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Research paper

Electrical Properties of Polymer Electrolytes Membrane and Keratin-PVA as Electrode for Supercapacitors

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Abstract

Polymer electrolytes membranes were synthesized from Polyvinil Alcohol (PVA) with variations of H_3PO_4, KI/I_2, and $H_3PO_4/KI/I_2$. Membranes were placed between two electrodes keratin-PVA and pressed at temperature of 50 ^{o}C The effect of polymer electrolytes on electrochemical properties of supercapacitors were investigated using LCR meter and charge discharge analysis. Semicircle indicates a movement of charge on electrode surface area and a charge transfer resistance (R_{ct}). Capacitance was increased up to 269 pF after the mixed electrolyte KI/I_2- PVA membrane. Spectra's impedance and permittivity identify polarizability a dielectric material. It is based on the interaction of an external field with the electric dipole moment of the sample and then trapped on the electrode surface. Redox pair I_3^- /I^- improves the process of charging energy and increases capacitance and power density.

Keywords: *supercapacitors, polymer electrolytes, keratin*

1. Introduction

Supercapacitors are energy storage which have high power density, large number of charging and discharging cycles and highly reversible stored charge. Supercapacitor is constructed from electrodes, separator between electrodes and electrolyte (Kumar & Bhardwaj, 2013).

The performance of supercapacitors is determined by the physical properties of both the electrode and the electrolyte materials. The principle of energy storage in a supercapacitor is electrostatic charge accumulation at the electrode/electrolyte interface (electrical double layer capacitance, EDLC), or charge transfer, via

reversible (Faradaic) redox reaction(s), to redox materials (e.g. conductive polymers, metal oxide nanoparticles) on the surface of electrode (pseudo-capacitance) (Chen & Dai, 2013).

Separator is a semipermeable membrane that allows the movement of electrolyte ions between the two electrodes. Polymer electrolytes can be classified as a two-phase system consisting of an ionic conductor and the polymer matrix. Ionic conductors can be obtained from the proton (H+) and lithium (Li+) electrolyte based. Yoo et al. ,2011) used an electrolyte membrane made from PVA-H3PO4 as a separator and graphene as an electrode. The highest capacitance is 394 µFcm-1. Gedam et al. (2013) combined PVA with acid or salts such as phosphoric acid (H3PO4), hypophophorus acid (H3PO2), heteropolyacid (HPA), dipotasium phosphate (K2HPO4) and sulphosuccinic acid (SSA) to increase the conductivity of PVA.

The electrode composite materials were researched and developed. The electode composite is formed by metal oxides, conductive polymers, activated carbon or carbon nanotubes (Yin, 2010). Supercapacitor electrode materials are required to have chemical properties and physical properties, as follows high conductivity, high surface area (~ 1 to > 2000 m2g-1), corrosion resistance, stable at high temperatures, controlled pore structure and low cost (Pandolfo & Hollenkamp, 2006).

In this research, we synthesized composite keratin-PVA as an electrode material. A two steps pyrolysis was developed for poultry keratin fibers (Senoz & Wool, 2010). The renewability and the cost of PCFF (Pyrolysis Chicken Feather Fibers) are the most important advantages. They are remarkably low in price because they are a waste material and require only relatively low temperature heat treatments. Keratin is micropore materials and has specific surface area 10-430 m2g-1 (Senoz & Wool, 2011). Keratin is composed of a cystine disulfide bonds, hydrogen bonds and hydrophobic interactions of molecules of keratin (Williams et al., 1991). Polymer electrolyte membranes were made from PVA with variations of electrolyte solution (PVA, PVA: H3PO4, PVA: KI: I2, and PVA: H3PO4: KI: I2).

2. Method

Keratin material is taken from poultry feathers that have been pyrolized in a vacuum. Pyrolysis temperature is done in two stages, first at or under temperature of 215 °C for 15 hours. Second is at 450 °C for one hour. Pyrolised keratin results is purified by using 15 cm^3 toluene and 45 cm^3 distilled water, And then it is soaked for one hour and dried in the air. Polymer electrolyte membranes were made from one gram PVA, 10 ml deionized water and dissolved in a variations electrolyte (H_3PO_4, H_3PO_4: KI: I_2, KI: I_2) of 0.5 M. The solution mixed for three hours at temperature 60 °C and allowed to gel. The Electrode slurry was fabricated by mixing keratin and PVA in weight ratio of 92:8 (%wt).

To measure electrochemical properties of supercapacitor, PVA membrane with variations electrolyte were placed between two electrodes and pressed at temperature of 50 °C for 10 minutes and coated silver on both sides as current collector. Conductivity of polymer electrolyte membrane, resistance and capacitance of supercapacitors were measured using the RCL meter Fluke PM 6306 in a frequency range from 1 kHz to 1 MHz with an ac amplitude of 1 V. Supercapacitor performance was tested with a charge-discharge methode, using a simple circuit which is connected to oscilloscope with a current 15.7 mA.

3. Result and Discussion

The conductivity of electrolyte membrane affected series resistance (R_S) which associated with a power density of supercapacitors, polarization of electrolyte ions in electrode material and the dielectric properties of electrolytes and related with capacitance supercapacitors (Conway, 1999). This study used an electrolyte solution such as H_3PO_4, $KI:I_2$ and $H_3PO_4:KI:I_2$ with a concentration 0.5 M and mixed into PVA as matrix. Membrane PVA conductivity is 5.501×10^{-6} Scm^{-1}. Conductivity increased with an addition of electrolyte solution $H_3PO_4/KI/I_2$ (M-PHKI) and H_3PO_4 (M-PH) which respectively are 7.745×10^{-6} Scm^{-1} and 6.818×10^{-5} Scm^{-1}.

Electric measurement of keratin-PVA electrode resulted cole-cole plot. Fig.1 shows the spectra semicircle. It showed one simple parallel RC circuit with a resistor (R_p) and a capacitor (C_p) connected in parallel. The R_p is associated with the material layer resistance and C_p is related to geometric capacitance of the layer (Varade. V. et al., 2013). Diameter of semicircle indicates a movement of charge on electrode surface area and a charge transfer resistance (R_{ct}) is about 6×10^4 Ω.

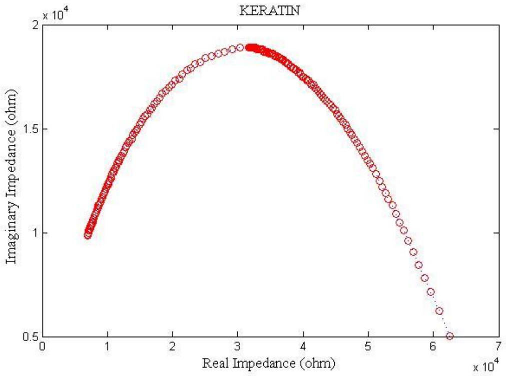

Fig. 1: Cole-Cole Plot Electrode Keratin-PVA at Frequency 1 kHz to 1 MHz

The Cole-Cole plots consist of a high frequency intercept on the real Z′ axis, and a semicircle in the high to low frequency region. The high frequency intercepts for all the four membranes are almost the same, indicating that the four supercapacitors with variation membranes have the same resistance combination of ionic resistance of the electrolyte, intrinsic resistance of keratin-PVA, and contact resistance between keratin-PVA and the current collector (Fig.2).

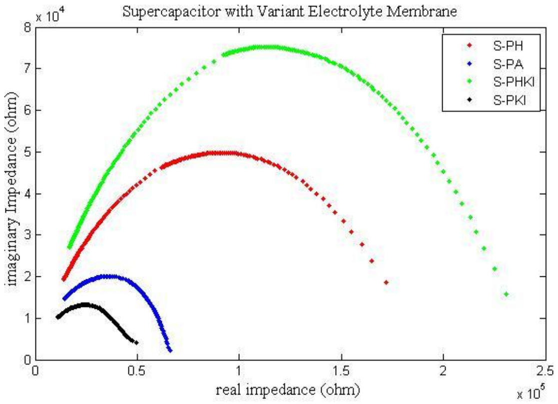

Fig. 2: Cole-Cole Plot Supercapasitors at Frequency 1 kHz to 1 MHz

The semicircle in the high to low frequency region corresponds to a parallel combination of charge transfer resistance (R_{ct}) and double layer capacitance (Xia et al., 2012). It can be seen that the R_{ct}, which is equal to the diameter of the semicircle, for the four electrolyte is in the order of S-PKI < S-PA < S-PH < S-PHKI.

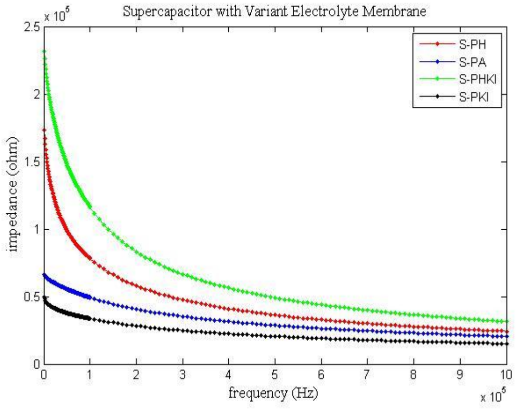

Fig. 3: Plot Frequency vs Impedance

Fig.3 is the result of a plot between impedance supercapacitors and frequency. Samples S-PA, S-PH, S-PKI and S-PHKI have curves which tend to rise at low frequency and slowly approached constant as rising frequency. An addition of electrolyte KI/I_2 and H_3PO_4 decreased the impedance value, but increased on addition of electrolyte $KI/I_2/H_3PO_4$. It suggests electrolytes KI/I_2 and H_3PO_4 can improve conductivity values.

By using the technique of impedance analysis we evaluated the real and imaginary parts of the dielectric constant (ε′) and dielectric loss (ε") of supercapacitors. The values obtained from that equation expressed in the form of complex permittivity spectrum are shown in Fig.4.

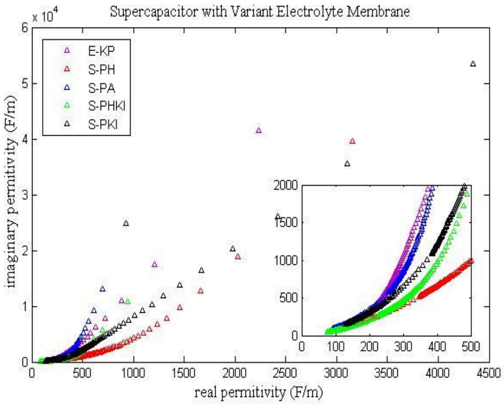

Fig. 4: Complex Permittivity Spectrum (Cole–Cole plot) of Supercapacitors with Variant Electrolyte Membrane

Cole and Cole showed that a feature of relaxation behaviour in accordance with the Debye equation. It formed small semicircle at high frequency and a straight line at a low frequency. From the experimental data, it is observed that the complex permittivity plots have become more circular with the addition of the electrolyte in polymer matrix. Therefore two relaxations are clearly observed in the complex permittivity spectrum.

Plot between real permittivity (ε') and imaginary permittivity (ε") on the function of frequency can identify polarizability a dielectric material. It is based on the interaction of an external field with the electric dipole moment of the sample and then trapped on the electrode surface which expressed by dielectric permittivity.

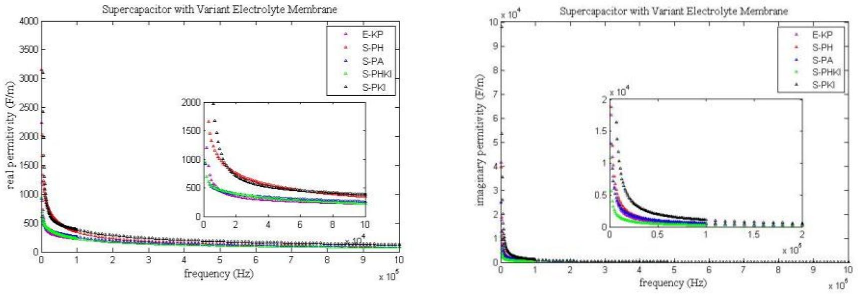

Fig. 5: Plots Frequency vs Real Permittivity and Imaginary Permittivity

The plots of real permittivity/dielectric constant and imaginary permittivity/dielectric loss against frequency supercapacitors for different electrolyte membrane are presented in Fig. 5a and 5b respectively. It is observed that dielectric constant (ε') is significantly increased with electrolyte loading especially at low frequency region. The increase in dielectric constant at lower frequency range is mainly due to the increase in space charge and interfacial polarization. Similarly, dielectric loss (ε") is increased with the addition KI/I_2 and H_3PO_4.

The charge-discharge mesurement was used to obtain performance of supercapacitors with variations electrolyte membrane. It is connected to the oscilloscope with a current of 15.7 mA.

Table 1: Performance of supercapasitors with variations electrolyte membrane

Sample	**Capacitance (pF)**	**Energy density (mWh/kg)**	**Power Density (Watt/kg)**
PVA	77,8	0,33	129,55
PVA:H_3PO_4	98,4	0,36	130,68
PVA:KI:I_2	269	0,60	130,65
PVA: H_3PO_4: KI:I_2	46,8	0,33	129,55

The addition of redox pair I_3^-/I^- improve the process of charging energy and increasing capacitance and power density. There are two possibilities, i.e improving access K^+ ion in the electrolyte membrane, and increasing K^+ charge transfer at the electrode surface. However, an addition of a redox pair I_3^-/I^- on the sample S-PHKI is decrease. Many concentration of H^+ and K^+ ions caused stack of charge on the materials.

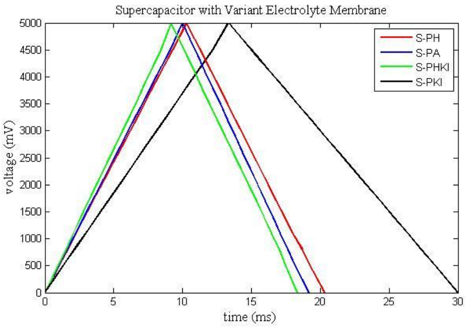

Fig.6: Charge-discharge Curve of Supercapacitors

Supercapacitors performance shows operating voltage of 5 volts. Discharge time S-PKI were longer than S-PH, S-PA and S-PHKI. The duration of the discharge process is influenced by time of the dielectric relaxation. Samples S-PKI in Fig.4 shows that there is a long straight line at low frequencies that indicate the length of relaxation time. This is equivalent with charge-discharge results in Fig.6.

4. Conclusion

Supercapacitors with a variations polimer electrolyte membrane consisting of a PVA, KI/I2, H3PO4 and electrode PVA-keratin have been successfully synthesized. An addition of the electrolyte solution in membrane increased conductivity of PVA. Conductivity of keratin-PVA composite electrode is very small compared to conductivity of activated carbon-PVA which is equal to 1.406 x 10-6 Scm-1. Electrical properties of supercapacitors showed a small capacitance value that is on order of pF. Keratin is typical microporous materials with low surface areas and narrow pore size distributions. So, increasing the size of the electrode/electrolyte interface, increasing the surface area of the electrodes or decreasing the separation between the ions and electrode the capacitance stored increases.

References

[1] Chen. T. & Dai. L. (2013). Carbon nanomaterials for highperformance supercapacitors. Materials Today. Volume 16, Numbers 7/8
[2] Conway, B.E. (1999). Electrochemical Supercapacitor : Scientific Fundamentals and Technological Aplications. New York: Kluwer Academic-Plenum Publisher
[3] Gedam, S.K., et al. (2013). Development of Solid Proton Conductors Based On Doped Polyvinyl alcohol. India: Department of Physics RTM Nagpur University
[4] Kumar V. & Bhardwaj. N. (2013). Introduction to Supercapacitors and Supercapacitor Assisted Engine Starting System. International Journal of Scientific & Engineering Research, Volume 4, Issue 8
[5] Pandolfo, A.G. & Hollenkamp, A.F. (2006). Carbon Properties and Their Role In Supercapacitor. Australia : CSIRO Division of Energy Technology
[6] Senoz. E & Wool. RP. (2010). Microporous carbon-nitrogen fibers from keratin fibers by pyrolysis. J Appl Polym Sci. 118
[7] Senoz. E. & Wool. RP. (2011). Hydrogen storage on pyrolyzed chicken feather fibers. International Journal of Hydrogen energy
[8] Varade. V., et al. (2013). Probing disorder and transport properties in polypyrrole thin-film devices by impedance and Raman spectroscopy. J. Phys. D: Appl. Phys. 46
[9] Williams, C.M., et al. (1991). Evaluation of a Bacterial Feather Fermentation Product, Feather Fermentation Product, Feather-Lysate, as a Feed Protein. Poultry Sci. 70:85-94
[10] Xia et al. (2012). Hydrothermal synthesis of MnO2/CNT nanocomposite with a CNT core/porous MnO2 sheath hierarchy architecture for supercapacitors. Nanoscale Research Letters. 7:33.
[11] Yin, Y. (2010). An Experimental Study on PEO Polymer Electrolyte Based All-Solid-State Supercapacitor. Open Access Dissertations. Paper 440
[12] Yoo, J.J., et al. (2011). Ultrathin Planar Graphene Supercapacitors. Nano Lett. 11, 1423-1427