Electrochemical characterization of supercapacitors based on carbons derived from Sorona activated by ZnCl_2

Jisha. M. R · Maria Christy* · Ae Rhan Kim** · Kee Suk Nahm** · Dong Jin Yoo[†]

Department of Hydrogen and Fuel Cells Engineering, Specialized Graduate School, Chonbuk National University, *School of Semiconductor and Chemical Engineering, Chonbuk National University

**School of Chemical Engineering and Technology, Chonbuk National University

(Received 3 August 2012, Revised 3 September 2012, Accepted 5 September 2012)

Abstract

Carbons derived by the pyrolysis of Sorona activated by ZnCl_2 in the ratio of 1:20 and non-porogen Sorona carbons are used as the electrode materials in asymmetric electrochemical supercapacitors and electrochemical behavior is investigated. Scanning electron microscopy (SEM) reveals the porogen free carbons show a flake-like structure and the ZnCl_2 -treated Sorona carbons have a loose, disjoint structure without any particular shape. Cyclic voltammetric (CV) studies show specific prolate rectangular shape and gives good capacitive properties.

Key words : Supercapacitors, porogen, zinc chloride, Sorona, chemical activations

1. Introduction

For applications such as high current loads, supercapacitors characterized by high capacitance values in the Farad ranges and low internal resistances are used. Thus electrochemical capacitors are attractive energy storage devices [1]. The energy storage in a supercapacitor is achieved either by faradaic or non-faradaic processes at the electrode-electrolyte interface. Since the reversibility of the double layer process at the surface of an electro active material determines the capacitor performance, a high surface area is a key factor in achieving a high capacitance. High surface area, porous carbons are widely employed as electrodes for energy storage in double layer capacitors [2-10]. In a supercapacitor, two symmetric capacitors are

connected in series and the total capacitance is halved [11]:

$$1/C_{\text{total}} = 1/C + 1/C$$

$$C_{\text{total}} = C/2$$

Normally active carbons consist of micro-meso pores in wide ranges. These active carbons have been reported by many for supercapacitor applications [4-9]. Synthesis of porous carbons which include mesopores with narrow range sizes is not possible with any known classical methods of preparing active carbons [10].

A better way to achieve this involves the use of organic or inorganic materials as templates or use of pore forming substances like ZnCl_2 . Most of the research on carbon has been done with precursors which are either directly or indirectly related to the petroleum products or fossil fuels and hydrocarbons like methane, benzene, acetylene, butane etc. For synthesizing novel carbon material as a viable product, it is necessary to select a precursor, which is not derived from fossil fuels or related to

[†]To whom corresponding should be addressed.

Department of Hydrogen and Fuel Cells Engineering,
Specialized Graduate School, Chonbuk National University, 567
Baekje-daero, Deokjin-gu, Jeonju-si, Jeollabuk-do 561-756,
Republic of Korea
Tel : 063-270-3608 E-mail : djyoo@jbnu.ac.kr

petroleum products.

Hence, we employed 'Sorona', a natural product, to synthesize activated carbons by pyrolysis. As shown in Figure 1, Sorona, poly(trimethylene terephthalate) is a unique polymer based on 1, 3-propanediol (PDO). It is a copolymer of 'Bio-PDO' and petroleum derived terephthalate. In this paper, carbons obtained from polymer Sorona are used as the carbon source and ZnCl_2 as the pore former. Comparing with other carbon materials, activated carbons from Sorona is one of the most promising materials for fabricating supercapacitors, because of its low cost, inherent surface area, structural stability and good electrochemical property in acidic aqueous electrolyte.

Hwang et al. reported production of disordered carbons by the pyrolysis of coffee shells and have shown higher capacities for lithium intake [12]. The surface area of the carbon materials has been increased to 1.3 and 19.9 orders upon the addition of ZnCl_2 and KOH as porogen, respectively. The high capacities in these disordered carbons are attributed to the binding of lithium on extra surfaces of the single layers of carbon and in the nano cavities formed by the porogens. In our previous study, we reported the lithium intercalation properties of pyrolytic carbon obtained from Sorona for lithium intercalation properties [13]. The thermogravimetric analysis (TGA) and X-ray diffraction (XRD) studies on the sample were carried out in our previous work.

The objective of this article is to prepare high-performance, low-cost carbon electrode materials from Sorona and study the relation between the carbon property and performance of the supercapacitor. In this study, at first we tried to synthesize activated carbon of high surface area by using simple pyrolysis technique. Only a few examples of the use of the aforementioned carbon source have been reported for use in double layer capacitor [14]. In the present study, symmetric supercapacitor has been assembled using these

Fig. 1. Molecular structure of Sorona, poly(trimethylene terephthalate).

carbons as electrode materials and ZnCl_2 as the pore former. The preparation and electrochemical properties of carbonaceous material derived from Sorona activated by ZnCl_2 were investigated for supercapacitor applications and the results will be presented.

2. Experimental Procedure

General

The Sorona were ground into a fine powder and then treated with concentrated aqueous solutions of ZnCl_2 (porogen) as a ratio of 1:20 (Sorona/porogen) by weight for 5 days at room temperature and dried. Pyrolysis was carried out by heating these ZnCl_2 -treated samples at 900°C under flowing nitrogen at a heating ramp of $10^\circ\text{C}/\text{min}$ for a hold period of 1 hr. Pyrolytic carbons were also obtained without treating with the porogen (ZnCl_2), where the Sorona were simply heat-treated under the above conditions. The pore size distribution changes from bimodal to unimodal after the addition of ZnCl_2 , indicating the dispersion effect of ZnCl_2 . The morphology of the pyrolytic carbons were examined by a (FESEM S-4700, Hitachi) scanning electron microscope. BET (Brunauer, Emmett and Teller) surface area measurements were studied by a (MicromeriticsASAP2010) surface area analyzer.

General

Activated carbons ($\text{Sorona}/\text{ZnCl}_2 = 1/20$) and the non-porogen carbons were mixed well and thus slurry was prepared. It was pressed, made in the

Fig. 2. SEM micrographs of pyrolyzed (at 900°C) carbons derived from (a) untreated Sorona (b) Sorona treated with 20% ZnCl_2 .

form of a pellet and was pasted on the nickel mesh current collector attached with a stainless steel plate. Then the electrodes were kept in the oven at 120°C for 1 hr and slowly cooled to room temperature. To study the electrochemical properties, asymmetrical supercapacitor cells were fabricated. The above prepared electrode was used as the working electrode; platinum wire was used as counter electrode; and Ag/AgCl as the reference electrode. The electrochemical behavior of the cells was analyzed in 1 M H_2SO_4 aqueous electrolyte solution. The cyclic voltammetry was characterized by using the electrochemical analyzer (BAS 100B).

3. Results and Discussion

SEM micrographs of pyrolyzed (at 900°C) Sorona carbons with and without porogen treatment are shown in Figure 2a and 2b. It is revealed that some parts of the carbons are blown off for the ZnCl_2 -treated Sorona carbons. It can also be seen that some parts of the carbons are blown off. It may be due to the elimination of gases during the pyrolysis process [15]. They have a loose, disjoint structure without any particular shape. The porogen free carbons show a flake-like structure. During the carbonization process the ZnCl_2 acts as a dehydration agent. It results in charring and

aromatization of carbon and in turn yields the pore formation. After carbonization, the Sorona carbons were washed thoroughly. During the washing process, untreated ZnCl_2 were fully removed from the samples and generated further pores [16]. The surface properties of the pyrolyzed carbon play a vital role in the electrochemical properties of double layer capacitors. N_2 adsorption analysis reveals an average BET (Brunauer, Emmett and Teller) surface area of 390 m^2/g for ZnCl_2 activated Sorona carbon and 4 m^2/g for non-porogen Sorona carbon. Typical N_2 -adsorption-desorption isotherms for porogen treated carbons and non-porogen carbons are shown in Figure 3a and 3b. It is worth mentioning that the hysteresis observed in the N_2 -adsorption-desorption isotherms is mainly attributed to the mesoporosity of the materials, and a similar behavior was observed for all the samples studied [17, 18].

Asymmetric Supercapacitor cells were fabricated and the electrochemical behavior such as cyclic voltammetry (CV) was characterized by using the electrochemical analyzer (BAS 100B) in 1 M H_2SO_4 aqueous electrolyte solution. The electrode prepared using activated Sorona carbon-slurry (Figure 4) was used as the working electrode; platinum wire as the counter electrode and Ag/AgCl as the reference electrode. Use of higher voltage scan rates was found to yield voltammograms dominated by capacitive charging currents. This

Fig. 3. BET isotherm for pyrolyzed (at 900°C) carbons derived from (a) untreated Sorona (b) ZnCl_2 treated Sorona.

meant that minor errors in the subtraction of these currents would have an increasing effect on the resulting peak current [19]. Thus higher scan rates have therefore not been used in this work and lowers scan rates such as 5 mV/s and 10 mV/s are used in a voltage window of 0-1 V range. Cyclic voltammograms of non-porogen carbons and carbons obtained from Sorona activated by ZnCl_2 in the ratios of 1:20 are shown in Figure 5a, b and Figure 5c, d, respectively, for two different scan rates i.e. 5 mV/s and 10 mV/s. The influence of scan rate on the specific capacitance is evident from the figures and it is seen that the increase of non-faradaic current is observed with increase in scan rate. For non-porogen carbon at the two scan rates, cyclic voltammograms are not prolate rectangular but capacitive current is observed; whereas, for ZnCl_2 activated Sorona carbons at both scan rates, a prolate rectangle is observed. This implies that the carbons obtained from ZnCl_2 activated Sorona have so excellent capacitor performance at both scan rates. The prolate shape may be due to the diffusion-limited capacitance, which may be due to the electrolyte tapped in micro pores of the carbon [20, 21 and 22]. The power property of the activated carbons and non activated carbons is also seen from the figures. The

Fig. 4. Graphical representation of Sorona carbon electrode.

1:20 ZnCl_2 activated carbons give a capacitance of 146 F/g at the scan rate of 10 mV/s. It is clear that 1:20 is superior, compared to non-porogen Sorona at the two scan rates. For these kinds of porous carbons, it is well known that the higher the capacitance the longer is the time needed to acquire/release charges.

The CV curves of the carbon electrodes reveal that the mechanism of electrochemical storage can be studied by the electrical double layer theory. Energy storage in these electrodes is by the accumulation of the ionic charge in the double layer at the electrode/electrolyte interface. This may be due to high surface area and porosity of the carbons

Fig. 5. Cyclic voltammograms for the carbons derived by the pyrolysis of non-porogen Sorona at (a) 5 mV/s (b) 10 mV/s and ZnCl_2 activated Sorona at (c) 5 mV/s (d) 10 mV/s.

obtained from Sorona. However, the capacitance obtained may not be commensurate with the surface area and this may be caused by the capacitance of mesoporous area. This may also be due to large microporous carbons synthesized using ZnCl_2 chemical activation similar to the reports obtained for paper mill sludge [7-10]. This is attributed to the dispersion effect of ZnCl_2 and the pore size distribution could have been changed from bimodal to unimodal upon the addition of ZnCl_2 .

From our BET measurements for activated Sorona it is revealed that, BET Surface area is 390 m^2/g , and Langmuir surface area is 424 m^2/g and there is abundance of mesopores and micropores in the sample. Micropores have a high surface area/volume ratio. When these are present in significant proportions, they have a major contribution to the measured area of high surface. Fine micropores also exhibited a greater adsorbent-adsorbate affinity. This is due to the overlap of adsorption forces from opposing pore

walls. Hence, adsorption takes place through pore filling mechanism rather than through surface coverage (Langmuir type). N_2 adsorption analysis reveals an average BET surface area of 3.59 m^2/g for non-porogen Sorona which attributes to the low capacitive property of it and which is very less compared to the ZnCl_2 activated carbon as the above explanation shows.

4. Conclusions

Activated carbons were obtained from a novel carbon source named Sorona which was treated with the pore forming agent ZnCl_2 . The presence of mesopores in the carbons was confirmed by SEM analysis. N_2 adsorption analysis revealed an average BET surface area of 390 m^2/g and suggested that these carbons have a predominance of micropores and mesopores. Cyclic voltammetry of carbons treated by ZnCl_2 showed prolate rectangular shapes and high capacitive currents. The 20% ZnCl_2

activated carbons give a capacitance of 146 F./g at the scan rate of 10 mV/s. Hence, the carbons obtained from the present method are highly suitable for supercapacitor applications and it is obvious that these carbons have enormous capacitive properties.

Acknowledgements

This work was supported by the New & Renewable Energy R & D program (2009T100100606) under the Ministry of Knowledge Economy, Republic of Korea. This work was supported by the Human Resources Development of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Korea government Ministry of Knowledge Economy (20114030200060).

References

1. Conway, B.E. *Electrochemical supercapacitors - Scientific Fundamentals and Technological Applications*; Kluwer Academic publisher, Plenum press: Dordrecht, New York, USA, 1999; pp. 183-220.
2. Niu, C.; Sichel, E. K.; Hoch, R.; Moy, D.; Tennent, H.; App. Phys. 1997, 70, 1480-1482.
3. Qu, D.; Shi, H. J. *Power Sources* 1998, 74, 99-107.
4. Shi, H. *Electrochim. Acta.* 1996, 41, 1633-1639.
5. Kotz, R.; Carlen, M. *Electrochim. Acta.* 2000, 45, 2483-2498.
6. Endo, M.; Takeda, T.; Kim, Y. J.; Koshiba, K.; Ishii, K. *Carbon Sci.* 2001, 1, 117-128.
7. Frackowiak, E.; Beguin, F. *Carbon* 2001, 39, 937-950.
8. An, K.H.; Kim, W.S.; Park, Y.S.; Choi, Y.C.; Lee, S. M.; Chung, D.C.; Bae, D.J.; Lim, S.C.; Lee, Y.H. *Adv. Mater.* 2001, 13, 497-500.
9. Emmanegger, Ch.; Mauron, Ph.; Sudan, P.; Wenger, P.; Hermann, V.; Gallay, R.; Zettel, A. *J. Power Sources* 2003, 124, 321-329.
10. Kyotani, T. *Carbon* 2000, 38, 269-286.
11. Park, G. J.; Kalpana, D.; Thapa, A.K.; Nakamura, H.; Lee, Y.-S.; Yoshio, M. *Bull. Korean Chem. Soc.* 2009, 30, 817-820.
12. Hwang, Y. J.; Jeong, S. K.; Nahm, K. S.; Shin, J. S.; Stephan, A. M. *J. Phys. Chem. Solids* 2007, 68, 182-188.
13. Maria Christy; Jisha M.R.; Kim, E.R.; Nahm, K.S.; Yoo, D.J.; Suh, E.K. *Indian J. engineering and material sci.* In Press (2010).
14. Lee, J.; Yoon, S.; Oh, M.S.; Shin, C.-H.; Hyeon, T. *Adv. Mater.* 2000, 12, 359-362.
15. Zhou, H.; Zhu, S.; Hibino, M.; Honma, I. *J. Power Sources* 2003, 122, 219-223.
16. Dandekar, M. S.; Arabale, G.; Vijayamohanan, K. *J. Power Sources* 2005, 141, 198-203.
17. Hwang, Y. J.; Jeong, S. K.; Nahm, K. S.; Stephan, A. M. *J. Alloys & Comp.* 2008, 448(1-2), 141-147.
18. Janes, A.; Kurig, H.; Lust, E. *Carbon* 2007, 45, 1226-1233.
19. Zhao, J.; Lai, C.; Dai, Y.; Xie, J. *Mater. Lett.* 2007, 61, 4639-4642.
20. Liu, Y.; Xue, J. S.; Dahn, J. R. *Carbon* 1996, 34, 193-200.
21. Rees, N.V.; Klymenko, O.V.; Maisonhaute, E.; Coles, B.A.; Compton, R.G. *J. Electroanalytical Chem.* 2004, 542, 23-32.
22. Chmiola, J.; Yushin, G.; Dash, R.; Gogotsi, Y. *J. Power Sources* 2006, 158, 765-772.