

Short Communication

Hydrogel-Polymer Electrolytes Based on Polyvinyl Alcohol and Hydroxyethylcellulose for Supercapacitor Applications

*Memoria Rosi, Ferry Iskandar, Mikrajuddin Abdullah, and Khairurrijal**

Physics of Electronic Materials Research Division; Faculty of Mathematics and Natural Sciences,
Institut Teknologi Bandung; Jalan Ganesa 10, Bandung 40132, Indonesia

*E-mail: krijal@fi.itb.ac.id

Received: 20 March 2014 / Accepted: 29 April 2014 / Published: 19 May 2014

A transparent polymer-hydrogel electrolyte was successfully synthesized on the basis of polyvinyl alcohol (PVA). Sulfuric acid (H_2SO_4) as a dopant electrolyte was used to dissolve PVA. Hydroxyethylcellulose (HEC) was then added into the PVA/ H_2SO_4 solution. By analyzing their FTIR spectra, it was found that HEC interacts with PVA/ H_2SO_4 in the form of a three dimensional polymeric network or HEC and PVA/ H_2SO_4 chains existed in the hydrogel-polymer electrolytes. From the AC impedance spectroscopy, it was shown that the hydrogel-polymer electrolyte with 1 wt.% of HEC has the highest ionic conductivity. The highest capacitance of 160 F/g was given by the supercapacitor employing the hydrogel-polymer electrolyte with 1 wt.% of HEC as confirmed by its cyclic voltammetry.

Keywords: Electrolyte, Hydrogel, Hydroxyethylcellulose (HEC), Ionic conductivity, Polyvinyl alcohol (PVA), Supercapacitor

1. INTRODUCTION

In the last decade, utilization of a hydrogel containing an electrolyte (a hydrogel electrolyte) has been considered as a substitute of a liquid electrolyte for supercapacitors because of its reliability, flexibility, leakage free and safety [1,2]. A few studies of hydrogel electrolytes for supercapacitors application including the hydrogels based on potassium poly(acrylate) (PAAK), poly(acrylamide) (PAAM), polyvinyl alcohol (PVA), and polyvinyl alcohol/poly(acrylic acid) (PVA/PAA) have been done [3-9]. Among the polymers, PVA is more attractive because it is biodegradable, nontoxic, inexpensive and chemically stable. The PVA hydrogels also have high structural integrity and good mechanical properties [10,11]. Moreover, the -OH groups of PVA absorbs a large of water that extend the water content absorbs consequently enhance its ionic conductivity [12].

The PVA hydrogels are usually prepared from dialdehyde (glutaraldehyde)-based cross linking agents under acidic condition [10,13]. However, the prevalent crosslinkers have drawbacks due to toxicity, cost, and difficulty in controlling the reaction. Fortunately, PVA has unique properties that allow the crosslinking without using a chemical reaction. It is a challenge to utilize gelatin substance to substitute glutaraldehyde and serve as an efficient route to produce the hydrogel. Hydroxyethylcellulose (HEC) as one of gelatin/thickening agents commonly known in industry application [14,15] is a nonionic polymer compound that is soluble in water and its ionic conductivity can be fine-tuned under acidic condition [16]. However, an elaborate study on PVA/HEC hydrogels for supercapacitor applications is still lack. This paper reports the syntheses of hydrogel-polymer electrolytes based on PVA dissolved in H_2SO_4 and added with HEC and the fabrication of supercapacitors using the hydrogel-polymer electrolytes.

2. EXPERIMENTAL

Polyvinyl alcohol (PVA), $(CH_2CHOH)_n$, (Bratachem, Indonesia) with an average molecular weight of 20,000 was dissolved in 4 M sulfuric acid (H_2SO_4) at $40^\circ C$. After complete dissolution, hydroxyethylcellulose (HEC) (Bratachem, Indonesia) was added into the solution and then stirred at room temperature for several minutes. A transparent hydrogel-polymer electrolyte was finally obtained. The concentration of HEC was varied from 1 to 5 wt.% to optimize the hydrogel-polymer electrolyte.

For making supercapacitors, the electrodes were the coconut shell-based nanoporous carbon (NPC) mixed with 10 wt.% graphite and 10 wt.% PVA solution. The resulting mixtures were then coated on an aluminum current collector to obtain an NPC electrode on the aluminum current collector. The resulting NPC electrodes were then dried at $110^\circ C$ for 2 h. A supercapacitor was assembled like a sandwich in which the hydrogel-polymer electrolyte is inserted between the electrodes. The detailed procedure was described in our previous work [17].

As-synthesized hydrogel-polymer electrolytes were characterized using a Fourier transform infrared spectrometer (FTIR) (Shimadzu IRPrestige-21). Their electrical impedance characteristics were investigated by using an AC impedance spectroscopy (Agilent E4980A). Cyclic voltammeteries of the supercapacitors were performed using a potentiostat (Hokuto Denko HB-501) with Ag/AgCl reference electrode.

3. RESULTS AND DISCUSSION

Figure 1 gives FTIR spectra and their peaks were identified by comparing to those in Ref. [18]. The FTIR spectrum of PVA/ H_2SO_4 solution (Fig. 1.(a)) has the following peaks. The broad peak in $3500-3450\text{ cm}^{-1}$ region (label A) is attributed to the O-H stretching of alcohol group. The sharp peak at 1637 cm^{-1} (B) is assigned to the C=O stretching of carboxyl group. The bands at 1288 cm^{-1} (C) and 1174 cm^{-1} (D) are due to the CH_2 and CH wagging vibrations, respectively. The bands at 1055 cm^{-1}

(E), 1002 cm^{-1} (F), and 883 cm^{-1} (G) belong to the C-C stretching, C-O stretching, and CH_2 out of plane vibrations, respectively. The others are the O-H plane bending motions at 669 cm^{-1} (H) and 584 cm^{-1} (I). The FTIR spectrum of HEC given in Fig. 1.(b) shows several typical peaks. The peaks at 3440 and 1635 cm^{-1} are originated from the O-H stretching and C=O stretching of carboxyl group, respectively. The wider peak at 678 cm^{-1} is due to the O-H plane bending.

Figures 1.(c)-1.(e) depict the spectra of hydrogel-polymer electrolytes with 1, 2.5, and 5 wt.% of HEC, respectively. It is seen that the peaks of O-H stretching, C=O stretching, and CH wagging are still found while that of CH_2 wagging disappeared. The peaks of C=O stretching in the spectra of hydrogel-polymer electrolytes are strengthened as compared to that in the spectrum of PVA/ H_2SO_4 solution. It is also observed from the spectra of the hydrogel-polymer electrolytes that the peak of CH wagging at 1174 cm^{-1} shifted to higher wavenumbers ($1199\text{-}1205\text{ cm}^{-1}$), indicating shortened bond lengths of gel-like structures in the electrolytes [19]. These indicate that HEC interacts with PVA/ H_2SO_4 in the form of a three dimensional polymeric network. In other words, HEC and PVA/ H_2SO_4 chains existed in the hydrogel-polymer electrolytes [20].

Moreover, a broad peak of O-H stretching in the spectra of hydrogel-polymer electrolytes with 1 wt.% of HEC reflects possible interactions through hydrogen bonds between PVA and HEC [21]. By increasing the concentration of HEC up to 5 wt.%, the peak of O-H stretching is narrowed due to the hydrolysis of the HEC as consequence of a large amount of HEC itself [22]. The hydrolysis breaks the molecular bonds of HEC under acid condition [23-24]. The higher the concentration of HEC, the more extensive hydrolysis of the hydrogel is. As the network junction of the HEC moves away, the hydrogen bond strength is therefore reduced. This phenomenon was observed physically from the stiffness of hydrogel-polymer electrolytes with 2.5 and 5 wt.% of HEC.

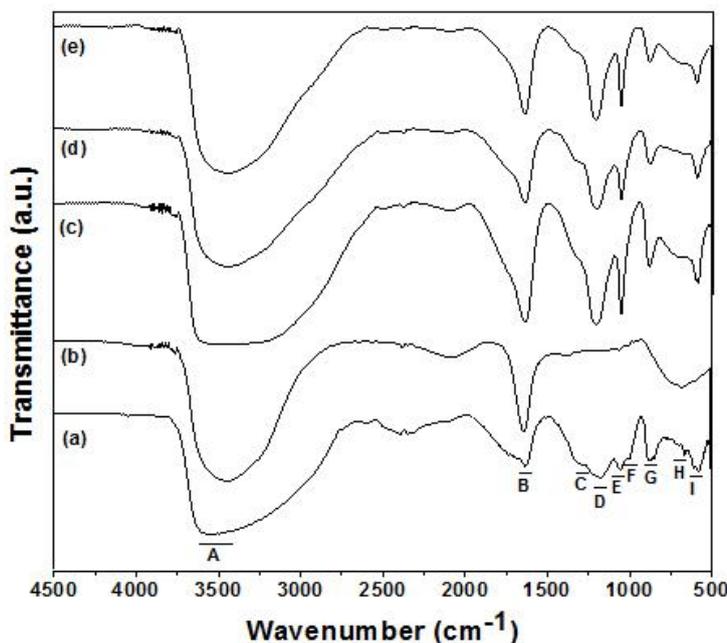


Figure 1. FTIR spectra of (a) PVA/ H_2SO_4 solution, (b) HEC solution, and hydrogel-polymer electrolytes with 1 (c), 2.5 (d), and 5 wt.% (e) of HEC.

The impedance spectra of as-synthesized hydrogel-polymer electrolytes are depicted in Fig. 2. The typical Nyquist plot includes a small semicircle part at higher frequencies corresponding to the ionic transport and a linear part at lower frequencies resulting from the interface between electrolyte and the electrode. The behavior of the hydrogel-polymer electrolyte can be clarified by an equivalent circuit shown by the inset of Fig. 2. The equivalent circuit includes the ohmic resistance (R_s) of the hydrogel-polymer electrolyte, the Warburg impedance (Z_w) of the electrode, the constant phase element (CPE), and the interface resistance (R_i) of the electrode and the electrolyte.

The point of an impedance spectrum in the range of high frequency intersecting the real axis (Z') represents the ohmic resistance (R_s) of the polymer electrolyte. Their ohmic resistances were estimated to be 0.3, 0.25, 0.9, and 2 Ω for the PVA/H₂SO₄ solution, hydrogel-polymer electrolytes with 1, 2.5, and 5 wt.% of HEC, respectively. The lowest ohmic resistance indicates the most rapid ionic transport which is contributed from the O-H groups throughout the chain of HEC in the hydrogel-polymer electrolyte with 1 wt.% of HEC. This finding is consistent with the broadest peak of O-H stretching of the FTIR spectra as discussed before. The increase of the resistance with increasing the concentration of HEC implies that the free-volume of the electrolyte to transport ions becomes less. This is supported by narrow peaks of O-H stretching of the hydrogel-polymer electrolytes with 2.5 and 5 wt.% of HEC.

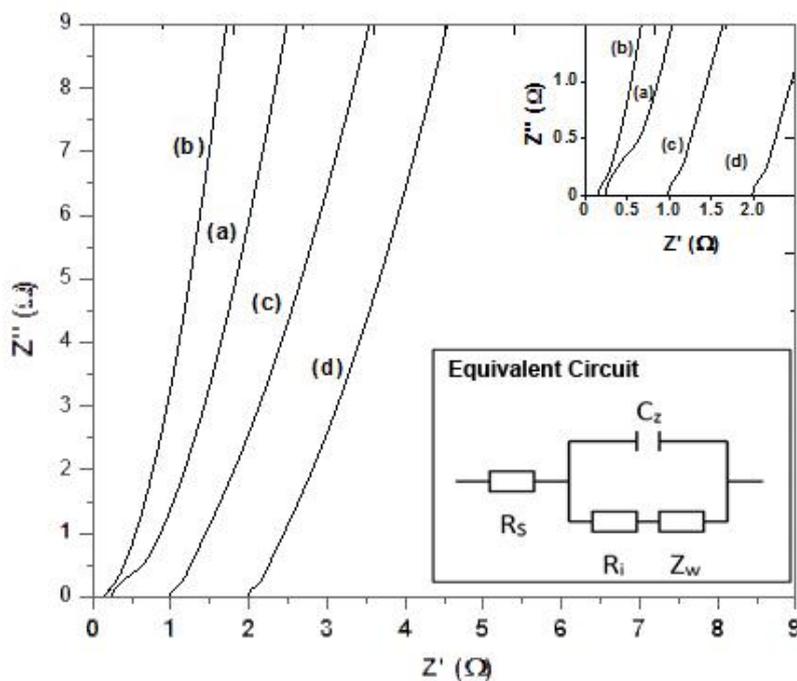


Figure 2. AC impedance spectra of the PVA/H₂SO₄ solution (a) and the hydrogel-polymer electrolytes with 1 (b), 2.5 (c), and 5 wt.% (d) of HEC.

Figure 3 shows the cyclic voltammeteries (CVs) of the supercapacitors at the scan rate of 10 mV/s. The specific capacitance was obtained by calculating the charge under the curves along the voltage applied as given by Eqs. (1) and (2):

$$C_{cell}(F) = \frac{\int IdV}{\Delta V \times v_s} \quad (1)$$

$$C_s = \frac{2C_{cell}}{m} \quad (2)$$

where C_{cell} is the capacitance (F), I is the charging/discharging current (A), ΔV is the potential range (V), v_s is the scan rate, C_s is the specific capacitance (F/g), and m is the mass of active material of the electrode.

The specific capacitances were 120, 160, 50 and 40 F/g for the supercapacitors employing the PVA/H₂SO₄ solution, hydrogel-polymer electrolytes with 1, 2.5, and 5 wt.% of HEC, respectively. The highest capacitance of the supercapacitor using the hydrogel polymer electrolyte with 1 wt.% of HEC corresponds with the lowest ohmic resistance of the electrolyte. As previously discussed, the lowest ohmic resistance of the electrolyte is due to the most rapid ionic transport contributed from the O-H groups throughout the chain of HEC in the electrolyte. By increasing the concentration of HEC in the hydrogel-polymer electrolyte, the specific capacitance decreases. Following the argument of Ref. 10, the decreased ionic conductivity could be due to the less free-volume of the hydrogel-polymer electrolytes with 2.5 and 5 wt.% of HEC.

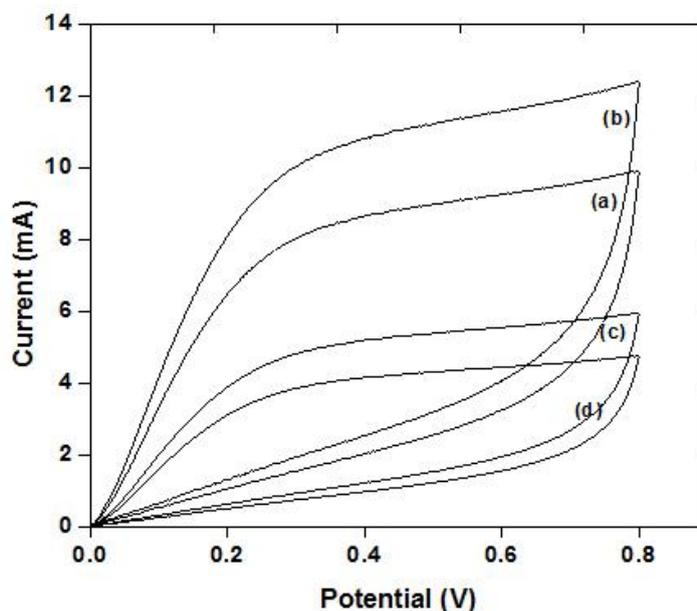


Figure 3. Cyclic voltammograms of the supercapacitors using PVA/H₂SO₄ solution (a), hydrogel-polymer electrolytes with 1 (b), 2.5 (c), and 5 wt.% (d) of HEC.

4. CONCLUSIONS

A hydrogel-polymer electrolyte based on polyvinyl alcohol (PVA) with the addition of hydroxyethylcellulose (HEC) has been produced and characterized. The FTIR spectra have demonstrated that HEC and PVA/H₂SO₄ chains existed in the hydrogel-polymer electrolytes. The highest ionic conductivity has been shown by the hydrogel-polymer electrolyte with 1 wt.% of HEC as

confirmed by its AC impedance spectrum. From the cyclic voltammetry, it has been found that the supercapacitor using the hydrogel-polymer electrolyte with 1 wt.% of HEC has the highest capacitance of 160 F/g.

ACKNOWLEDGMENT

This research was financially supported by Institut Teknologi Bandung through the “Outstanding Doctor Program” Research Grant of the IMHERE Project.

References

1. C. Iwakura, S. Nohara, N. Furukawa, H. Inoue, *Solid State Ionics*, 148 (2002) 487-492.
2. N. A. Choudhury, S. K. Prashant, S. Pitchumani, P. Sridhar, A. K. Shukla, *J. Chem. Sci.*, 121, 5 (2009) 647–654.
3. C. Iwakura, H. Wada, S. Nohara, N. Furukawa, H. Inoue, M. Morita, *Electrochem. Solid-State Lett* 6, 2 (2003) A37-A39.
4. F. Jianqi, G. Lixia, *Eur. Poly. J.* 38 (2002) 1653-1658.
5. S. Nohara, H. Wada, N. Furukawa, H. Inoue, M. Morita, C. Iwakura, *Electrochim. Acta* 48 (2003) 749-753.
6. I. Stepniak, A. Ciszewski, *Electrochim. Acta* 54 (2009) 7396-7400.
7. H. Wada, S. Nohara, N. Furukawa, H. Inoue, M. Morita, C. Iwakura, *Electrochim. Acta* 49 (2004) 4871-4875.
8. N. A. Choudhury, A. K. Shukla, S. Sampath, S. Pitchumani, *J. Electrochem. Soc.* 153 (2006) A614-A620.
9. S. Patachia and C. B. Florea, *Rev. Roum. Chim.* 52 (2007) 1145-1149.
10. S. Sampath, N. A. Choudhury, A. K. Shukla, *J. Chem. Sci* 121 (2009) 727-734.
11. P. B. Bhargav, B. A. Sarada, A. K. Sharma, V. V. R. N. Rao, *J. Macromol. Sci. Part A Pure Appl. Chem.* 47 (2010) 131-137.
12. N. A. Choudhury, S. Sampath, A. K. Shukla, *J. Electrochem. Soc.* 155 (2008) A74-A81.
13. H. Wada, K. Yoshikawa, S. Nohara, N. Furukawa, H. Inoue, N. Sugoh, H. Iwasaki, C. Iwakura, *J. Pow. Sourc.* 159 (2006) 1464–1467.
14. S. Gorgieva, V. Kokol, *Carbohydr. Polym.* 85 (2011) 664-673.
15. R. Dash, M. Foston, A. J. Ragauskas, *Carbohydr. Polym.* 91 (2013) 638-645.
16. Aqualon, “Natrosol Hydroxyethylcellulose a Nonionic Water-soluble Polymer”, Hercules Incorporated (1999).
17. M. Rosi, F. Iskandar, M. Abdullah, Khairurrijal, *Mater. Sci. Forum* 737 (2013) 191-196.
18. R. M. Silverstein, F. X. Webster, D. J. Kiemle, “Spectrometric Identification of Organic Compounds”, 7th ed., John Wiley & Sons, United States of America, 2005.
19. K. Pal, A. K. Banthia, D. K. Majumdar, *AAPS Pharm.Sci.Tech.* 8, 1 (2007) E1- E5.
20. W. Wang, J. Wang, Y. Kang, A. Wang, *Composites: Part B* 42 (2011) 809-818.
21. S. M. Pawde, K. Deshmukh, *J. App. Polym. Sci.*, 109 (2008) 3431-3437.
22. H. S. Mansur, C. M. Sadahira, A. N. Souza, A. A. P. Mansur, *Mater. Sci. Eng. C* 28 (2008) 539–548.
23. H. Vink, *Die Makromolekulare Chemie* 94 (1966) 1-14.
24. Antonio Martínez-Richa, *Carbohydrate Polymers* 87 (2012) 2129– 2136.