

Short communication

ZnCl₂- and NH₄Cl-hydroponics gel electrolytes for zinc–carbon batteries

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Abstract

Absorbency testing is used to determine the percentage of ZnCl₂ or NH₄Cl solution absorbed by a hydroponics gel (HPG). It is found that the absorbency of ZnCl₂ or NH₄Cl solution decreases with increasing solution concentration. The conductivity of ZnCl₂- and NH₄Cl-HPG electrolytes is dependent on the solution concentration. A mixture of salt solution with HPG yields excellent gel polymer electrolytes with conductivities of 0.026 and 0.104 S cm⁻¹ at 3 M ZnCl₂ and 7 M NH₄Cl, respectively. These gel electrolytes are then used to produce zinc–carbon cells. The fabricated cells give capacities of 8.8 and 10.0 mAh, have an internal resistance of 25.4 and 19.8 Ω, a maximum power density of 12.7 and 12.2 mW cm⁻², and a short-circuit current density of 29.1 and 33.9 mA cm⁻² for ZnCl₂- and NH₄Cl-HPG electrolytes, respectively.

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1. Introduction

Super-absorbent polymer hydrogels can be defined as polymers that can absorb and retain extremely large amounts of liquid relative to their mass. For this unique characteristic, they have been widely used in various applications such as disposable diapers, soil replacement in agriculture, and drug delivery systems in medicine [1].

The advantages of super-absorbent polymer hydrogels have been identified by polymer electrolyte researchers. Hopefully by utilizing this type of polymer, the problems in polymer batteries such as low conductivity and leakage can be overcome. To date, several types of super-absorbent polymer hydrogel have been examined as gel polymer electrolytes (GPEs), e.g., Nafion® [2,3], hydroponics gel (HPG) [4–8], poly(acrylic acid) [9] and poly(acrylic acid)–poly(ethylene glycol) [10]. Meanwhile, the absorbency property of the electrolyte solution also plays an important role in a GPE, in order to retain the obtained maximum conductivity.

Therefore, the aim of this work is to obtain a suitable concentration of electrolytes to yield optimum conductivity and then to use them to produce batteries. The percentage of solution absorbed by the gel has been identified and the

conductivity of various concentrations of ZnCl₂- and NH₄Cl-HPG are determined. The ZnCl₂- and NH₄Cl-HPG electrolytes with the highest conductivity are used to prepare zinc–carbon cells. The fabricated cells are characterized according to their current–voltage curves (*I–V*), current density–power density curves (*J–P*) and discharged profiles.

2. Experimental

Electrolyte solutions were prepared by mixing ZnCl₂ (R&M Chemical) or NH₄Cl (Merck) with 10 ml distilled water. Then, a 0.5 g sample of HPG grains made from poly(acrylic acid) copolymer (YMWoo Corp., Malaysia, product code: 770453) was added to the solution and homogeneously mixed. The mixture was left at room temperature (25 °C) for 60 min. Absorbency testing was used to determine the percentage of solution that had been absorbed by the gel. The swollen gel was separated from the unabsorbed solution by pouring the unabsorbed solution into a graduated cylinder. The percentage of absorbency was calculated using the following equation:

$$\% \text{ absorbency} = \frac{V_i - V_f}{V_i} \times 100 \quad (1)$$

where *V_i* and *V_f* are the original volume of solution and the volume of unabsorbed solution, respectively.

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Impedance testing was used to measure the conductivity of ZnCl_2 - and NH_4Cl -HPG electrolytes. A frequency response analyser (FRA) module in an Autolab PGSTAT 30 (Eco Chemie, B.V.) system was used to analyze the electrolyte impedance. The high-frequency intercept on the real axis provides the bulk resistance (R_b) of the electrolyte. The conductivity (σ) of the HPG electrolyte can be calculated using the following equation:

$$\sigma = \frac{t}{R_b A} \quad (2)$$

where t and A are the thickness and the area of electrolyte, respectively.

The anode pellet consists of Zn powder (Merck), polytetrafluoroethylene (PTFE, Fluka) and acetylene black (AB, Gunbai) in a weight ratio of 96.0:3.0:1.0. Meanwhile, the cathode pellet was a mixture of MnO_2 (Aldrich), PTFE, and AB in a weight ratio of 90.0:8.0:2.0. A hydraulic press was used to compress the pellets. The cells were then assembled by sandwiching the GPEs between the two electrodes. The I - V curves were measured using different current values. The internal resistance of the cell was then calculated by using equation:

$$V = E - Ir \quad (3)$$

where V is the voltage, E the electromotive force, I the current and r is the internal resistance. The discharge characteristics were measured using a constant current of 1.0 mA. The characteristics of the cells were measured by means of a galvanostatic Autolab PGSTAT 30 GPES instrument (Eco Chemie, B.V.).

3. Results and discussions

3.1. Analysis of ZnCl_2 - and NH_4Cl -HPG electrolytes

HPG grains have a significant impact on the solution uptake which, in turn, determines the ionic conductivity. When HPG grains are mixed with solution, the grains expand and form loosely bound, elastic, jelly granules. The expansion of grains strictly depends on the solution concentration. Fig. 1 shows the variation of percentage absorbency for different concentrations of ZnCl_2 - and NH_4Cl -HPG. Two distinct observations can be made from the plot, namely, (i) the absorbency of pure dis-

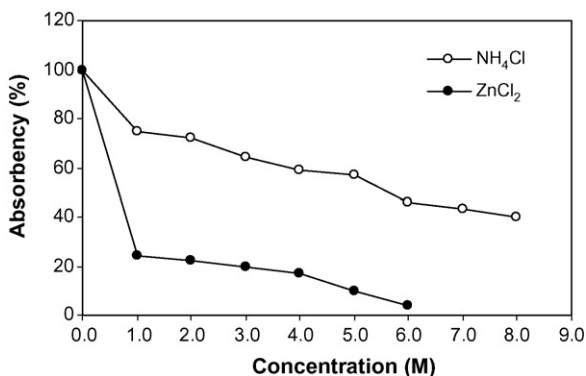


Fig. 1. Variation of percentage absorbency for different concentrations of ZnCl_2 and NH_4Cl to HPG.

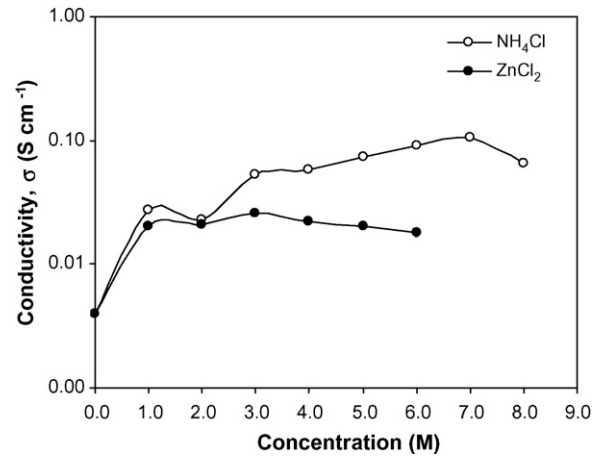


Fig. 2. Variation of conductivity for different concentrations of ZnCl_2 and NH_4Cl to HPG.

tilled water and (ii) the absorbency of electrolyte solution. HPG absorbed 100% of pure distilled water. In fact, HPG grains can absorb almost 500% of pure water, but in this work the volume of water was controlled to only 10 ml in order to minimize the use of salts. It is found that the percentage absorbency of ZnCl_2 -HPG is lower than that of NH_4Cl -HPG. In addition, there is a drastic decrease to about 76% absorbency in the concentration region of 0–1 M for ZnCl_2 -HPG. On the other hand, there is only a small decrease of 25% for NH_4Cl -HPG.

The conductivity for different concentrations of ZnCl_2 - and NH_4Cl -HPG electrolytes is found to depend on the concentration of ZnCl_2 - and NH_4Cl -HPG, see Fig. 2. The conductivity of pure distilled water-HPG is 0.004 S cm^{-1} . The conductivities within the concentration range of 0–1 M for ZnCl_2 - and NH_4Cl -HPG electrolytes increase drastically. Above a concentration of 1 M, the conductivity of ZnCl_2 -HPG electrolyte shows a small increase when compared with NH_4Cl -HPG electrolyte. The conductivity behaviour is also consistent with the absorbency observation, where NH_4Cl -HPG electrolyte shows higher conductivity than ZnCl_2 -HPG electrolyte. The conductivities reach maximum values of 0.026 and 0.104 S cm^{-1} for 3 M of ZnCl_2 -HPG and 7 M of NH_4Cl -HPG electrolyte, respectively. After both electrolytes reached their optimum values, a decrease in conductivity takes place.

Generally, conductivity (σ) is given by equation $\sigma = nq\mu$, where: n is the number of free mobile ions; q the electronic charge; μ is the ionic mobility. When the concentration of the ZnCl_2 - or NH_4Cl -HPG increases, or in other words the number of n increases, the conductivity will increase. Therefore, the increase in conductivity in the concentration region of 0–3 M for ZnCl_2 -HPG and 0–7 M for NH_4Cl -HPG electrolytes is attributed to the increase of n inside the HPG granules. Since absorbency of NH_4Cl solution into HPG grains is higher, its conductivity will be higher compared with ZnCl_2 -HPG electrolytes. On the other hand, the reduction in conductivity after the maximum point is due to decreasing μ when ions start to pair up. The highest conductivity of the gel electrolytes at a concentration of 3 M of ZnCl_2 -HPG and 7 M of NH_4Cl -HPG was selected as

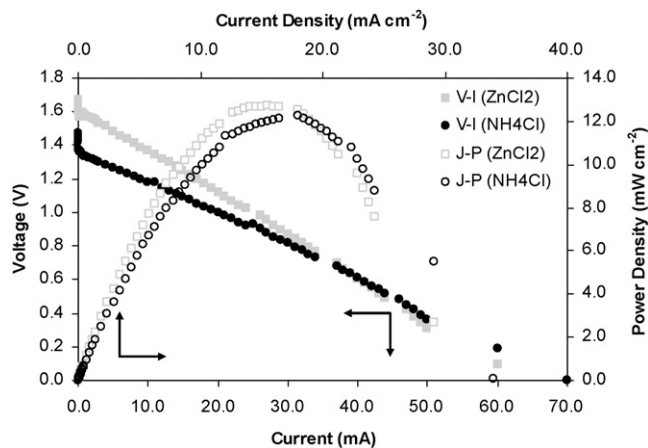


Fig. 3. I - V and J - P curves for ZnCl_2 - and NH_4Cl -HPG cells.

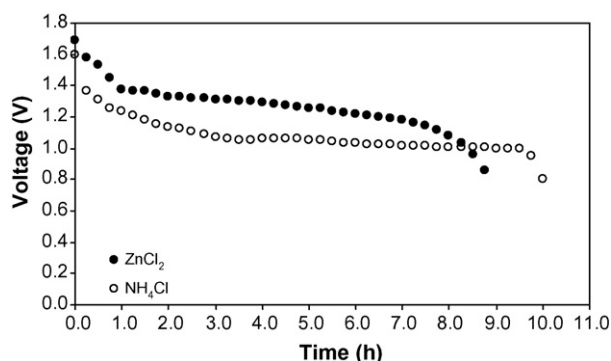


Fig. 4. Discharge characteristics of ZnCl_2 - and NH_4Cl -HPG cells.

an optimum concentration and therefore a suitable candidate for use in zinc-carbon cells.

3.2. Batteries analysis

Fig. 3 shows I - V and J - P curves for cells based on ZnCl_2 - and NH_4Cl -HPG electrolytes. The r values were calculated from the slopes of the former curves and found to be 25.4 and 19.8 Ω for ZnCl_2 - and NH_4Cl -HPG, respectively. Based on J - P curves, the curves clearly indicate that the highest power densities (P_{\max}) for ZnCl_2 - and NH_4Cl -HPG are almost the same, namely, 12.7 and 12.2 mW cm^{-2} , respectively. In addition, the short-circuit current density (J_{SC}) for ZnCl_2 - and NH_4Cl -HPG is 29.1 and 33.9 mA cm^{-2} , respectively. Fig. 4 shows the discharge characteristic of cells for discharge at constant current of 1.0 mA. It is seen that the open-voltage circuit (V_{OC}) of the cell using ZnCl_2 -HPG electrolyte is comparatively higher than that of the cell employing NH_4Cl -HPG electrolyte. The V_{OC} results from the discharge curves are also consistent with the I - V curves. After discharging the cells for 8.8 and 10.0 h at 1.0 mA, the V_{OC} of the cells is 1.7 and 1.6 V and then falls to a cut-off of ~ 0.8 V for ZnCl_2 - and NH_4Cl -HPG, respectively. The average nominal

voltages are 1.3 and 1.0 V and the capacities obtained are 8.8 and 10.0 mAh, ZnCl_2 - and NH_4Cl -HPG, respectively.

From the electrochemical properties, of the cells, it is observed that the NH_4Cl -HPG cell system exhibits a small improvement compared with ZnCl_2 -HPG. This is in agreement with the data that show the absorbencies and conductivities of NH_4Cl -HPG are both higher than those of ZnCl_2 -HPG electrolyte. Meanwhile, the differences in cell electrochemical observations can be explained by considering the electrolyte-electrode reaction. Since the concentration of NH_4Cl -HPG and ZnCl_2 -HPG was 7 and 3 M, respectively, the surface degradation of the electrode of the NH_4Cl -HPG cell is assumed to be higher. The formation of thick surface degradation during the discharge process hampers a continuous reaction between the electrode and the electrolyte [11].

4. Conclusions

A mixture of ZnCl_2 or NH_4Cl with HPG shows that the conductivity of NH_4Cl -HPG is greater than that of ZnCl_2 -HPG. The conductivity is dependent on the ability of HPG grains to absorb the solution and NH_4Cl -HPG exhibits greater absorbency. Meanwhile, the electrochemical properties of the cells show that the r , P_{\max} , J_{SC} , operation voltage and capacities of the cells range between 19.8–25.4 Ω , 12.2–12.7 mW cm^{-2} , 29.1–33.9 mA cm^{-2} , 1.0–1.3 V and 8.0–10.0 mA h, respectively. Since the electrolyte properties of NH_4Cl -HPG are superior to those of ZnCl_2 -HPG electrolytes, the electrochemical properties of a cell fabricated with NH_4Cl -HPG electrolyte are slightly higher than those of cell using ZnCl_2 -HPG electrolyte.

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References

- [1] F.L. Buchholz, T. Graham, Modern Superabsorbent Polymer Technology, Wiley-VCH, New York, 1998.
- [2] M. Cappadonia, J.W. Erning, S.M.S. Niaki, U. Stimming, Solid State Ionics 77 (1995) 65.
- [3] E. Skou, P. Kauranen, J. Hentschel, Solid State Ionics 97 (1997) 333.
- [4] R. Othman, W.J. Basirun, A.H. Yahaya, A.K. Arof, J. Power Sources 103 (2001) 34.
- [5] R. Othman, A.H. Yahaya, A.K. Arof, J. New Mater. Electrochem. Syst. 5 (2002) 177.
- [6] R. Othman, A.H. Yahaya, A.K. Arof, J. Appl. Electrochem. 32 (2002) 1347.
- [7] A.A. Mohamad, J. Power Sources 159 (2006) 752.
- [8] S.C. Yap, A.A. Mohamad, Electrochem. Solid State Lett. 10 (2007) A139.
- [9] C. Iwakura, K. Ikoma, S. Nohara, N. Furukawa, H. Inoue, J. Electrochem. Soc. 150 (2003) A1623.
- [10] Z. Lan, J. Wu, J. Lin, M. Huang, J. Power Sources 164 (2007) 921.
- [11] M.S. Rahmanifar, M.F. Mousavi, M. Shamsipur, M. Ghaemi, J. Power Sources 132 (2004) 296.