

# Performance of Electric Double Layers Capacitor Using Activated Carbon Materials from Rice Husk as Electrodes

Tuan Dung Nguyen<sup>1</sup>, Jae Kyung Ryu<sup>2</sup>, Bramhe Sachin N.<sup>1</sup> and Taik-Nam Kim<sup>1,3†</sup>

<sup>1</sup>Department of Materials Science and Engineering,

Graduate School of PaiChai University, Daejeon 302-735, Korea

<sup>2</sup>Department of Dental Technology, ShinHan University, 95 Hoamro, Eujungbu Si, Gyong Gi Do, Korea

<sup>3</sup>Department of Information and Electronic Materials Engineering, PaiChai University, Daejeon 302-735, Korea

(Received October 5, 2013 : Received in revised form October 25, 2013 : Accepted October 31, 2013)

**Abstract** Activated carbon (AC) was synthesized from rice husks using the chemical activation method with KOH, NaOH, a combination of (NaOH + Na<sub>2</sub>CO<sub>3</sub>), and a combination of (KOH + K<sub>2</sub>CO<sub>3</sub>) as the chemical activating reagents. The activated carbon with the highest surface area (around 2000 m<sup>2</sup>/g) and high porosity, which allows the absorption of a large number of ions, was applied as electrode material in electric double layer capacitors (EDLCs). The AC for EDLC electrodes is required to have a high surface area and an optimal pore size distribution; these are important to attain high specific capacitance of the EDLC electrodes. The electrodes were fabricated by compounding the rice husk activated carbons with super-P and mixed with polyvinylidene difluoride (PVDF) at a weight ratio of 83:10:7. AC electrodes and nickel foams were assembled with potassium hydroxide (KOH) solution as the electrolyte. Electrochemical measurements were carried out with a three electrode cell using 6 M KOH as electrolyte and Hg/HgO as the reference electrode. The specific capacitance strongly depends on the pore structure; the highest specific capacitance was 179 F/g, obtained for the AC with the highest specific surface area. Additionally, different activation times, levels of heating, and chemical reagents were used to compare and determine the optimal parameters for obtaining high surface area of the activated carbon.

**Key words** supercapacitor, EDLC, activated carbons, specific capacitance, rice husk.

## 1. Introduction

Electric double-layer capacitor(EDLC) is a part of new type of electrochemical capacitors called supercapacitor, also known as ultracapacitor, which differs from regular capacitor in that it has very high capacitance.<sup>1,2)</sup> As a new potential energy storage device with great application prospects, supercapacitors have recently attracted great attention owing to their good power property, high capacitance and cycling performance. It stores electric charge physically in the EDLC, at the electrode/electrolyte interfaces which are readily accessible to ions present in the electrolyte.<sup>3)</sup> Supercapacitors or EDLC have been found application in solar cell power storage, electric and hybrid vehicle, electric devices, etc.<sup>4,5)</sup> Activated carbon materials have become popular electrode materials for supercapacitors or EDLC because of its porous structure, which ac-

commodates electrolyte ions providing great cycling performance and stable electrochemical behavior.<sup>6-9)</sup>

Activated carbons are carbonaceous materials which can be synthesized from low cost natural precursors such as coconut shell,<sup>10-12)</sup> wood,<sup>13)</sup> different seed shells,<sup>14)</sup> etc. In this study, activated carbon was prepared from rice husk by chemical activation method using KOH, NaOH, combination of NaOH + Na<sub>2</sub>CO<sub>3</sub> and combination of KOH + K<sub>2</sub>CO<sub>3</sub> as the chemical activating reagents. The main objective of this study is to synthesize activated carbon sample with very high specific surface area at various activation conditions and investigate the applicability of activated carbons as supercapacitor electrodes. The prepared activated carbons were characterized to determine their porous structure, pore size distribution and electrochemical properties, which influence the performance of the supercapacitor. The electrochemical properties of the

<sup>†</sup>Corresponding author

E-Mail : [tnkim@pcu.ac.kr](mailto:tnkim@pcu.ac.kr) (T.-N. Kim, PaiChai Univ.)

© Materials Research Society of Korea, All rights reserved.

This is an Open-Access article distributed under the terms of the Creative Commons Attribution Non-Commercial License (<http://creativecommons.org/licenses/by-nc/3.0>) which permits unrestricted non-commercial use, distribution, and reproduction in any medium, provided the original work is properly cited.

electrodes were investigated by CV, the charge-discharge cycling test and electrochemical impedance spectroscopy.

## 2. Experimental procedure

### 2.1 Preparation of activated carbon

The rice husk(RH) from Hyunduk industry production (Korea) was used as the starting material. RH was first washed with DI water in the ultrasonic cleaner and dried in the oven at 60 °C for 24 hours. The dried rice husk was milled at 700 rpm for 30 minutes by the attrition milling with alumina balls ( $\varnothing$  2 mm) and sieved through standard testing sieve with aperture 425  $\mu$ m and then carbonized at 700 °C for 2 hours in the presence of nitrogen. Next, chemical activation of the carbonized product was performed by strong corrosive solution at high temperature to create porous structure. KOH, NaOH and combination of NaOH + 10 % Na<sub>2</sub>CO<sub>3</sub> and combination of KOH + 10 % K<sub>2</sub>CO<sub>3</sub> were chosen as the activating agent. The black carbonized RH was soaked in activating reagent solution with a weight ratio of 2:1 (KOH/sample, NaOH/sample, (NaOH + 10 % Na<sub>2</sub>CO<sub>3</sub>)/sample and (KOH + 10 % K<sub>2</sub>CO<sub>3</sub>)/sample). The RH soaked in activating reagent solution were stirred and dried until paste state on the hot plate at 60-70 °C and then the paste samples were dried at 60 °C for 12 hours in oven. When soaking the carbonized RH in combination of KOH + 10 % K<sub>2</sub>CO<sub>3</sub> (or NaOH + 10 % Na<sub>2</sub>CO<sub>3</sub>), the sample was mixed with a concentrated KOH (or NaOH) solution at 60 °C and then 10 % K<sub>2</sub>CO<sub>3</sub> (or Na<sub>2</sub>CO<sub>3</sub>) was added into the slurry after 5 minutes. Next, the samples were activated under nitrogen flow (400 cm<sup>3</sup>/min) at 900 °C for 1-3 hours. Finally, the activated product was washed with DI water and filtered before drying at 80 °C overnight to form porous carbon. The activated carbons(ACs) prepared by physically mixing KOH, NaOH, the combination of KOH + 10 % K<sub>2</sub>CO<sub>3</sub> and NaOH + 10 %Na<sub>2</sub>CO<sub>3</sub> were designated as sample ACK, ACN, ACKK and ACNN respectively.

### 2.2 Characterization of activated carbons

Activated carbons were characterized by X-ray diffractomet(XRD, CuK $\alpha$ <sub>1</sub> radiation, Shimadzu, Japan) over the 2 $\theta$  range of 20° to 80° at a scan rate of 2°/min. The specific surface area, average pore size and micropore volume of the samples were measured using an ASAP 2010 micromeritics. The Brunauer-Emmett-Teller(BET) equation was applied to N<sub>2</sub> adsorption isotherms at 77 K (-196 °C) to obtain the apparent BET surface area, S<sub>BET</sub>.

The activity level(higher number indicates higher degree of activation) and micropore content of activated carbons were measured by adsorption of iodine from solution. Iodine number is defined as the milligrams of iodine adsorbed by one gram of carbon. By knowing the amount

of iodine adsorbed, the pore volume of the activated carbon can be calculated. Iodine solution was prepared by mixing crystal iodine in KI solution and AC was dropped into the above solution during ultrasonication. The Iodine number was measured by adding sodium thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>) solution until the change of color in sample solution is observed.

The iodine number was calculated by Korean Granular Activated Carbon Test Method KSM 1802 using following Eq.

$$I = \frac{(10 \times f' - K \times f)}{S \times \frac{10}{50}} \times 12.69 \quad (1)$$

where I is the Iodine number (mg/g), S is mass of activated carbon material (g), K is adsorption volume of 0.1M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution, *f* and *f'* are the density of 0.1M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution and adsorptive solution, respectively.

### 2.3 Preparation of electrodes

Firstly, 0.083 g activated carbon(AC) powders were well mixed and ground with the 0.01 g super-P(conductive carbon black). Then, 0.007 g Polyvinylidene difluoride(PVDF) binder and 0.5 ml N-methyl-2-pyrrolidone (NMP) solution was dropped into the above mixture and stirred for 24 hours until formation of coating slurry. The coating slurry was smeared onto the nickel foam with a surface area of (2 × 2) cm<sup>2</sup> and thickness of 350  $\mu$ m. These precursor electrodes were dried at 120 °C for 12 hours under vacuum and pressed in order to get the working electrodes with the thickness of 280  $\mu$ m.

### 2.4 Electrochemical measurement

In the present work, electrochemical measurements were performed in a Protentiostat- Galvanostat(Model 273A) at room temperature using 6M KOH solution as electrolyte. All experiments were carried out in a typical three-electrode cell with Hg/HgO (1M NaOH) as reference electrode, commercial activated carbon Maxorb msc-30 as counter electrode and the prepared working electrode.

Cyclic voltammograms were recorded at various scan rates (5 mV/s - 500 mV/s) in the potential range of (-1;-0.1) V. The discharge capacitance (*C*) of the electrodes in EDLCs was calculated from the slope of the discharge using the following Eq. (2).<sup>15)</sup>

$$C = \frac{Q}{\Delta V} \quad (2)$$

where *Q* is the electric charge(Coulomb) and  $\Delta V$  is the potential change in discharge (V).

The specific capacitance *C<sub>m</sub>* in farads per gram of a single electrode (F/g) was calculated from the capacitance of the cell *C*:

$$C_m = \frac{C}{m} \quad (3)$$

where  $m$  is the mass of the active material in a working electrode.

AC impedance spectra were measured by using a Hg/HgO reference electrode after the AC electrodes were charged to the cell in the frequency range of 10 kHz to 10 mHz.

### 3. Results and discussion

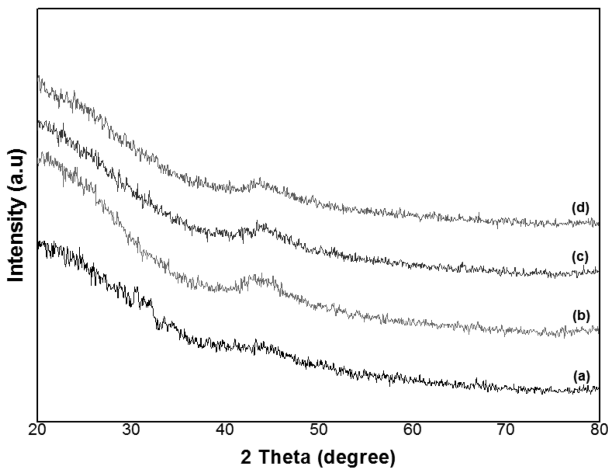
#### 3.1 Characteristics of porous carbons

The XRD results of activated carbons synthesized by activating at 900 °C for 1-3 hours after soaking in KOH or combination of KOH + 10 % K<sub>2</sub>CO<sub>3</sub> are shown in Fig. 1. The XRD pattern of activated carbon basically appears non-crystalline and this amorphous structure was consistent in all samples.

In this study, various experimental parameters were studied and labeled as described in Table 1. The activated carbons (ACs) prepared by physically mixing KOH in 2:1 ratio with sample and activated for 1, 2 and 3 hours at

900 °C were designed as samples ACK9112, ACK9212 and ACK9312, respectively. Likewise, label ACN9312 designate that the sample was synthesized by using NaOH as activating reagent and activated for 3 hours at 900 °C. The other samples ACKK9312 and ACNN9312 were soaked in combination of (KOH + 10 % K<sub>2</sub>CO<sub>3</sub>) and (NaOH + 10 % Na<sub>2</sub>CO<sub>3</sub>) before activating at 900 °C for 3 hours. Table 1 gives information about porous structure of activated carbon at various conditions. It can be clearly seen that porous properties of ACs changes with change in activation time and activating reagents. As can be seen, the specific surface areas and micropore volumes of ACs soaked in KOH tends to increase significantly with the increase in activation time. The S<sub>BET</sub> of the sample prepared in KOH and activated for 1 hour (ACK9112) was 1475 m<sup>2</sup>/g which increases to 1667 m<sup>2</sup>/g and further increased to 1793 m<sup>2</sup>/g when activated for 2 hours and 3 hours, respectively. Likewise, micropore volume of the carbon also increases from 0.294 to 0.383 cm<sup>3</sup>/g when activation time increases from 1 to 2 hours and reached a maximum of 0.406 cm<sup>3</sup>/g when activated for 3 hours (ACK9312). This is because during the activation process the carbon layer is burn out, which leaves many small micropores in the bulk carbon creating porous structure.<sup>16)</sup>

According to the Table 1, it is evident that activating reagents effect on BET surface areas of AC at the same ratio of 2:1 and 3 hours of activation. ACs prepared by NaOH reagent have larger pore diameter than the ACs prepared with KOH. This is because boiling point of potassium (759 °C) is lower than that of sodium (883 °C) [16], so potassium diffuses into the interior of carbon structure easily as compared to sodium at the high activation temperature used in the experiment. As a result, the sample prepared by NaOH activation (ACN9312) had lower S<sub>BET</sub> and larger pore diameter than the sample prepared with KOH (ACK9312) at the same activation condition. In addition, we also attempted synthesis of AC activated with combination of (KOH + K<sub>2</sub>CO<sub>3</sub>) and (NaOH + Na<sub>2</sub>CO<sub>3</sub>). As can be ascertain from the Table 1, at the same activation conditions the sample activated with NaOH had S<sub>BET</sub> (1269 m<sup>2</sup>/g) slightly higher than S<sub>BET</sub> of the sample soaked with combination (NaOH + Na<sub>2</sub>CO<sub>3</sub>) which was 1232 m<sup>2</sup>/g. On the other hand, the S<sub>BET</sub> increased



**Fig. 1.** XRD Patterns of activated carbon synthesized by activating at (a) 900 °C for 1 hr after soaking in KOH, (b) 900 °C for 2 hrs after soaking in KOH, (c) 900 °C for 3 hrs after soaking in KOH, (d) 900 °C for 3 hrs after soaking in combination of KOH + 10 %K<sub>2</sub>CO<sub>3</sub>.

**Table 1.** Experimental parameters and porous structure parameters of activated carbon derived from RiceHusk in various activation conditions at 900 °C.

Samples	ACN9312	ACNN9312	ACK9112	ACK9212	ACK9312	ACKK9312
BET(m <sup>2</sup> /g)	1269	1232	1475	1667	1793	1982
Iodine number(mg/g)	1221.4125	1198.5000	1241.5142	1284.8625	1296.1928	1332.4500
Micropore area(m <sup>2</sup> /g)	489.1409	422.8011	540.5819	709.3630	747.7136	579.5124
Micropore volume(cm <sup>3</sup> /g)	0.260975	0.231563	0.294138	0.383441	0.406235	0.319240
Average Diameter(nm)	2.8682	3.4301	2.6604	2.6517	2.5616	2.5922

considerably from 1793 to 1982  $\text{m}^2/\text{g}$  when activation reagent KOH was replaced with the combination (KOH +  $\text{K}_2\text{CO}_3$ ). This result, apparently, indicates the influence of chemical activating reagent on  $S_{\text{BET}}$  of ACs. The reason, as to why only (KOH +  $\text{K}_2\text{CO}_3$ ) combination showed increased  $S_{\text{BET}}$ , is uncertain and needs further investigation.

The  $\text{N}_2$ -adsorption isotherm obtained for the samples prepared under the various conditions is shown in Fig. 2. Nitrogen adsorption is a standard method for the determination of porosity of carbonaceous adsorbents. The adsorption isotherm is the information source about the porous structure of the adsorbent, heat of adsorption and characteristics of physics and chemistry.<sup>17)</sup> In Fig. 2, it can be seen that volume adsorbed curves relatively increased in initial adsorption region and had flatter plateau region at higher relative pressure. According to IUPAC classification, these isotherms belong to Type I, which represents dense micropore structures. It shows that the ACs synthesized from rice husk would be more porous

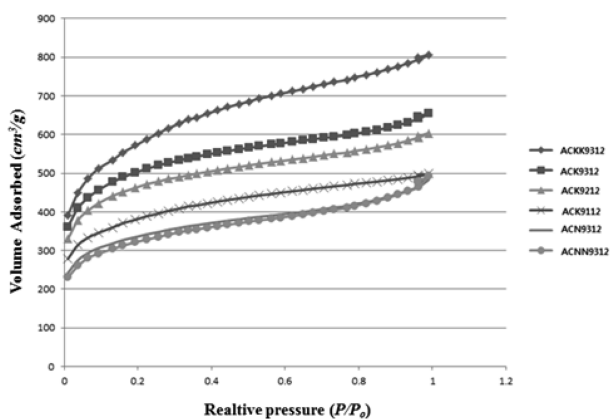


Fig. 2. Nitrogen (77 K) adsorption isotherms of the Rice Husk based activated carbon.

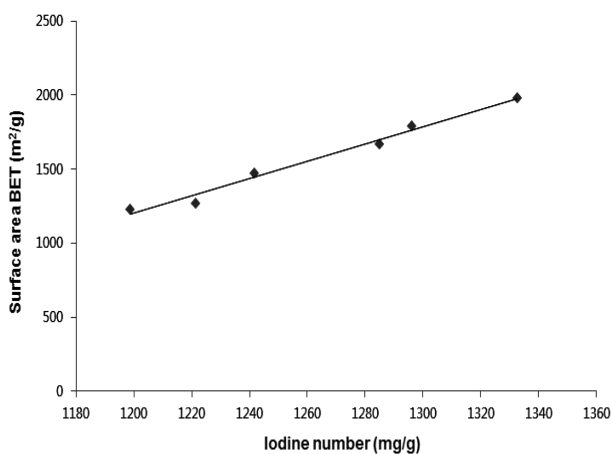


Fig. 3. Correlation between the surface area calculated according to the BET method and the iodine adsorption number as measured by the KS M 1802.

with a narrow pore size distribution. The saturated  $\text{N}_2$  volume adsorbed at  $P/P_0 = 1$  on sample ACKK9312 was clearly higher than that of other samples. Clearly, the use of  $\text{K}_2\text{CO}_3$  combined with KOH as activating reagent resulted in more porous structure and increased adsorbed property of AC.

Fig. 3 illustrates correlation between the surface area calculated by the BET method and the iodine adsorption number as measured by the KS M 1802. The Iodine adsorbed number increases with increasing specific surface area and can be represented by a straight line. In other words, the strength of Iodine adsorption on the ACs surface is stronger if the ACs internal structure is more porous.

### 3.2 Electrochemical performances of the activated carbon

Electrochemical properties of AC samples were investigated using cyclic voltammogram (CV) tests in the potential range of (-1; -0.1) V vs. Hg/HgO. The CV for the AC sample ACKK9312 as electrodes in 6M KOH solution is

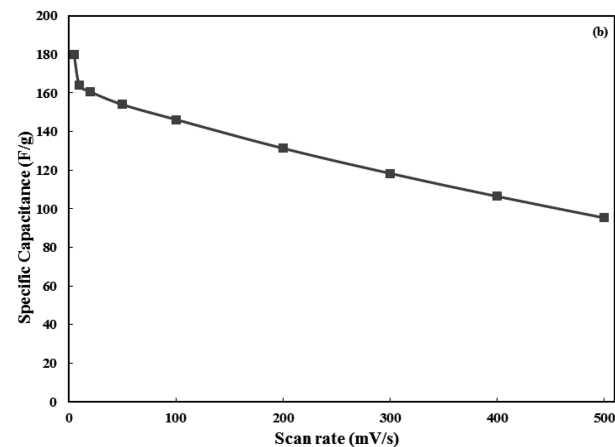
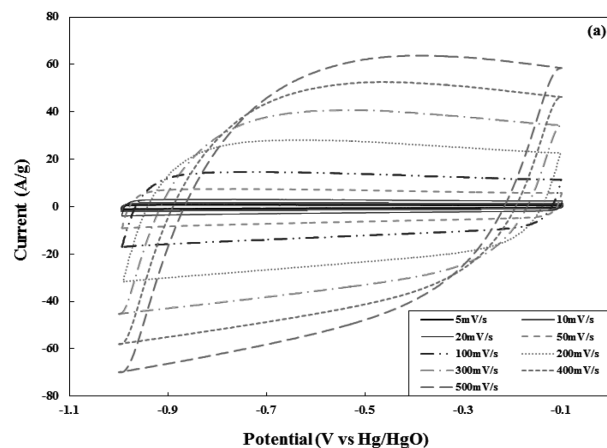
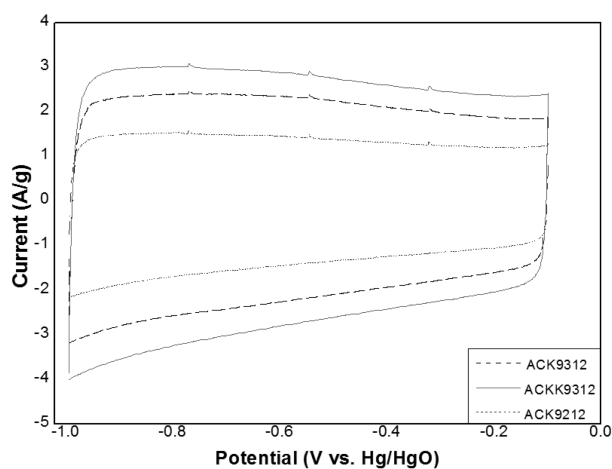


Fig. 4. (a) Cyclic voltammograms of the activated carbon electrode ACKK9312 in 6M KOH at various scan rates; (b) specific capacitance based on activated carbon (ACKK9312) as a function of scan rate.

shown in Fig. 4(a), which was recorded at different scan rates of 5, 10, 20, 50, 100, 200, 300, 400 and 500 mV/s. As shown in Fig. 4(a), the capacitor with ACKK9312 electrode exhibits charge propagation evident by the rectangular shape voltammograms as a reversible system up to a scan rate of 500 mV/s. At higher scan rates, the CV curves deviate from the rectangular shape to an extended shape. This can be explained as the effect of electrochemical polarization and diffusion resistance on the electrodes.<sup>18)</sup> As the scan rate increases, the AC electrode in the electrolyte suffers from higher diffusion resistance and larger electrochemical polarization, which would influence the capacitive behavior and interaction between the AC electrode and the electrolyte. According to the Eq. (2) and Eq. (3), the specific capacitance of ACKK9312 electrode calculated from the area of the CV curve was found to be 179 F/g. The dependence of the specific capacitance on the scan rates is shown in Fig. 4(b). It can be clearly seen that the capacitance decreased slightly with the increase of scan rate. The increase of scan rate makes the ion access to the electrode surface limited, limiting it only to the outer electrode surface and not to the internal pores leading to the capacitance decrease.<sup>19)</sup> However, as the scan rate rises to 100 mV/s, the specific capacitance of ACKK9312 electrode remained at 146 F/g which is over 80 % of the value measured at 5 mV/s (179 F/g) before decreasing to 131 F/g at 200 mV/s. This slight capacitance decay phenomenon at higher scan rates indicates the good performance of the AC electrodes.

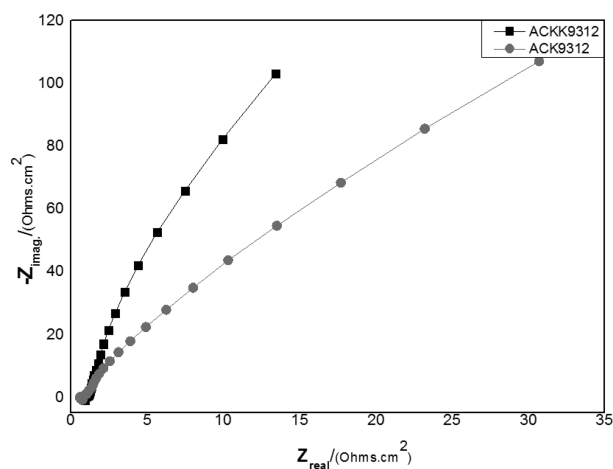
Fig. 5 displays the cyclic voltammograms of ACs electrodes ACK9212, ACK 9312 and ACKK9312 measured at 20 mV/s in 6M KOH solution. The results show that the CV curves of ACKK9312 electrode had the enclosed area larger than that of other electrodes. It is well known that with the larger enclosed area of the CV curve, greater specific capacitance of AC samples can be obtained



**Fig. 5.** Cyclic voltammograms of ACs electrodes ACK9212, ACK 9312 and ACKK9312 as measured at 20 mV/s in 6M KOH.

i.e. the specific capacitance of electrode ACKK9312 (179 F/g) was higher than that of electrode ACK9312 (145 F/g) and ACK9212 (98 F/g). The use of (KOH + K<sub>2</sub>CO<sub>3</sub>) combination as an activating reagent is a more adept idea for high capacitance AC synthesis compared to KOH alone as a chemical activating reagent mentioned in previous researches.

The electrochemical behavior at the electrodes/electrolyte interface was investigated by measurement of AC impedance from 10<sup>-2</sup> to 10<sup>5</sup> Hz frequency. The impedance spectra for the electrode ACKK9312 and ACK9312 expressed as Nyquist plots are illustrated in Fig. 6. It was found that the Nyquist plots contain a high-frequency range and low-frequency spike range. The high-frequency range corresponds to charge transfer resistance at electrolyte/electrode interface and the low-frequency spike range corresponds to cations diffusion in the electrode solid. There was similarity between the high-frequency curves of the two electrodes; however, in the low frequency range, Nyquist plots of electrode ACK9312 exhibited a line close to 45°, but a line close to 90° was observed for the impedance spectra of ACKK9312 electrode, which suggest the pure capacitive behavior and fast transfer character of electrolyte ions in the structure of the AC electrode.<sup>20,21)</sup> The overall impedance of sample ACK9312 was larger than that of sample ACKK9312. Therefore, it can be said that the cations diffuse in the electrode ACKK9312 more quickly and easily, than in electrode ACK9312. This also shows that the sample ACKK9312 had more porous structure and reflected higher capacitance than other samples in these experiments. Therefore by comparing the results obtained, it can be said that AC prepared by soaking in combination of (KOH + K<sub>2</sub>CO<sub>3</sub>) gave better porous structure, capacitance and conductivity thus making it a promising material for supercapacitor electrodes.



**Fig. 6.** Nyquist plot of the electrodes ACKK9312 and ACK9312 prepared in 6M KOH electrolyte.

#### 4. Conclusion

In this study, high surface area activated carbons were synthesized by using potassium hydroxide(KOH), sodium hydroxide(NaOH) and combination of (KOH + K<sub>2</sub>CO<sub>3</sub>) & (NaOH + Na<sub>2</sub>CO<sub>3</sub>) as activating agents. The sample prepared by NaOH activation (ACN9312) had lower S<sub>BET</sub> and larger pore diameter than the sample prepared with KOH (ACK9312) at the same activation conditions. The S<sub>BET</sub> considerably increased from 1793 to 1982 m<sup>2</sup>/g when the samples prepared by soaking in KOH and combination of (KOH + K<sub>2</sub>CO<sub>3</sub>) is compared. This indicates the positive effect of combination chemical reagent on the porous structure. The strength of Iodine adsorption on the ACs surface is stronger if the ACs internal structure is more porous. The specific capacitance of the electrodes decreased with the increase of scan rate. The specific capacitance of electrode ACKK9312 (179 F/g) was higher than that of other electrodes. In addition, from ac-impedance analysis, the overall impedance of sample ACK9312 was larger than that of sample ACKK9312 implying that the ACKK9312 electrode can be a better material for the purpose of energy storages.

#### Acknowledgement

The research project was supported by the Korea Research Foundation Grant funded by the Korean Government(Contraction No.: K21003002146-12B1200-03800).

#### References

1. B. E. Conway, *Electrochemical Supercapacitors*, Kluwer-Plenum Pub. Co. New York (1999).
2. A. Burke, *J. Power Source*, **91**, 37 (2000).
3. H. Wang, J. Varghese and L. Pilon, *Electrochimica Acta.*, **56**, 6189 (2011).
4. L. Wang, T. Morishita, M. Toyoda and M. Inagaki, *Electrochimica Acta.*, **53**, 882 (2007).
5. L. Zhang, H. Liu, M. Wang and L. Chen, *Carbon*, **45**, 1439 (2007).
6. H. Shi, *Electrochimica Acta.*, **41**, 1633-1639 (1996).
7. H. Teng, Y. J. Chang and C. T. Hsieh, *Carbon*, **39**, 1981 (2001).
8. G. Salitra, A. Soffer, L. Eliad, Y. Cohen and Aurbach D. *J. Electrochem. Soc.*, **147**, 2486 (2000).
9. C. T. Hsieh and H. Teng, *Carbon*, **40**, 667 (2002).
10. K. Y Foo and B. H Hameed, *Bioresour. Technol.*, **102**, 9814 (2011).
11. G. Afrane and O. W Achaw. *Bioresour. Technol.*, **99**, 6678 (2008).
12. S. H Guo, J. H Peng, W. Li, K. B Yang, L. B Zhang and S. M Zhang, *Appl. Surf. Sci.*, **255**, 8443 (2009).
13. J. Acharya, J. N Sahu, B. K Sahoo, C. R Mohanty and B. C Meikap, *J. Chem. Eng.*, **150**, 25-39 (2009).
14. A. Elmouwahidi, Z. Z Benabithé, F. C Marin and C. M Castilla, *Bioresour. Technol.*, **111**, 185 (2012).
15. A. Yuan, X. Wang, Y. Wang and J. Hu, *Energy Conversion and Management.*, **51**, 2588 (2010).
16. Y. Guo, J. Qi, Y. Jiang, S. Yang, Z. Wang and H. Xu, *Mater. Chem. Phys.*, **80**, 704 (2003).
17. W. Li, L. Zhang, J. Peng, N. Li and X. Zhu, *Industrial Crops and Products*, **27**, 341 (2008).
18. Y. Zhang, G. Li, L. Wang, A. Zhang, Y. Song and B. Huang, *Int. J. Hydrogen Energy*, **36**, 11760 (2011).
19. V. Subramanian, H. Zhu and B. Wei, *J. Power Sources*, **159**, 361 (2006).
20. W. H Wang and X. D Wang. *Electrochimica Acta.*, **52**, 6755 (2007).
21. M. Ghaemi, F. Ataherian, A. Zolfaghari and S. M Jafari, *Electrochimica Acta.*, **53**, 4607 (2008).