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Hydroponics Polymer Gels for Zn–MnO_2 Alkaline Batteries

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Gel polymer electrolytes (GPEs) were prepared by mixing hydroponics polymer gel (HPG) with 6 M potassium hydroxide (KOH), and the control sample was produced by mixing HPG with distilled water (H_2O). The optimum absorbed volumes obtained for HPG + 6 M KOH and HPG + H_2O were 40 and 10 ml, respectively. The swelling percentage for HPG + 6 M KOH was lower than that for HPG + H_2O. However, both samples reached maximum expansion within 60 min. The engineering strain experienced by HPG + 6 M KOH was lower than that of HPG + H_2O, whereas the compressive stress–strain for HPG + 6 M KOH was higher than that for HPG + H_2O. The maximum conductivity of the gels was obtained at 40 ml of 6 M KOH. Subsequently, Zn–MnO_2 alkaline batteries were fabricated, which provided a discharge capacity ca. 148 mAh g^{-1} and the maximum power density was 7.8 mW cm^{-2}. Moreover, the double-layer capacitances before and after discharge were found to be different.

Keywords: Gel polymer electrolytes (GPEs); mechanical properties; swelling; Zn–MnO_2 alkaline batteries.

1. INTRODUCTION

Superabsorbent polymers (SAPs) are cross-linked three-dimensional networks of hydrophilic polymers that can absorb considerable amounts of H_2O or aqueous fluids to form a stable hydrogel. The absorbed H_2O is hardly removable even under some pressure because the hydrophilic polymer backbone in SAP contains H_2O-loving carboxylic acid groups [1]. In general, an ideal SAP material features the highest absorption capacity (maximum equilibrium swelling) in salt solution, highest absorbency under load, and highest durability and stability in the swelling environment and during storage [2]. SAPs possess a number of characteristics that make them outstanding in many different applications. These excellent characteristics make the conducting hydrogel available for use in fuel cells, dye-sensitive solar cells, and rechargeable batteries [3].

Batteries require solid or gel electrolytes instead of liquid electrolytes because batteries with solid or gel electrolytes are more attractive particularly in terms of reliability, safety, design, and processing ability [4]. Currently, gel electrolytes are commercially of great interest as they are seen as an attractive alternative to solvent-free systems, particularly with regard to achieving higher, more practical ionic conductivities. To date, several types of SAP hydrogels have been examined as gel polymer electrolytes (GPEs), such as hydroponics polymer gels (HPGs), poly(acrylic acid), and poly(acrylic-acid)-poly(ethylene glycol) [5]. HPG is made of poly(acrylic acid) copolymers and has grain sizes of about 1 to 3 mm. It is a well-known polymer because of its high H_2O-holding capacity that is 20 to 100 times its weight, high gel strength, and relatively low cost. When added with a solution, the gel expands, swells, and becomes elastic. As a result, the amount of electrolyte required to occupy a particular cell volume is reduced.

Despite their superb characteristics as multifunctional materials, the low mechanical strength of hydrogels is disadvantageous in practical applications [3]. The most important mechanical properties of GPEs, particularly those for batteries, are their expansion and compression strength, because they act as a medium of ion movement between the anode and cathode. Therefore, GPEs should have sufficient volume for them to make better contact with electrodes particularly during the morphological deformation of the electrode in repeated charge and discharge processes [6].

Therefore, the current work aims to study the mechanical properties of HPG + 6 M potassium hydroxide (KOH) that can be used as minimum standard for the preparation of superabsorbent GPEs. Meanwhile, for application purposes, the ionic conductivity of the HPG + 6 M KOH system was characterized to determine the optimum electrolyte volume and, hence, the maximum conductivity, which were used to fabricate Zn–MnO_2 alkaline batteries.

2. EXPERIMENTAL

The electrolytes were prepared by adding 0.5 g of HPG (poly(acrylic acid) copolymer, YMWOO Corporation, Malaysia; product code: 770453) into KOH solution (ChemAR System). The absorption test was done to determine the optimum volume that can be absorbed by the gel. HPG was also added with distilled H_2O to produce the control sample. The amount of absorbed solution (V) was calculated as follows:

$$V = V_o - V_f \tag{1}$$

where V_o is the volume poured into graduated cylinder and V_f is the volume after absorption. This optimum volume will be used as constant volume in tests such the equilibrium swelling, expansion, and compressive stress–strain tests. The equilibrium swelling test was conducted to estimate the time required for the gel to reach the equilibrium state. The swelling of a single grain of HPG was observed under a Stereo Zoom Microscope. The percentage of swelling (% S) of the gel was calculated as

$$\%S = \frac{m_t - m_o}{m_o} \times 100 \tag{2}$$

where m_t is the mass of the swollen gel at time t and m_o is the mass of the dry gel at time zero. An 8.4 g Teflon load that is 22 mm in diameter was used for the expansion test. The stress applied by this load was approximately equal to 210.5 Pa. The original length (l_o) of the HPG and the final length (l_f) of the swollen gel were measured, and the engineering strain (ε) of the gel can be calculated as

$$\varepsilon = \frac{l_f - l_o}{l_o} = \frac{\Delta l}{l_o} \tag{3}$$

The schematic diagram of the measurement process is shown in Fig. 1(a).

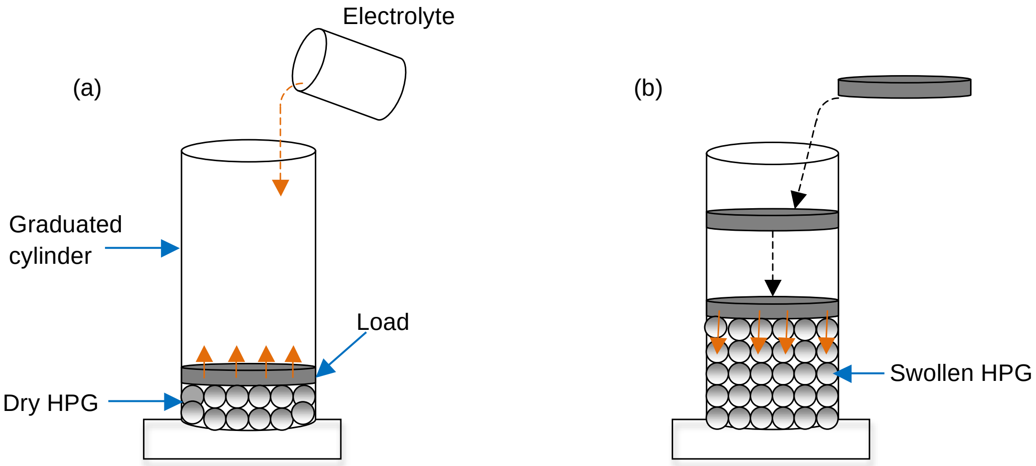

Figure 1. Experimental setup for HPG absorption via (a) expansion and (b) compression.

The test was performed until the swollen gel reached maximum expansion. In other words, the ε of the swollen gel becomes constant no matter how much solution is added. Initially, the l_o of the swollen gel was determined, and then, a Teflon load was applied on top of the swollen gel and left for 5 min before measurement. All grains were assumed to be expended at the same rate. The compressive stress (σ) can be calculated as

$$\sigma = \frac{F}{A} \tag{4}$$

The schematic diagram of the measurement process is shown in Fig. 1(b). A brass load (F) was occasionally added, and the change in length was recorded as the final length l_f. The area (A) of each load was approximately 314.16 mm^2.

The main purpose of the impedance test was to measure the bulk resistance (R_b) of the HPG with different volumes of 6 M KOH. The gel polymer electrolytes were prepared from 0 ml (pure

HPG) to 100 ml of 6 M KOH and were connected to the Frequency Response Analyzer module in the Autolab PGSTAT-30 system. The gel electrolytes were sandwiched between two stainless-steel disk electrodes, which act as blocking electrodes for the ions. The study was performed in the frequency range of 0.1 Hz to 1.0 MHz. R_b can be obtained from the plot of the negative imaginary impedance against real impedance, with the horizontal and vertical axes having the same scale. The GPE conductivity was calculated from the bulk impedance as follows:

$$\sigma = \frac{t}{R_b A} \tag{5}$$

where σ, t, and A are the electrolyte conductivity, thickness, and area, respectively. The conductivity was due to the mobile ions from the salt, and increasing the number of mobile ions enhances conductivity.

The anode pellet consisted of Zn powder (Merck), polytetrafluoroethylene (PTFE, Fluka), and acetylene black (AB, Gunbai). Meanwhile, the cathode pellet was a mixture of MnO_2 (Aldrich), PTFE, and AB. The cells were assembled by sandwiching the GPEs between the anode and cathode electrodes, and the electrochemical impedance spectroscopy (EIS) properties of the cells were obtained using the similar method to test the electrolyte conductivity. At the same time, the double-layer capacitances (C_{dl}) of the cell before and after discharge can be calculated as;

$$C_{dl} = \frac{1}{2\pi f' R_{ct}} \tag{6}$$

where f' is the frequency corresponding to the maximum value of the imaginary component of the semicircle and R_{ct} is the charge transfer resistance.

The cells were then characterized according to their discharged profiles at a constant current using an Arbin system. The I–V curve was measured using different current values. The internal resistance of the cell can then be calculated as

$$V = E - Ir \tag{7}$$

where V is the voltage, E is the electromotive force, I is the current, and r is the internal resistance. Moreover, the J–P curve was also obtained as the secondary result of the I–V curve.

3. RESULTS AND DISCUSSION

3.1. HPG Electrolyte

Initially, the HPG are grains. However, when they were added into a solution, they expanded and form loosely bound jelly-like particles. Fig. 2 shows the variation of the absorbed solution for different volumes of KOH and H_2O solutions. At low solution volumes (10 ml), the HPG added with KOH was slightly different from that added with distilled H_2O. When the solutions were increased to 100 ml, HPG absorbed only about 5 ml of KOH, whereas the H_2O absorption of HPG showed a linear relationship.

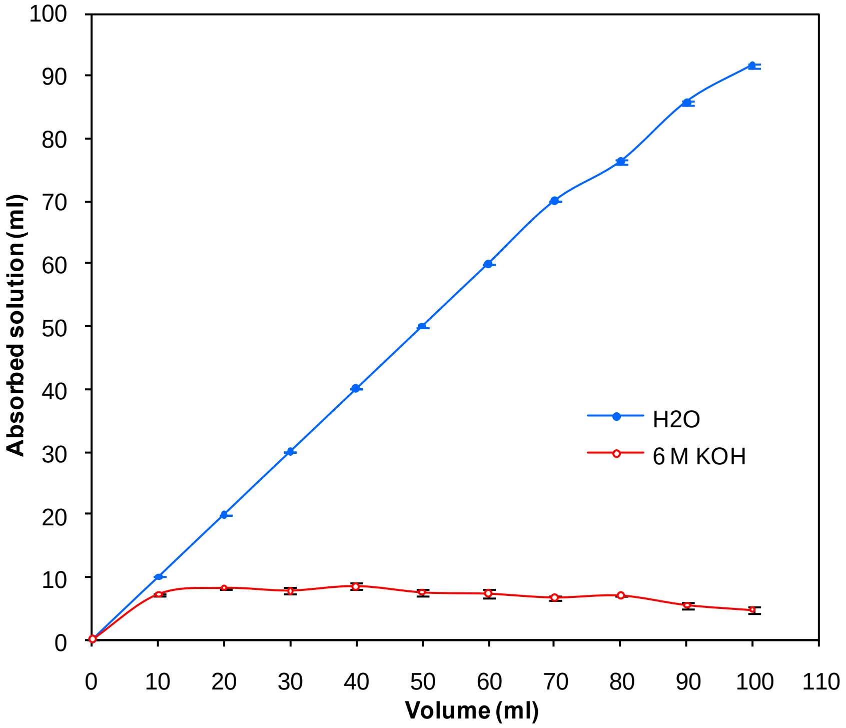

Figure 2. Absorbed solution in HPG at various volumes.

The H_2O absorption of HPG occurred through H bonding with H_2O molecules. Low osmotic pressure in HPG made H_2O easier to diffuse into the spaces between polymeric chains. However, the presence of valence cations in the KOH solution impeded the polymer's ability to bond with the H_2O molecules and thus resulted in HPG swelling. According to Bajpai and Giri [7] and Ramazani-Harandi [8], the ionic dependence of swelling balances between the osmotic pressure and elastic response of the polymeric material. Increasing ionic concentration reduces the mobile ion concentration difference between the polymer gel and external medium (osmotic swelling pressure) and thus reduces the gel volume. In other words, the gel shrinks. This explanation agrees well with the current results. With 40 ml of KOH, the HPG absorption was reduced.

Figs. 3 and 4 show the HPGs in 40 ml of KOH and H_2O, respectively. The figures show that the % of swelling in both length (Y-axis) and width (X-axis) increase with time. Initially, the HPG grains were mostly sugar-like particles with irregular shapes. When added with a solution, the gel started to swell into loosely bound jelly-like particles (soft and elastic). The longer the gel stayed in the solution, the more it expanded. The swelling of the HPG + KOH was lesser than that of the HPG + H_2O.

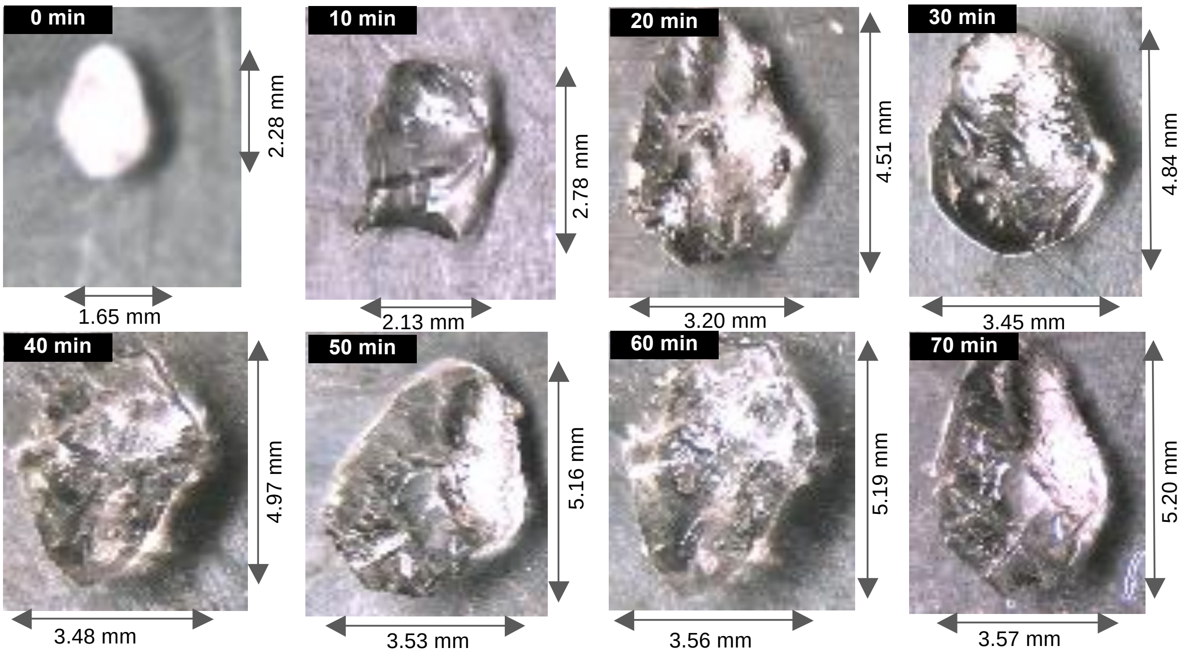

Figure 3. HPG after immersion in 40 ml of 6 M KOH.

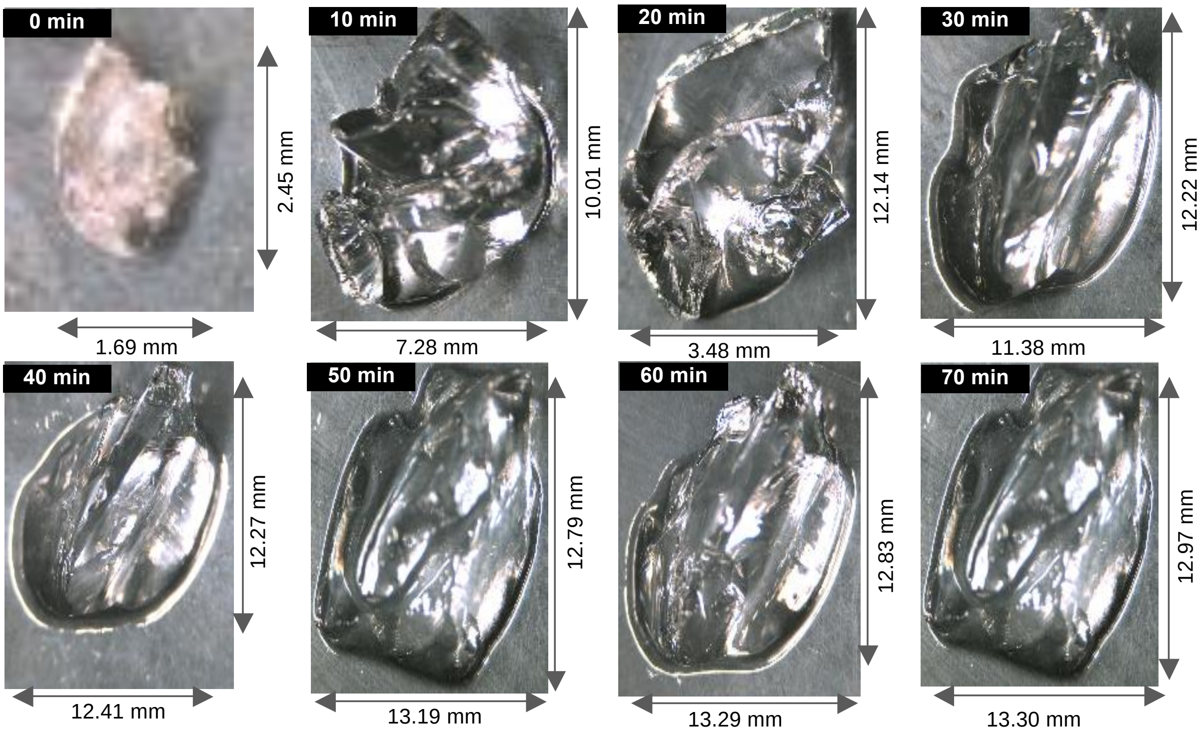

Figure 4. HPG after immersion in 40 ml of H_2O.

This observation can be proven mathematically by calculating % of swelling using Eq. 2 and can be represented by plotting the % of swelling in the X- and Y-axes (width and length) against volume, as shown in Figs. 5(a) and 5(b), respectively. HPG + KOH showed a gradual increment in % of swelling. Unlike HPG + H_2O, the % of swelling in the X- and Y-axes significantly increased during the first 10 min and then continuously increased with time. However, regardless of the solution with which HPG gels, both samples reached the equilibrium % of swelling at the same time within an average of 60 min, indicating that the osmotic pressure difference between the gel and the solvent already became zero.

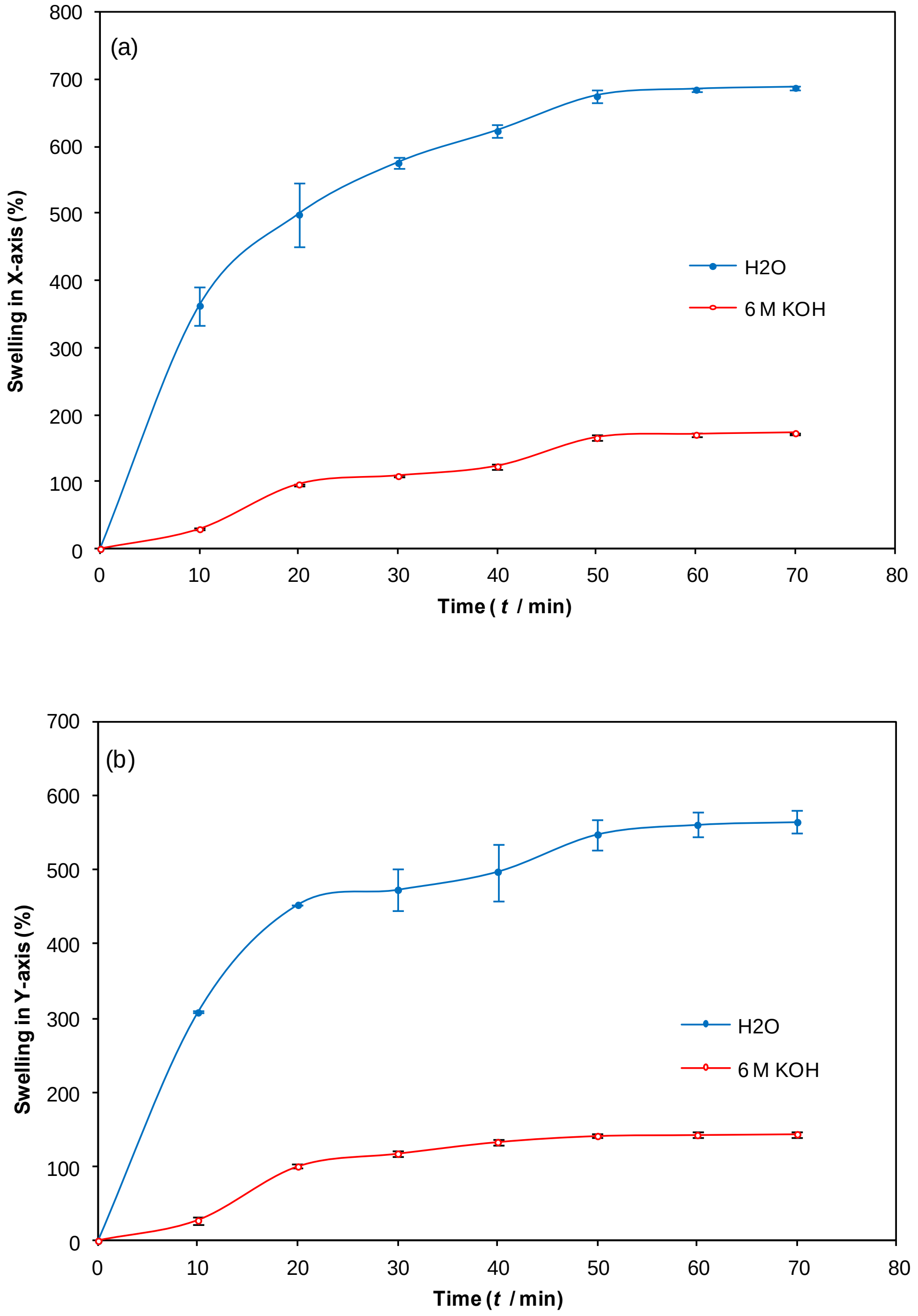

Figure 5. Variation of % of swelling in the (a) X-axis (width) and (b) Y-axis of HPG in 6 M KOH and H_2O.

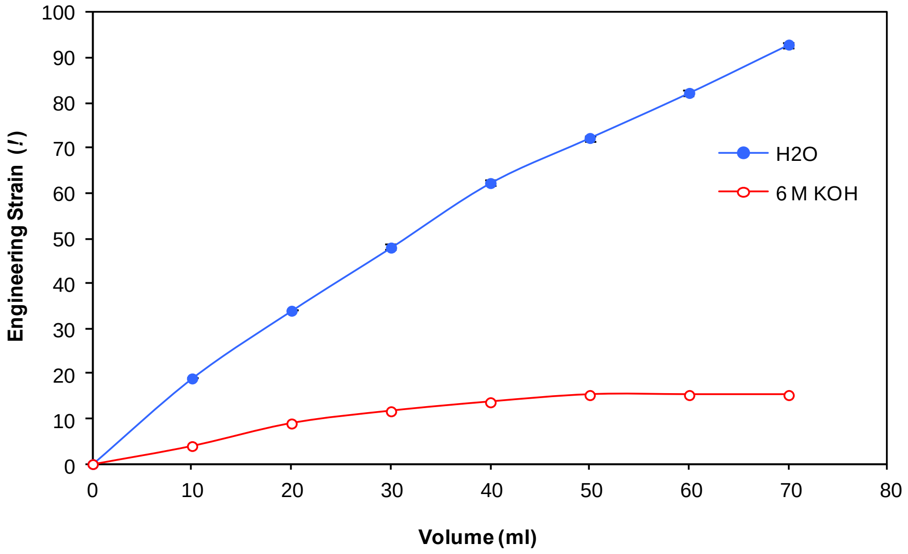

Figure 6. Variation in engineering strain value for different volume of 6 M KOH and H_2O.

Fig. 6 shows the variation in the engineering strain values for different volumes of KOH and H_2O. The HPG immersed in 6 M KOH experienced lower strain compared with those immersed in H_2O. Considering that HPG can absorb higher amounts of H_2O, it expands and increases the strain value more than the HPG + KOH. Meanwhile, the compressive stress–strain curves for KOH and H_2O are shown in Fig. 7.

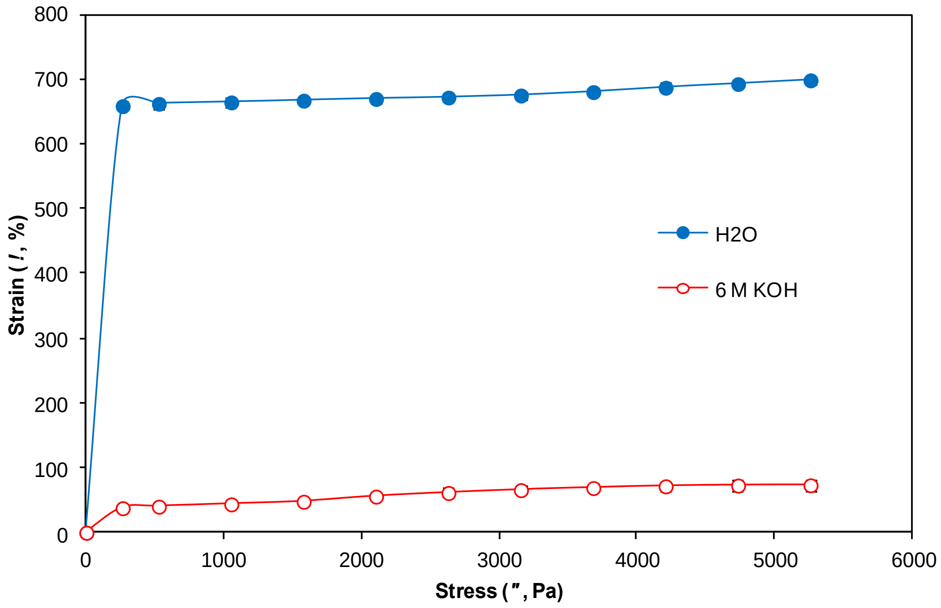

Figure 7. Compressive stress–strain curve for H_2O and 6 M KOH.

The strain amplitude increased with increasing applied stress, and the strain amplitude for the HPG + KOH was lower compared with that of HPG + H_2O. The strain amplitude was more likely to follow the trend of the percentage absorbency of the gel. Considering that the gel absorbed only a small amount of KOH, the gel only expanded slightly. Hence, it yielded a smaller strain amplitude. On the other hand, the percentage absorbency of the HPG + H_2O was relatively high, and as a result, the gel was able to expand more, becoming a big bloated gel. However, the gel was relatively soft and thus experienced larger strain amplitude. Strain amplitude can be used to interpret roughly the compressive strength of the gel. A larger strain amplitude means that the gel experienced larger deformation and hence indicates that the compressive strength of the gel was lower and vice versa.

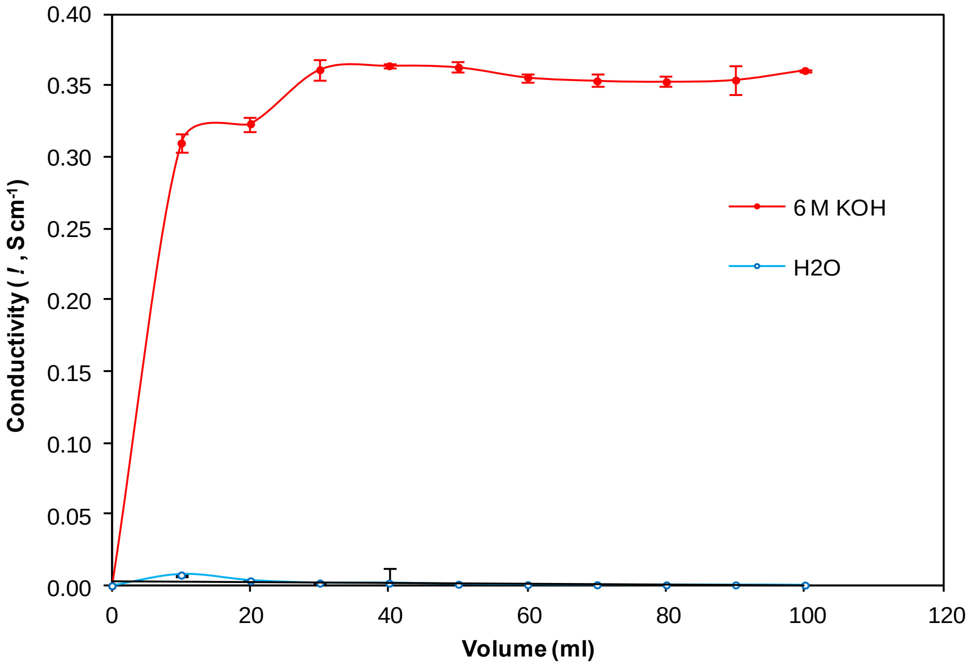

Figure 8. Variation in conductivity for different concentrations of 6 M KOH and H_2O.

The varying conductivities at different volumes of KOH and H_2O absorbed by HPG are shown in Fig. 8. Evidently, the addition of KOH significantly improved ionic conductivity. The conductivity of pure HPG (compressed pellet) was about 10^{-8} S cm^{-1} and sharply increased to about 10^{-1} S cm^{-1} with the addition of 10 ml of KOH solution. The conductivity of the HPG + KOH jelly granule reached the maximum conductivity at 0.3642 ± 0.0018 S cm^{-1} using 40 ml of electrolyte solution, whereas the maximum conductivity achieved by HPG + H_2O was only about 0.0075 ± 0.0006 S cm^{-1}.

Since there have no free charge carrier was introduced to the pure HPG, the results show that pure HPG has lower conductivity. This observation agrees with the HPG + H_2O system that shows a lower conductivity value, which could be contributed by the impurities or H_2O molecules. Meanwhile, the absorption of the KOH solution into the HPG granule provided a free charge carrier, namely, OH^-. HPG with 40 ml of KOH, the conductivity was almost similar to the KOH solution [9]. Thus, 40 ml of KOH and immersion within 60 min are the optimum conditions targeted for our next battery.

3.2. Application of HPG in Zn–MnO_2 Batteries

The typical discharge curve for Zn–MnO_2 alkaline batteries with HPG + KOH is shown in Fig. 9. The starting point of the open-circuit voltage was about 1.5 V. Meanwhile, the discharge curve showed a voltage plateau at about 1.0 V. The calculated discharge capacity was ca. 148 mAh g^{-1}, and the battery and capacity curves were almost comparable with those obtained by Zhang and Zhang [10].

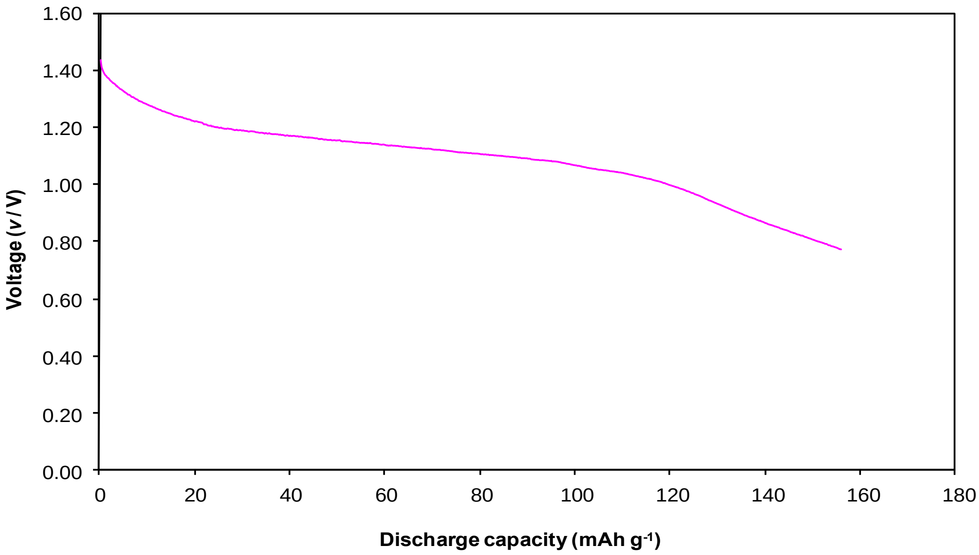

Figure 9. Typical discharge capacity of battery.

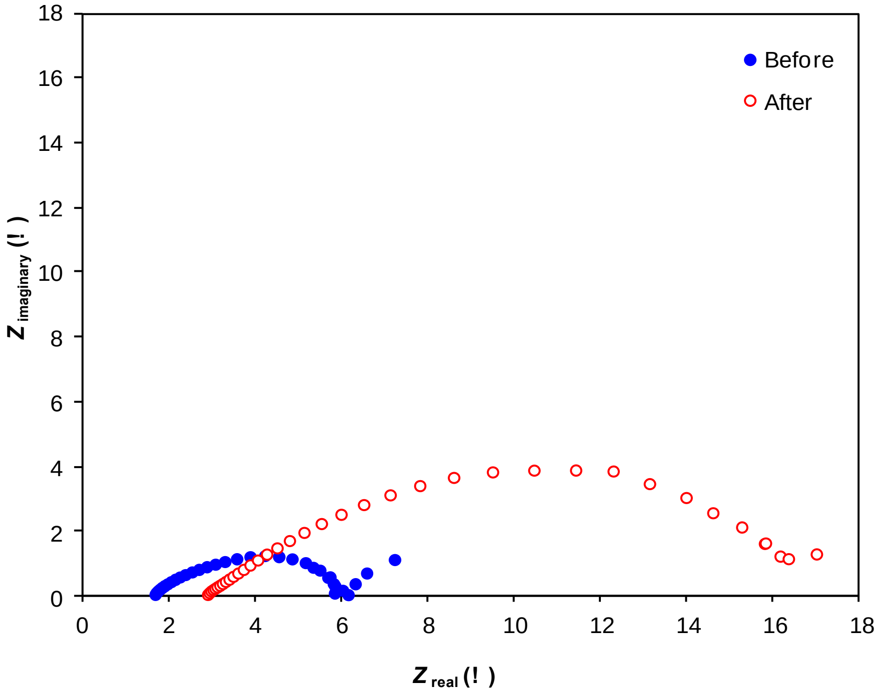

Figure 10. EIS spectra of battery before and after discharge.

The EIS spectra of the Zn–MnO_2 alkaline battery with 40 ml of HPG + KOH electrolyte are shown in Fig. 10. All impedance plots showed a typical semicircular impedance behavior at high frequencies followed by a short spike (residual tail) at low frequencies. The semicircular behavior depends on the parallel combination of R_{ct} and C_{dl} to explain the possible reactions occurring between the electrolyte and electrode. The diameter of the semicircle after discharge was wider than that before discharge. Kumar and Sampath [11] also observed an increase in the semicircle diameter in the Zn/GPE/Zn system caused by the lost electrolyte and the growth of the surface film on the Zn electrode. These reactions could be the causes for the decreased battery discharge. As a result, R_{ct} and, hence, C_{dl} increased. Thus, the polarization of the electrode surface increased, as indicated by the C_{dl} values (Table 1).

Table 1. Impedance parameters of the batteries determined from Nyquist plots.

Condition	R_{ct} (Ω)				C_{dl} (x 10^{-4} F)			
	Battery 1	Battery 2	Battery 3	Average	Battery 1	Battery 2	Battery 3	Average
Before discharge	5.1	5.0	6.4	5.5	1.5	1.5	1.5	1.5
After discharge	14.8	13.5	11.9	13.4	2.8	4.0	3.5	3.4

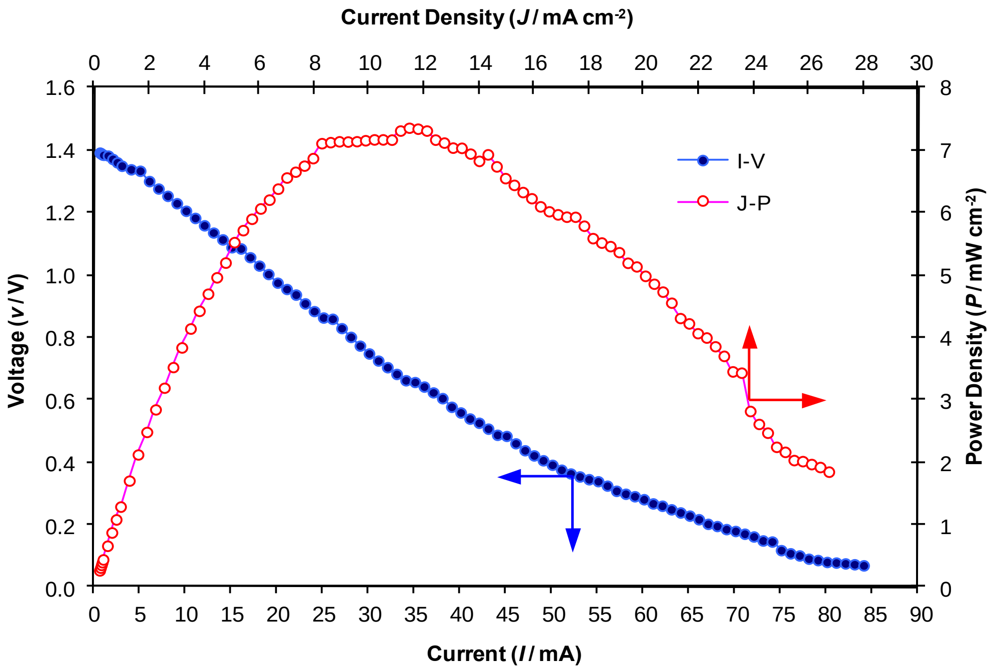

Figure 11. *I–V* and *J–P* curves for the battery.

Fig. 11 shows the *I–V* and *J–P* curves for the battery. The internal resistance value was calculated from the slope of the former *I–V* curve as 16 Ω. The values of the internal resistance obtained from the *I–V* curve were almost comparable with the R_{ct} obtained from the EIS after completed discharge. Therefore, the internal resistance values obtained can be used to predict the R_{ct} of the battery and vice versa. Both results indicate the internal resistance of charge transfer between anode/electrolyte/cathode. The maximum power density for the battery was 7.8 mW cm^{-2}.

4. CONCLUSION

Equilibrium swelling studies are important in determining the time required for gels, particularly those used in GPE batteries, to reach maximum expansion. The results show that 0.5 g of HPG could absorb a maximum of 40 ml of 6 M KOH, and the time required to achieve maximum absorption was 60 min. The batteries application of HPG + 6 M KOH showed promising results with voltage plateau approximately 1.0 V, and a discharge capacity ca. 148 mAh g^{-1} was achieved.

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References

1. Y.T. Xie, A.Q. Wang, *J Polym Res*, 16 (2009) 143-150.
2. M.J. Zohuriaan-Mehr, K. Kabiri, *Iran Polym J*, 17 (2008) 451-477.
3. S.J. Fan, Q.W. Tang, J.H. Wu, D. Hu, H. Sun, J.M. Lin, *J Mater Sci*, 43 (2008) 5898-5904.
4. C. Iwakura, S. Nohara, N. Furukawa, H. Inoue, *Solid State Ionics*, 148 (2002) 487-492.
5. N.H. Khalid, Y.M.B. Ismail, A.A. Mohamad, *J Power Sources*, 176 (2008) 393-395.
6. S.H. Kim, J.K. Choi, Y.C. Bae, *J Appl Polym Sci*, 81 (2001) 948-956.
7. A.K. Bajpai, A. Giri, *Carbohydr Polym*, 53 (2003) 271-279.
8. M.J. Ramazani-Harandi, M.J. Zohuriaan-Mehr, A.A. Yousefi, A. Ershad-Langroudi, K. Kabiri, *Polym Test*, 25 (2006) 470-474.
9. C.K. Yap, W.C. Tan, S.S. Alias, A.A. Mohamad, *J Alloys Compd*, 484 (2009) 934-938.
10. G.Q. Zhang, X.G. Zhang, *Solid State Ionics*, 160 (2003) 155-159.
11. G.G. Kumar, S. Sampath, *Solid State Ionics*, 160 (2003) 289-300