maintained below 70 wt.% to ensure the acceptable mechanical properties.

On addition of salt, the conductivity continued to increase by increasing the ion content up to a certain amount. It can be inferred that the salt was responsible for the conductance of the chitosan-based films. However the EC did not increase the ion numbers, but the role of the EC was to dissociate the salt thereby increasing the numbers of mobile ions, which lead to conductivity enhancement [10,11].

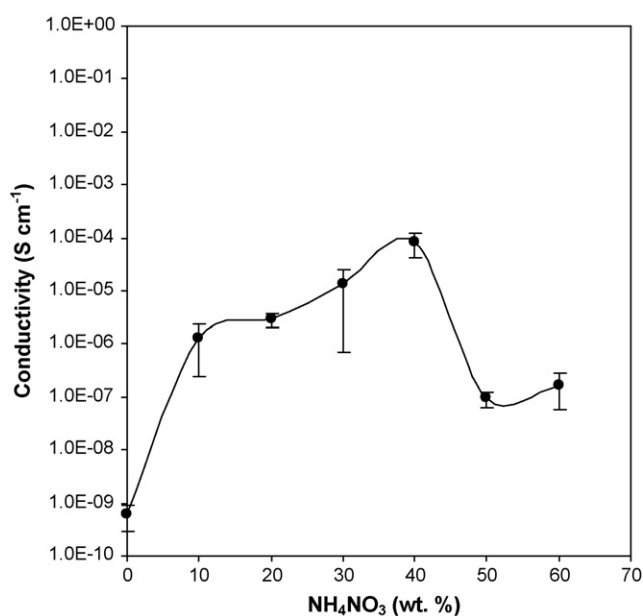


Fig. 1. Electrical conductivity vs. NH<sub>4</sub>NO<sub>3</sub> concentrations in CA at room temperature.

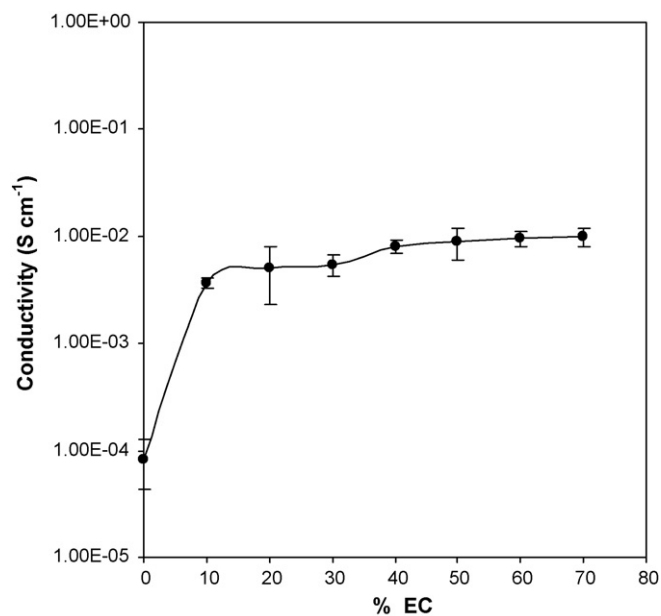


Fig. 2. Electrical conductivity vs. EC concentrations in CA-40 wt.% NH<sub>4</sub>NO<sub>3</sub> at room temperature.

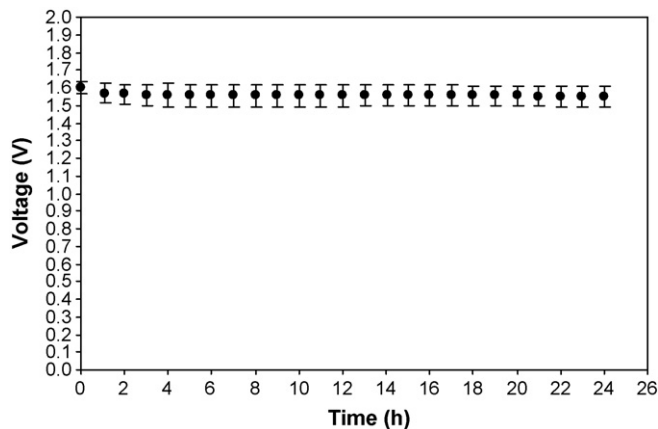


Fig. 3. Protonic battery open-circuit voltage during 24 h of storage.

### 3.3. Battery characterization

The OCV characteristic of the proton batteries at room temperature is shown in Fig. 3. There seems to be a voltage delay at the time of assembly when the voltage was observed higher in the first 2 h and later stabilized at  $\sim 1.56$  V. The OCV remained constant at  $1.56 \pm 0.06$  V until the 24th hour of storage.

Fig. 4 shows the discharge characteristic of three batteries at a constant current of 1 mA. It can be observed that the voltage of the batteries drop immediately before reaching a flat discharge plateau at  $1.30 \pm 0.04$  V. This phenomenon may be due to the activation polarization. The activation polarization was present when the rate of an electrochemical reaction at an electrode surface was controlled by sluggish electrode kinetics [12]. It also shows that the discharge was sustained for  $17.0 \pm 2.6$  h until the cut-off voltage of 1.00 V. The discharge capacity was  $17.0 \pm 2.6$  mAh, which was greater compared to reports elsewhere [13].

Fig. 5 shows the  $I$ - $V$  and  $I$ - $P$  characteristics for the protonic batteries at room temperature. The  $I$ - $V$  curve had a simple linear form, which indicates that the polarization on the electrode was primarily dominated by ohmic contributions. The plot of the operating  $I$ - $P$  suggests that the contact between electrolyte/electrodes was good. The voltage

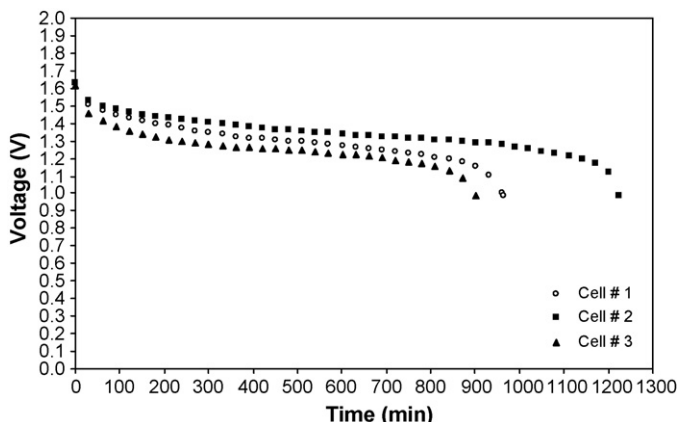


Fig. 4. Discharge curves using a constant current at 1 mA.

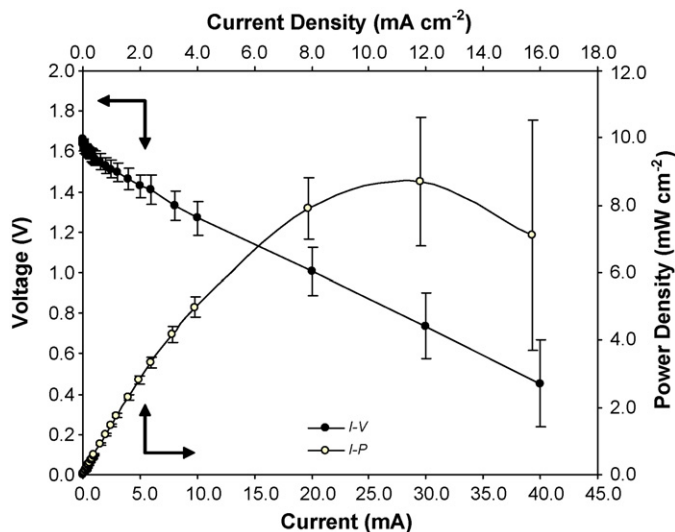


Fig. 5. The plot of  $I$ - $V$  and  $I$ - $P$  for proton batteries.

of the battery dropped to a short circuit current density of  $16.0 \text{ mA cm}^{-2}$  and the maximum power density was determined to be  $8.70 \pm 1.91 \text{ mW cm}^{-2}$ . The internal resistance of the battery was obtained from the gradient of the  $I$ - $V$  graph, which was  $29.8 \pm 5.1 \Omega$ , which was lower than other chitosan-based SPE batteries [4,5].

## 4. Conclusion

The conductivity of  $\text{CA-NH}_4\text{NO}_3$  was successfully increased from  $10^{-5}$  to  $10^{-3} \text{ S cm}^{-1}$  employing a plasticization method using EC. This proton conductor was evaluated for protonic batteries at room temperature with the achievement of an OCV of  $1.56 \pm 0.06$  V, the discharge capacity of  $17.0 \pm 2.6$  mAh and a maximum power density of  $8.70 \pm 1.91 \text{ mW cm}^{-2}$ . These results imply that  $\text{CA-NH}_4\text{NO}_3$ -EC is a promising proton conductor for proton batteries.

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