

Application of Liquid Gel Polymer Electrolyte Based on Chitosan–NH₄NO₃ for Proton Batteries

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ABSTRACT: Liquid gel polymer electrolyte (LGPE) based on chitosan, ammonium nitrate, and acetic acid with a ratio of 1.9 : 0.17 : 96.3 wt % gives the highest conductivity of $(1.46 \pm 0.07) \times 10^{-1} \text{ S cm}^{-1}$ at room temperature. This optimized composition of electrolyte is then used in proton batteries with the configuration of Zn + ZnSO₄·H₂O/LGPE/MnO₂. The open circuit voltage of battery is 1.41 V during

48 h of storage. The battery obtained a discharge capacity of 27.90 mA h⁻¹ upon discharge at 1.0 mA current. The maximum power density for the battery is 3.67 mW cm⁻². © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 1240–1243, 2010

Key words: polymer gel electrolytes; ionic conductivity; chitosan; ammonium nitrate; proton battery

INTRODUCTION

Gel polymer electrolytes (GPE) are currently of great interest commercially as they are seen as an attractive alternative to solvent-free systems because of their higher ionic conductivity.¹ GPEs are composed of gel-type polymer matrices with or without solvents or plasticizers. The GPE can be divided into two categories: (a) liquid gel polymer electrolyte (LGPE) and (b) solid gel polymer electrolyte (SGPE). LGPE is liquid flowing gel and SGPE normally use superabsorbent polymers to trap electrolytes. The advantages of using GPE in proton batteries are, first, they can obtain good surface contact and filling property with electrodes. Second, they show high ionic conductivity by trapping volatile organic solvents in polymer cages formed in polymer matrices, and their fabrication methods are simple.

Chitosan polymer-based electrolytes have normally been used as solid polymer electrolytes (SPE) in the fabrication of proton batteries.^{2,3} Chitosan is a neutral polymer; when it swells in water, its amine group may be protonated and this will lead to ionic conductivity.⁴ The conductance behavior of the chitosan polymer electrolytes is affected by the dopant addition that is added to make the chitosan a proton (H⁺) conductor. The addition of ionic salt helps to increase the conduction of electrolyte as the mobile

charge carrier whether in solid, liquid, or gel forms.⁵ The use of NH₄NO₃ as the salt in chitosan acetate (CA) SPE gives conductivity in the order of 10⁻⁵ to 10⁻³ S cm⁻¹.^{2,6}

In this work, LGPEs of chitosan–NH₄NO₃ are prepared to improve the conductivity and interface problem that are presented during the characterization of proton batteries. The highest conductivity of chitosan + NH₄NO₃ + acetate acid solvent is used for electrochemicals with an optimum composition to obtain the highest proton characteristics of batteries. Electrochemical characterizations, such as open circuit voltage (*V*_{oc}), discharge characteristics and current-voltage (*I*-*V*), and current density-power density (*J*-*P*) measurement will be presented in this report.

EXPERIMENTAL

LGPE was prepared by dissolving 1.0 g chitosan powder (Chito-Chem, Malaysia) in 50 mL of 1% acetic acid solution. Acetic acid was used to dissolve chitosan powder. Ammonium nitrate salt (NH₄NO₃, Riedel-de Haën, Hanover, NH) was then added into the mixture with different concentrations and stirred thoroughly for 5 h at room temperature (25°C). The samples were coded as CA-0N (control sample, without NH₄NO₃), CA-30N, CA-60N, and CA-90N for pure CA, CA with 30 wt % NH₄NO₃, CA with 60 wt % NH₄NO₃, and CA with 90 wt % NH₄NO₃, respectively. The ionic conductivities of the GPE samples were measured by impedance spectroscopy using Auotolab PGSTAT 30 Frequency Response Analyzer (Eco Chemie B.V., Netherlands) between

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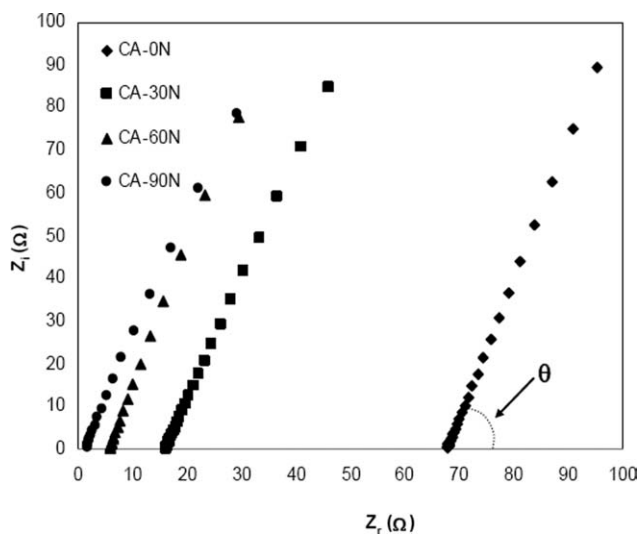


Figure 1 Impedance spectrum for chitosan gel electrolyte at various concentrations of NH₄NO₃ at room temperature.

frequencies of 0.1 Hz and 1.0 MHz. Viscosities of the samples were measured at room temperature with Haake viscotester VT550.

Anode pellet was prepared by mixing zinc powder (Zn, Merck), zinc sulfate heptahydrate (ZnSO₄·7H₂O, Univar), polytetrafluoroethylene (PTFE, Fluka), and acetylene black (AB, Gunbai). All mixtures for anode pellets were pressed using hydraulic pressing to sandwich a stainless steel mesh as current collector in the middle of the pellets. A mixture of MnO₂ (Sigma-Aldrich), PTFE (Fluka), and AB (Gunbai) was prepared to form cathode pellet following the same method used for anode.

Proton batteries were fabricated using the optimum composition of CA-NH₄NO₃ with the highest ionic conductivity. Three batteries were tested to get an average value. The V_{oc} was measured for 48 h at room temperature with no current flow between the electrodes. The batteries were discharged at the constant current of 1.0 mA. To plot the I - V and J - P curves, the batteries were discharged with various current ranges. The galvanostat of Autolab PGSTAT 30 GPES (Eco Chemie B.V.) was used to characterize the batteries.

RESULTS AND DISCUSSION

Liquid polymer gel electrolytes characterization

Figure 1 shows the impedance spectrum of the LGPE sample with various concentrations of NH₄NO₃. Bulk resistance (R_b) was obtained from the interception of impedance spectrum on the real-axis. R_b values decreased when concentration of NH₄NO₃ was increased. Normally, blocking electrodes were used to analyze the impedance spectrum where the interface between electrodes and electrolyte can be

regarded as a capacitance. The ideal capacitance should be a vertical line in the impedance spectrum. However, the spike angles (θ) shown in Figure 1 are about 70°. This can be explained by the roughness interface and inhomogeneous surface contact between the electrodes and electrolyte. However, these θ are higher compared to solid-state chitosan polymer electrolyte system that gave only about 50°. This shows that the chitosan LGPE in this work gave better electrodes and electrolyte surface contact.

The conductivity of GPE was then calculated using the value of R_b . The conductivity value for pure chitosan was $(0.34 \pm 1.23) \times 10^{-4} \text{ S cm}^{-1}$. However, the highest conductivity obtained was $(1.46 \pm 0.07) \times 10^{-1} \text{ S cm}^{-1}$ at 90 wt % of NH₄NO₃, which is higher than previous results used for proton batteries.² When the concentration of NH₄NO₃ was beyond 90%, the gel became less viscous. Therefore, to ensure the best performance of LGPE, the optimum amount of NH₄NO₃ is 90%. Figure 2 shows the values of conductivity obtained at different amounts of NH₄NO₃. The increase in conductivity was contributed by the increase of charge carrier movement with added NH₄NO₃.

Further understanding of the conductivity behavior of this chitosan GPE can also be explained by the plot of dielectric constant (ϵ_r) versus log frequency as plotted in Figure 3. The plot shows the frequency dependence of ϵ_r for different concentrations of NH₄NO₃ at room temperature. The ϵ_r values are very high at low frequency. As the concentration of NH₄NO₃ increased, the ϵ_r values also increased at the same value of frequency. Meanwhile, the increased number of H⁺ free mobile ions was contributed by NH₄NO₃. The values of ϵ_r can be used as an indicator to show that the increase in

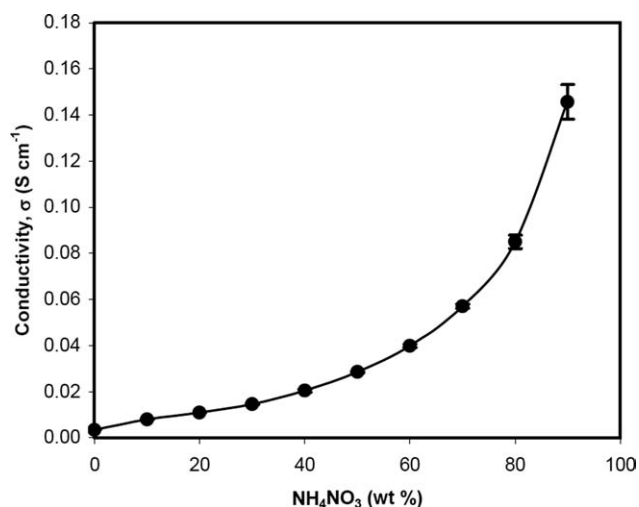


Figure 2 Dependence conductivity of chitosan electrolyte with different compositions of NH₄NO₃ at room temperature.

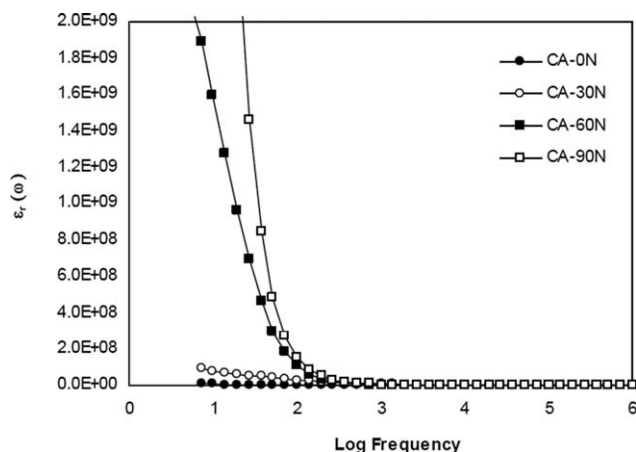


Figure 3 Frequency dependence of dielectric constant (ϵ_r) for different NH_4NO_3 concentrations at room temperature.

conductivity is due to an increase in the number of free H^+ mobile ions; ϵ_r likewise implies that the fraction increases in stored energy (E) per unit voltage (V) or

$$\epsilon_r = \frac{E}{V} \quad (1)$$

and

$$E = qV \quad (2)$$

where q is the charge, combining eq. (2) and eq. (1), we get eq. (3):

$$\epsilon_r = q \quad (3)$$

In other words eq. (3) shows that the ϵ_r represents the fraction increase in charge. The charge is due to H^+ ions and therefore it can be deduced that the

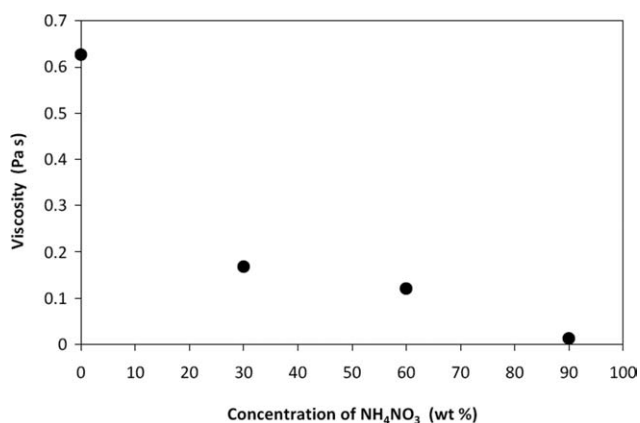


Figure 4 Viscosity of chitosan gel electrolytes with different compositions of NH_4NO_3 at room temperature.

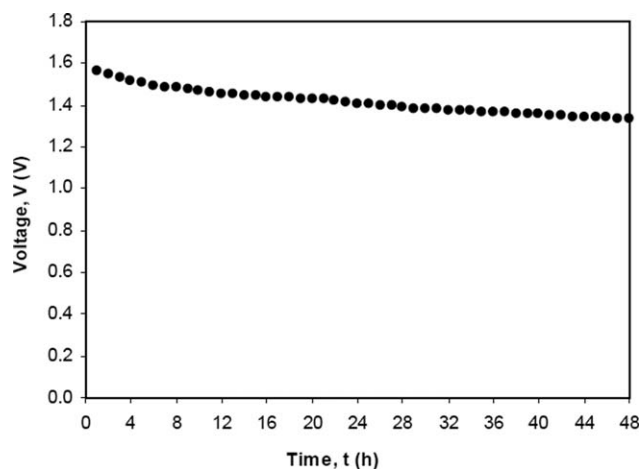


Figure 5 Open circuit voltage of proton battery during 48 h of storage.

increase in ϵ_r reflects the increase in the number of ions.

The intrinsic viscosities of CA- NH_4NO_3 are shown in Figure 4. The value for CA-0N, CA-30N, CA-60N, and CA-90N are 0.63, 0.17, 0.12, and 0.04 Pa s, respectively. It can be seen that CA mixed with NH_4NO_3 salt had significantly lower viscosity than pure CA. Chitosan is a biological product with cationic (positive electrical charge) properties. It poses monomer structure containing amine group, R-NH_3^+ . At the same time, addition of NH_4NO_3 salt supplies H^+ to the system. As a result, repulsion between cations of R-NH_3^+ and H^+ is believe to occur due to the similar charge polarity. Furthermore, this repulsion promotes disentanglement among the main polymer chains. As the polymer chain is separated by each other, the acetate-based solvent could penetrate in between them and contributes to the reduction of the electrolyte viscosity.

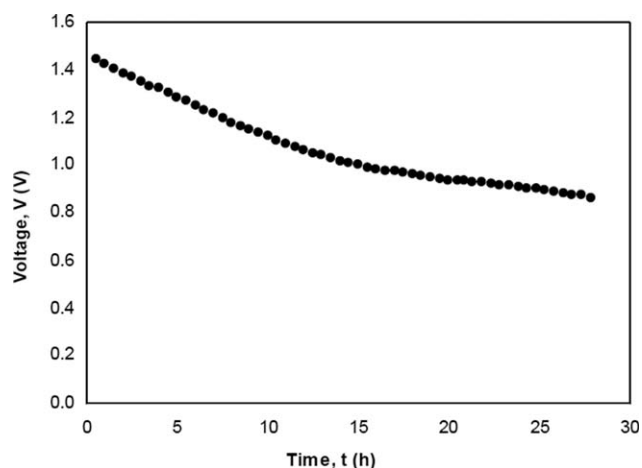


Figure 6 Discharge characteristics of proton batteries 1.0 mA constant current.

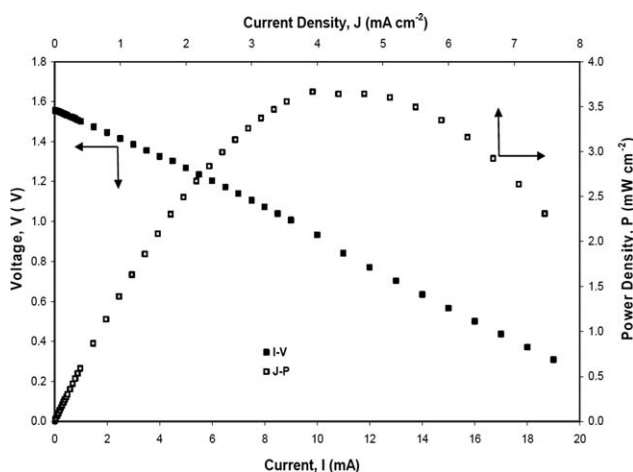


Figure 7 *I-V* and *J-P* for proton batteries.

The decrease in viscosity also agrees with conductivity values.

Batteries characterization

Figure 5 shows the characteristics of open circuit voltage (V_{OC}) of proton batteries with CA-90N. It can be observed that the voltage is initially higher for a few hours and then remains stable. This shows that the fabricated proton batteries are practically stable in an open circuit condition. The batteries give an V_{OC} of 1.41 V after 48 h of storage under no-load condition, comparable with our previous polymer proton batteries.^{2,8}

The discharge profiles for the proton batteries are shown in Figure 6. The plot shows a sloping discharge pattern rather than a plateau region. From our previous reports, the proton batteries discharge pattern can be characterized into two types: (a) for solid-state electrolyte^{2,3} and (b) for gel electrolyte.⁸ For solid-state electrolyte, the voltage plateau region can be well defined. Meanwhile, the sloping pattern only can be produced by gel-type electrolyte. As the electrolyte used in this work is gel-type electrolyte, the sloping pattern can be seen and the batteries are

sustained for 27.90 mA h⁻¹. This is higher than what was reported by Ng and Mohamad,² which is 17.0 mA h⁻¹ for batteries with chitosan-NH₄NO₃ solid-state electrolyte.

Figure 7 shows the *I-V* and *J-P* characteristics for the proton batteries. From the *J-P* plot, it can be observed that the voltage of the battery dropped to a short circuit current density of 7.46 mA cm⁻². The highest power density for proton battery is 3.67 mW cm⁻². *I-V* curve had a simple linear form that gives the internal resistance (r) value calculated from the gradient. Ohmic contributions that primarily dominated the polarization on the electrode gave this linear-type plot. The r value obtained is 66.55 Ω . The r value from this work could be attributed to oxide of the electrode developed during the contact with electrolyte.

CONCLUSION

As expected, this chitosan-NH₄NO₃ LGPE gives the highest conductivity in the order of 10⁻¹ S cm⁻¹. Meanwhile the batteries' properties, namely, V_{OC} of 1.41 V, the highest power density of 3.67 mW cm⁻², and discharge capacity at 27.90 mA h⁻¹, can be considered as good properties for proton batteries. The batteries' properties can be improved with the modification of electrode materials.

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