Development of Supercapacitor System Based on Ionic Liquid and Rice Hull Ash Silica Gel

Reynaldo T. Diego Jr.[1] Ma. Liliana Viktoria M. Maramba,[1]
Jose Paolo O. Bantang,[1] and Drexel H. Camacho[1,2]

[1] *Chemistry Department, De La Salle University, 2401 Taft Avenue, Manila, Philippines*
[2] *Organic Materials and Interfaces Unit, CENSER, De La Salle University, 2401 Taft Avenue, Manila, Philippines*
**Corresponding Author: drexel.camacho@dlsu.edu.ph*

Abstract: Supercapacitors are known for their capability of storing high energy with longer cycling durability. Considering its advantages, a new design of supercapacitors is highly sought. In this study, gel-electrolyte system based on ionic liquid and silica gel ash was developed. The silica gel of high purity was extracted from rice hull ash and was characterized using SEM and FTIR. The ionic liquid was synthesized through ion exchange method followed by the FTIR characterization. In the fabrication of the supercapacitor, stainless steel deposited with MnO_2 was prepared and used as the electrode. The incorporation of the gel electrolyte system into the two MnO_2 electrodes formed a symmetric solid-state supercapacitor. The fabricated supercapacitor was successful as evidenced by favorable capacitive behavior using Cyclic Voltammetry (CV), Galvanostatic charge – discharge measurement and Electrochemical impedance spectroscopy (EIS). The solid-state capacitor demonstrated a favorable potential window of 0.7 V, ideal capacitance behavior with 78.49% capacity retention, retaining an energy density of 0.97 mWh cm^{-2} with power density of 0.631 Wcm^{-2} at the maximum current density of $0.35mA^{-2}$. The study demonstrates the ionic liquid gel electrolytes with MnO_2 – based electrodes as a good system for supercapacitor.

Key Words: supercapacitor, ionic liquid, rice hull ash silica gel, potentiostat

1. INTRODUCTION

Development of MnO_2 – based solid state supercapacitors is beneficial for many applications in flexible electronics. Electrolytes play an important role in the charge storage process of supercapacitors. The match between the ions on the surface of the electrodes influences the capacitive behavior and working potential window of supercapacitors. With proper design of electrolyte formula in conjunction with the MnO_2 – based electrodes, specific capacitance can be maximized and energy density of supercapacitors could significantly be enhanced [1]. However, the encapsulation and sealing of electrolytes pose a problem in integrating the materials into storage systems. Designing a lightweight and flexible supercapacitors are accomplished by incorporating liquids with gel electrolytes. Only a few applications have been reported by ionic liquid gel electrolytes with MnO_2-based electrodes. Considering its advantages, a new design of supercapacitors is highly sought, hence this study.

2. RESULTS & DISCUSSION

Silica SiO_2 was produced from rice hull ash at pH 7.0 rather than at the normal xerogel production at pH 4.0. At pH 7.0, gel formation was rapid and rigid, due to the covalent Si – O bonds that were responsible for the gel structure. Since SiO_2 was responsible for silioxane (-Si-O-Si-) bonding, the decrease in pH could lead to the decrease in the extent of silioxane bonding. The major chemical groups present in silica were identified by the FTIR spectra: 2800 and 3750 cm^{-1} peaks were due to the silanol OH groups and adsorbed water, 1100 cm^{-1} peak was due to the silica gel network, silioxane (-Si-O-Si-) [2]. The morphology and particle size of lyophilized silica were examined by SEM as amorphous form in the range of 5 -15 μm. The synthesis of ionic liquid, 1 – ethyl – 3 – methyl imidazolium bromide was done using a protocol developed by Wang, et al., [3] and the FTIR assignments were consistent with previous literature reported by Sadlej et al. [4].

The gel-polymer electrolytes were prepared by entrapping the ionic liquid electrolytes into the host silica gel network. The characteristics of the gel-electrolyte systems are high ionic conductivity, mechanical stability and good interfacial stability [5]. Incorporating the ionic liquid in the silica gel minimized the leakage of the liquid electrolyte and made the fabrication of the solid-state supercapacitor effective because it ensured the adhesion of the gel-electrolyte system to both electrodes efficiently.

The fabrication of MnO_2 – based electrodes was done via chemical bath deposition in an acidic medium. The process afforded MnO_2 layer with thickness of ~1.0μm. At low magnification the substrate surface is well covered with highly porous 2D thin microstructures. At high magnification the thin microstructures are interconnected with spaces that serve as the site for intercalation of electrolyte ions in the active electrode material. The EDX spectrum of the MnO_2 film showed the presence of the elements manganese and oxygen and SEM confirmed the highly porous MnO_2 microflakes deposited on the stainless steel surface.

The assembly of the symmetric supercapacitor device consists of the MnO_2 film electrodes and ionic liquid – silica gel –electrolyte. Cyclic voltammetric investigation on the fabricated supercapacitor revealed that within the potential window range of 0.4 to 0.7 V, a smaller current response is observed and it exhibited potential pseudo – capacitive behavior due to its quasi – rectangular nature. At a potential window of 0.7V, the supercapacitor run over a scan rate of 10, 20, 50 and 100 mV s^{-1} showed that the area under the cyclic voltammetry curves persists with increasing scan rate, attributed to the enhanced supercapacitive behavior due to the increasing electrode/electrolyte interaction [6]. The maximum specific capacitance was reached at 61.4 mF/g at a scan rate of 10 mV/s, and can retain a specific capacitance of 14.2 mF/g at 100mV/s, which is lower compared to the specific capacitances reported by MnO_2 – based electrodes with gel – electrolytes. This is attributed to the microstructure of the MnO_2 thin film, which provides the pathway for the penetration of electrolyte ions in the inner side of the active electrode material that enhance the energy storing capacity [6].

The cycling stability of the supercapacitor, showed that after 100 cycles, the supercapacitor still exhibited a quasi - rectangular nature with a capacity retention of 78.49%. The capacitor retention measured shows enhanced electrochemical stability due to the the use of silica gel. This avoids the dissolution of the active electrode material which causes the limited cycling stability for MnO_2 - based electrodes [6] Moreover, the electrochemical performance showed that the device retains the energy density of 0.97 $mWhcm^{-2}$ with power density of 0.631 Wcm^{-2} at the maximum current density of $0.35mA^{-2}$. Although the supercapacitor has exhibited only a minimal amount of energy and power density, this observation leads to potential charge storage of the fabricated supercapacitor [7].

3. CONCLUSIONS

This investigation practically evidenced simple and cost-effective synthesis of MnO_2 – based electrode coupled with the fabrication of quasi – solid – state supercapacitor containing 1 – ethyl – 3 – methylimidazolium bromide. The ionic liquid – gel electrolyte in a MnO_2 – based electrode demonstrated ideal specific capacitance, energy and power density, and cycling stability with conventional set-up. Further, symmetric solid-state supercapacitor based on MnO_2 electrodes on ionic liquid –silica gel – electrolyte demonstrates a potential window (0.7 V) with excellent electrochemical stability. Additionally, it shows an energy density of 0.97 mWh cm^{-2} with power density of 0.631 Wcm^{-2}. This intellectual design of supercapacitors gives promising direction towards the development of energy storage devices with efficient and cost effective materials.

REFERENCES

[1] Wang, J., Kang, F., Wei, B. (2015) Progress in Material Science, 51 – 124.
[2] Kalapathy, U., Proctor, A., & Shultz, J. (2000). Bioresource Technology, 73, 257-262.
[3] Wang, L., Xu, S., Chang, L., Su, Z., Zeng, M., Wang, L., Huang, Y. (2011). Journal of Solid State Chemistry, 720 – 724.
[4] Sadlej, J. Jaworski, A., Miaskiewicz. (1992). Journal of Molecular Structures, 274, 247-257.
[5] Pandey, G. P., & Hashmi, S. A. (2013). Electrochimica Acta, 105, 333-341.
[6] Chodankar, N., Dubal, D., Gund, G., Lokhande, C. (2016). Journal of Energy Chemistry 25, 463-471.
[7] Tiruye, G., Torrero, D., Palma, J. Anderson, M., Marcilla, J. (2016). Journal of Power Sources, 1 – 9.