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Supercapacitors from Activated Carbon Derived from Banana Fibers

V. Subramanian,^{†,‡} Cheng Luo,[‡] A. M. Stephan,^{§,∇} K. S. Nahm,[∇] Sabu Thomas,[⊥] and Bingqing Wei^{*,†,‡}

Department of Mechanical Engineering, University of Delaware, Newark, Delaware 19716, Department of Electrical and Computer Engineering, Louisiana State University, Baton Rouge, Louisiana 70803, Electrochemical Energy Systems Division, Central Electrochemical Research Institute, Karaikudi–630 006, India, Department of Chemical Engineering, Chonbuk National University, Chonju 561-756, South Korea, and School of Chemical Sciences, Mahatma Gandhi University, Priyadarshini Hills P. O., Kottayam–686 560, India

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Carbon materials were synthesized from banana fibers by treating the fibers with pore-forming substances such as ZnCl₂ and KOH with an intention to improve the surface area and their electrochemical performance as electrical double-layer capacitor electrodes. The performance of these materials was studied in a neutral electrolyte for the first time. There has been a substantive increase in the specific surface area of the treated carbon material because of the effective pore generations. The structural and surface properties of the prepared carbon materials were studied using scanning electron microscopy and N₂ adsorption/desorption studies. The surface area of the 10% ZnCl₂ treated sample was found to be 1097 m²/g. The electrochemical properties of untreated and porogen treated carbons were evaluated by using cyclic voltammetry and galvanostatic charge–discharge studies, and the specific capacitance as high as 74 F/g in 1 M Na₂SO₄ neutral electrolyte was obtained for 10% ZnCl₂ treated carbon as determined by constant current charge–discharge studies. The system showed excellent cyclability with a Coulombic efficiency of ~88% at a high current density of 500 mA/g for 500 cycles. The electrochemical performance of the high surface area carbon in the neutral electrolyte medium is significantly high, and the reasons are discussed.

1. Introduction

Energy consumption relying on fossil fuels is forecasted to cause a severe problem in the world economics and ecology mainly because of depleting resources and increasing environmental concerns. Developing alternative energy storage or conversion devices with high power and energy densities is under serious consideration as a viable alternative. Lithium-ion batteries, fuel cells, and supercapacitors (SCs) are considered strongly as major contenders for power source applications. SC or ultracapacitor is one of the most promising electrochemical energy storage systems which have attracted much attention due to their potential applications ranging from mobile devices to electric vehicles. SCs are divided into two categories, namely, electrical double-layer capacitors (EDLCs) and pseudocapacitors, which are distinguished by their charge storage mechanism. EDLCs show a non-faradic reaction with accumulation of charges at the electrode and electrolyte interface, while pseudocapacitors exhibit faradic redox reactions.¹

In recent years, efforts in developing better EDLCs have gained importance because of their excellent power density which will provide rapid charge and discharge capabilities, leading to an ideal power source for applications such as mobile phones, laptop computers, etc. A variety of carbonaceous

materials such as activated carbon, carbon nanotubes, etc., are currently investigated for use as electrode materials for EDLCs.² However, activated carbon enjoys a place of pride mainly because of its abundance, cost effectiveness, and environmentally benign nature. Comparing with conventional capacitors, EDLCs with activated carbon electrodes are known to exhibit higher energy density mainly owing to their extremely high surface areas.^{1,2}

Fundamentals behind activation of carbon materials have been well studied and have been extensively reported in the open literature.^{3–5} The activation of carbon materials is generally done either by a physical or chemical process. In the case of physical activation process, removal of a large amount of internal carbon mass is necessary to impart well-developed carbon structures, while in the chemical activation process, all the chemical agents used are dehydrating agents which influence pyrolytic decomposition resulting in the formation of tar, which increases the carbon yield.^{3,5} However, there is no single mechanism by which the effective increase in surface area and formation of pores has been proposed.

Activated carbons such as activated carbon powder (ACP), activated carbon fiber cloth (ACF-cloth), and synthetic carbon aerogel have been investigated for EDLC applications. According to the characteristics of EDLCs, the capacitance and resistance of EDLCs are largely influenced by the specific surface area and pore size distribution.⁶ The characteristics of EDLCs are also influenced by the particle morphology and size of the activated carbon particles. ACF-cloth electrodes exhibit high performance since the ACF-cloth has a high specific surface area and suitable pore size distribution for forming an

* Author for correspondence. Tel.: 302-831-6438. Fax: 302-831-3619. E-mail: weib@udel.edu.

[†] University of Delaware.

[‡] Louisiana State University.

[§] Central Electrochemical Research Institute.

[∇] Chonbuk National University.

[⊥] Mahatma Gandhi University.

electric double layer.⁶ Moreover, the free-standing nature of the ACF-cloth prevents the usage of any binder for the electrode formation, which greatly improves the electrical properties of the electrode. On the other hand, the ACPs are composite electrodes involving conducting carbon black and binder with a specific capacitance of 49 F/g in the 5.35 M aqueous KOH electrolyte or 28 F/g in the 1 M aqueous solution of KCl electrolyte.⁶ The high surface area and the porosity of the activated carbon are the basic advantages to form an effective double layer, which results in an EDLC with a high power density and long cycle life. The capacitive behavior of carbon materials may be improved by different activation processes.

In the present study, activation of carbon derived from banana fibers were performed with KOH or ZnCl₂, where the KOH and ZnCl₂ act as pore-forming agents thereby improving the specific surface area of the material. The main advantage of the present carbon material is its source, banana fibers. The banana fibers are naturally occurring, and carbonization process is simple and environmentally benign. Generally, it is believed that the activation process of the carbon fibers increases the pore structure and morphology with a substantial increase in the specific surface area which is very critical for a better double-layer capacitance. It has been reported that activation of carbon using KOH provides a very large surface area of over 2000 m²/g.⁶ Graphitized carbons activated with KOH are reported to show a large capacitance of 40 F/g by weight in two electrode systems.⁵ Although a variety of carbon materials from different sources were prepared and activated for the use as an EDLC electrode, there are only a few studies that reported on the synthesis of carbon from a natural precursor for EDLC applications utilizing neutral precursors.^{7–9} Particularly, the use of carbon material obtained by the pyrolysis of a cellulose-based natural precursor such as banana fiber has not been addressed so far in the double-layer capacitance perspective. This motivated us to explore the possibility of utilizing the carbon materials derived from banana fiber in a neutral electrolyte medium. In this paper, we report the EDLC performance of carbon materials derived from banana fibers with and without activation. The structural and electrochemical properties of the untreated and the activated carbon materials are discussed in detail.

2. Experimental Section

The banana fiber carbons were prepared as follows. High-quality banana stems were obtained from the fields of Kerala, India. Sheets of herbaceous stems were dried in the sun, and fibers were drawn from them. Then the fibers were soaked, washed, and dried. The brownish white dry fibers were then treated with concentrated solutions of KOH or ZnCl₂ for 5 days at 110 °C at a fiber:porogen ratio of 1:5 by weight and dried. Pyrolysis was then carried out at 800 °C for 1 h under flowing nitrogen at a heating rate of 10 °C/min.

The nature of the carbon and their pore structures before and after activation were characterized with X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM). The electrochemical performance was studied using cyclic voltammetry (CV) and galvanostatic charge and discharge measurements. The electrodes for evaluating the electrochemical properties of the as-synthesized and activated carbons were fabricated by mixing with 20 wt % carbon black (Black Pearl 2000, Cabot Corp., U.S.A.) and 5 wt % PVdF-HFP binder using *N*-methyl-2-pyrrolidone (NMP) as a solvent. A slurry of the above mixture was subsequently brush-coated onto a Ni mesh. The mesh was dried at 110 °C in

air for 30 min for the removal of the solvent. After drying, the coated mesh was pressed to more completely adhere to the electrode material with the current collector.

CV studies were performed using a potentiostat/galvanostat (PGSTAT30, Autolab, EchoChemie, The Netherlands) in a three-electrode configuration using the Ni mesh coated with activated carbon as the working electrode, Pt wire as the counter, and saturated calomel electrode (SCE) as the reference. CV studies were recorded between −0.2 and 0.8 V in a 1 M Na₂SO₄ neutral electrolyte at different scan rates. The specific capacitance was evaluated from the area of the charge and discharge curves of the CV plot. Galvanostatic charge–discharge experiments were performed in a similar setup as described above using Arbin Instrument, with a specific high current of 500 mA/g and between −0.2 and 0.8 V. The specific capacitance of the system has been evaluated using the formula

$$C(\text{F/g}) = i\Delta t/m\Delta V \quad (1)$$

where i is the current used for charge–discharge, Δt is the time elapsed for the charge or discharge cycle, m is the mass of the active electrode, and ΔV is the voltage interval of the charge or discharge.

3. Results and Discussion

Two different chemical activation processes involving KOH and ZnCl₂ respectively have been employed to improve the specific surface areas and pore structures of the carbon materials derived from the banana fibers. Figure 1 depicts the SEM micrographs of carbon fibers with and without treatment. The untreated carbon fibers show a micrometer-sized tube-like structure. The carbon fibers treated with ZnCl₂ seem to have large aligned fibrous stacks with parts of the structure blown off because of the eliminating gases during the pyrolysis process, while the KOH treated carbon fibers have a loose, disjointed structure without any definite shape. This is very interesting in terms of applications mainly because of the different morphological end structures. In other words, just by changing the chemicals used for activation we can achieve completely different structures for the carbon.

Surface properties of the synthesized carbon materials are very critical for the electrochemical performance when used as an electrode material in double-layer capacitors. Table 1 summarizes the value of average pore diameter and BET surface area of the different carbon structures. As an example, a typical N₂-adsorption–desorption isotherm for the banana fiber carbon treated with 10% ZnCl₂ is shown in Figure 2. The BET surface area of the untreated carbon is 36 m²/g and increases to 686 m²/g and 1097 m²/g for the carbons after treatments with KOH and ZnCl₂, respectively. Thus, the surface area increased up to 35 times because of the action of the porogens. It is shown below that the increase in the specific surface area can significantly influence the electrochemical performance of the different carbon structures. On the other hand, the pore diameter does not show any significant increase after the treatments. The pore diameter is from 19 Å for the untreated fiber carbon to 25 and 23 Å for the structures treated with KOH and ZnCl₂, respectively. Another important point worth mentioning is the observed hysteresis in the case of the N₂ adsorption/desorption isotherms which is mainly due to the mesoporosity of the materials. This behavior is observed in all the three carbon materials studied and is predominantly due to the similar pore diameters in the mesoporous region for the untreated and the porogen treated carbons.

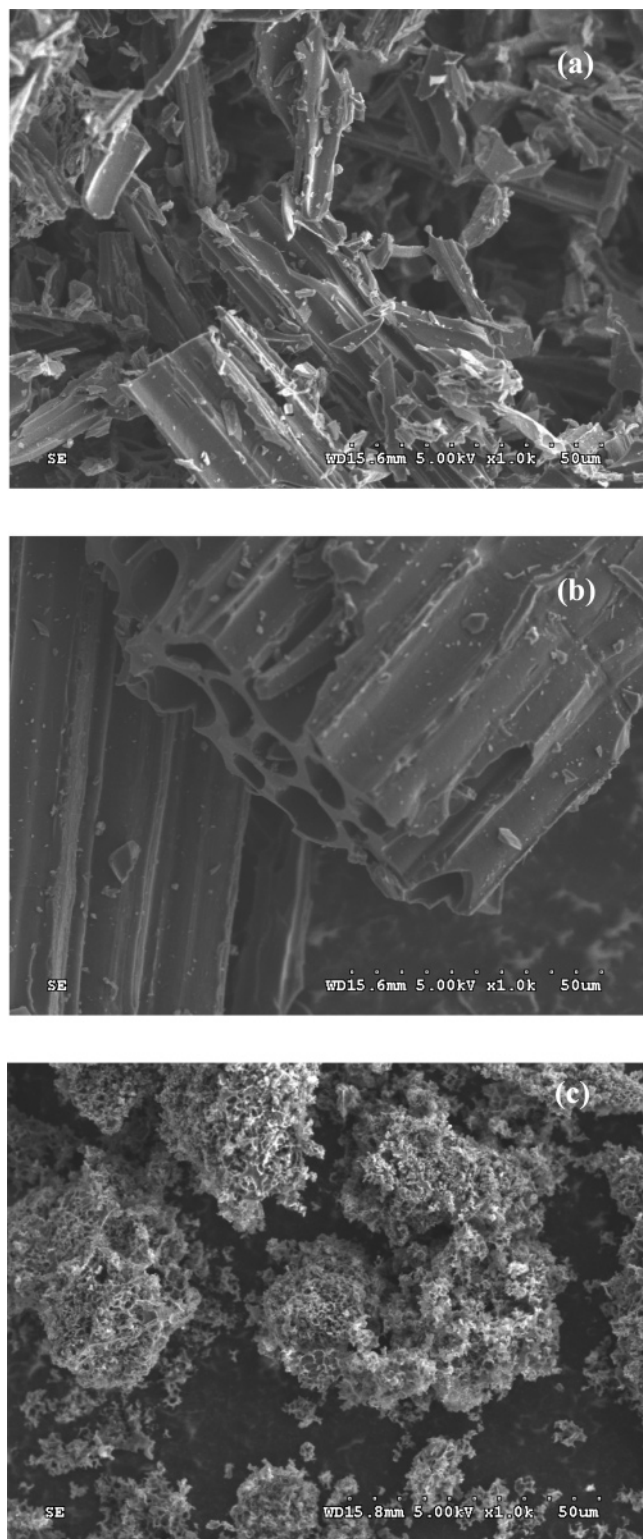


Figure 1. SEMs of (a) untreated carbon fibers, (b) carbon fibers treated by ZnCl_2 , and (c) carbon fibers treated by KOH.

To further explore the surface properties of the synthesized carbon materials, FTIR studies were employed and the details are given elsewhere.¹⁰ It was evident from the previous study that the oxygens exist as surface functional groups such as carboxyls, carboxyl anhydrides, phenols, carbonyls, lactones, quinines, quinine-like structures, etc., which are formed during the pyrolysis process and appear at edge carbon atoms.^{11–12}

The fundamentals behind the chemical activation using KOH and ZnCl_2 are well-known for various carbon materials.³ The

TABLE 1: Average Pore Diameter and BET Surface Area of the Different Carbon Structures

carbon sample	pore diameter (Å)	BET surface area ($\text{m}^2 \text{g}^{-1}$)
untreated	19	36
10% KOH treated	25	686
10% ZnCl_2 treated	23	1097

pore generation in carbon materials treated with KOH is mainly due to the presence of oxygen in KOH which results in the elimination of cross-linking and the stabilization of carbon atoms in the crystallites.³ At the pyrolysis temperature, the metallic potassium intercalates into the carbon structure and disrupts the lamellae arrangement of the crystallite.³ The porous nature is governed by the removal of potassium salts during washing and the removal of interior carbon atoms during the pyrolysis process. Mostly the pores exist in the mesoporous region. In the case of ZnCl_2 , it acts as a dehydration agent during the carbonization process, resulting in charring and aromatization of carbon and in turn yielding the pore formation. It is believed that during the washing stage after the carbonization process, the removal of unreacted ZnCl_2 salts results in further pore generations. In all these cases, the pore exists in the mesoporous region, as supported with the results from SEM and N_2 -adsorption studies.

XRD studies of the untreated and the activated carbons are discussed in detail in our earlier study.¹⁰ Briefly, the XRD patterns of the carbon samples revealed the disordered nature of the samples with still discernible characteristic (002) and (100) peaks of graphite. The (100) reflection corresponds to the honeycomb structure formed by sp^2 hybridized carbons, while the broad (002) reflections between 20° and 30° indicate small domains of coherent and parallel stacking of the graphene sheets. According to Liu et al.¹³ the empirical parameter, R , defined as the ratio of the height of the (002) Bragg reflection to that of background is a measure of the quantity of single-layered carbon sheets in disordered carbons prepared by low-temperature pyrolysis. Low values of the R factor for the samples (untreated: 2.31; ZnCl_2 treated: 2.27; KOH treated: 2.02) suggest large concentrations of nonparallel single layers of carbon.¹³ The decrease in the R value upon treatment with the porogens suggests a breakdown of aligned structural domains in the carbon matrix.¹³

Typical CV curves for the untreated banana fiber carbon and that treated with 10% KOH and 10% ZnCl_2 at different scan rates are shown in Figure 3. The CV curves exhibit a typical capacitor behavior showing a nearly rectangular shape for all scan rates except for that recorded at 100 mV/s. Similar results have been observed for other activated carbons when the scan rate is higher than 50 mV/s.^{14–16} As discussed above, the main idea behind the activation process using KOH and ZnCl_2 is to improve porosity of the carbon thereby increasing the specific surface area. The specific capacitance values for the untreated carbon at all scan rates are low because of the smaller surface area of the material; however, there has been an interestingly stable performance as shown in Figure 3. As expected, the activated carbons show an improved specific capacitance mainly because of the increased surface area. In the case of the carbon activated using KOH, the specific capacitance was 66 F/g at 5 mV/s, whereas it decreased to 54 F/g at a scan rate of 100 mV/s. A similar trend was found for the sample treated with 10% ZnCl_2 , but the decrease of the capacitance from 86 F/g at 5 mV/s to 83 F/g at 100 mV/s is relatively small, indicating that this activation process has more stabilized

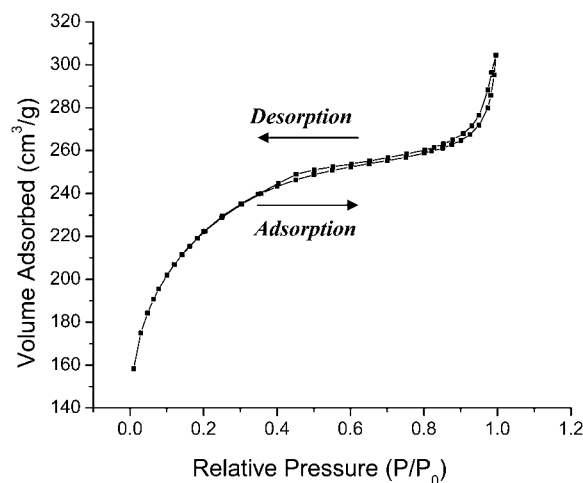


Figure 2. Typical N₂ adsorption–desorption curve for carbon synthesized from banana fiber and activated with 10% ZnCl₂.

structure for a high rate capability. It is worth mentioning that all the values in this report are after subtracting the contribution from the conducting carbon black (BP 2000). For this purpose we performed the CV studies for the BP 2000 alone in the same electrolyte (1 M Na₂SO₄) at different scan rates similar to the studies performed for the untreated and treated carbons. The specific capacitance values derived from this study for BP 2000 were used to eliminate the contribution from the double-layer capacitance of the untreated and KOH and ZnCl₂ treated carbons.

In order to evaluate the cycling stability of the synthesized carbon materials, galvanostatic charge–discharge studies were performed at a fairly high current of 500 mA/g between -0.2 and 0.8 V in the 1 M Na₂SO₄ electrolyte. The long cycle performance is shown in Figure 4, and the typical charge discharge curves are shown as an inset. The curve profile in the inset clearly indicates a typical capacitor behavior without any plateaus. The specific reversible capacitance for the 10% ZnCl₂ treated sample was found to be 74 F/g in the first cycle and 65 F/g after 500 cycles with a coulombic efficiency of 88%. For the 10% KOH treated sample, it was 66 and 46 F/g for the first and 500th cycle, respectively, with an efficiency of 70%. However, in the case of untreated carbon, the capacitance was extremely low with a value of ~ 1 F/g for the first cycle with a stabilized capacity of 4 F/g after 500 cycles. The specific capacitance values agree well with that derived from the CV studies.

The main reason for the enhanced specific capacitance for the 10% ZnCl₂ treated sample is its high specific surface area (1097 m²/g). The increase in the specific surface area by at least 30 times that of the untreated carbon has resulted in the significant increase in the double-layer capacitance. In the case of the KOH treated carbon, there is also an increase in the specific surface area; however, the surface area was not as high as the ZnCl₂ treated carbon. Also, particle morphology of the formed carbons after treatment with ZnCl₂ and KOH are completely different. As can be seen from the SEM images shown in Figure 1, the ZnCl₂ treated sample shows carbon with a tube like structures whereas that treated with KOH reflects fine agglomerated particles. This basic difference in structure always affects the double-layer formation and the associated capacitance.

There has been well-documented data on the electrochemical performance of the activated carbon supercapacitor electrodes.¹⁷ However, most of the works have been reported using either

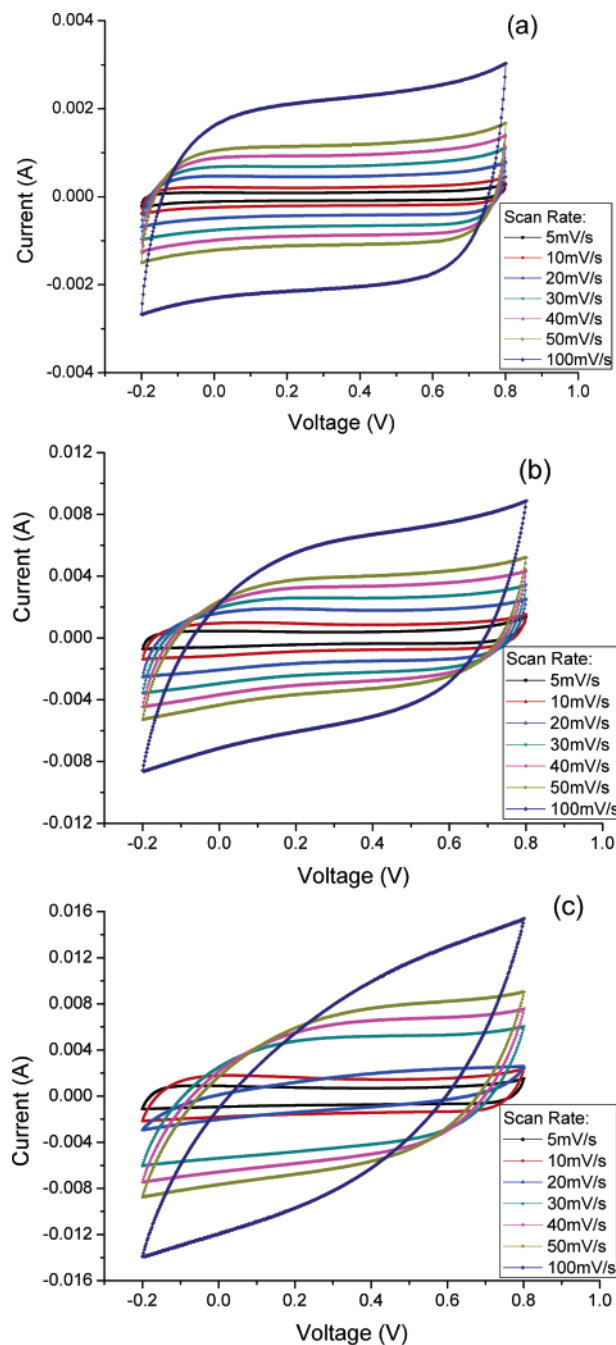


Figure 3. Cyclic voltammograms for (a) untreated carbon, (b) 10% KOH activated carbon, and (c) 10% ZnCl₂ activated carbon, at different scan rates from 5 to 100 mV/s.

an acidic electrolyte such as H₂SO₄ or highly basic electrolyte such as 6 M KOH. In general, the double-layer formation and the resulting capacitance show a strong dependence on the concentration of the electrolyte supported by the high surface area arising from the porous structure of the carbon. In the case of the H₂SO₄ based electrolyte, because of the presence of H⁺ ions as the mobile species, better ionic diffusion is observed into the pores of the carbon, resulting in an enhanced EDLC performance. Despite these advantages, the main disadvantage of the high corrosion rate of the current collectors because of the extreme conditions of the electrolyte limits the use of such an electrolyte system. In the case RuO₂, a potential pseudocapacitor material, use of 5.3 M H₂SO₄ is mandatory to extract the full potential of the pseudocapacitance property.¹⁸ Here, both ion dissolution into the electrolyte combined with corrosion of

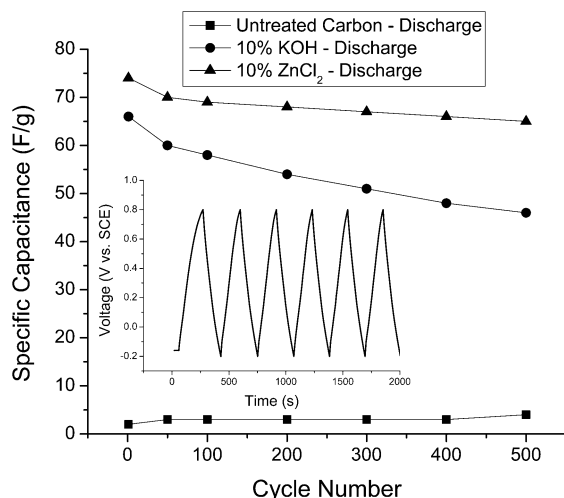


Figure 4. Cycling performance of untreated and KOH/ZnCl₂ treated carbons at 500 mA/g between -0.2 and 0.8 V in a 1 M Na₂SO₄ neutral electrolyte. Inset: Typical galvanostatic charge–discharge cycling for activated carbon treated by 10% KOH at a constant current of 500 mA/g in the first six cycles.

the current collector has been reported to deteriorate the cycling performance of the capacitor. The aforementioned disadvantages prompted us to investigate the activated carbon performance in a neutral electrolyte such as 1 M Na₂SO₄. In our earlier study utilizing carbon nanotubes and MnO₂ in 1 M Na₂SO₄, we found no major disadvantages discussed above when cycled for more than 1000 times.¹⁹

Hulicova et al. reported the electrochemical performance of carbon derived from melamine resin heat treated at different temperatures in two different electrolytes— 1 M H₂SO₄ and 3 M NaCl.²⁰ In the case of neutral electrolytes, the specific capacitance is mainly governed by the non-faradic electrostatic sorption of ions at the double layer.¹³ Comparing the electrochemical capacitance of the carbon derived from melamine resin and that prepared from banana fiber in our experiments in the neutral electrolyte medium, the specific capacitance and electrochemical performance are much better in the latter. For the melamine resin based carbon, the best reported specific capacitance was 75 F/g at a low constant current, 20 mA/g.²⁰ In the present case, the specific capacitance is 74 F/g at a much higher constant current of 500 mA/g, which is 25 times higher than the former. The main difference between the carbon derived from melamine resin and banana fiber is the specific surface area. For the melamine resin based carbon, the maximum surface area reported was 345 m²/g.²⁰ Hence, the improved rate capability and enhanced long cycle performance in the present case is mainly due to the larger surface area.

Generally, systems using organic electrolytes such as Et₄NBF₄/propylene carbonate (PC) and acetonitrile (AN) solutions can be cycled in a wider potential window, up to 2.5 V, than that for a system in an aqueous electrolyte medium.²¹ However, it has been reported that the use of nonaqueous electrolytes in some form of porous carbons results in a lower specific capacitance. In the case of large surface area carbon materials used as electrodes for EDLCs, there has been an observed increase in the internal resistance upon charging. Conway et al.²² studied the details of such a behavior in nonaqueous electrolyte and attributed that the decrease in the free ion concentrations in the electrolyte was due to the electrostatic adsorption at the high surface area carbon and the electrolyte interface.²¹ The possible reason for the activated carbon fibers in the organic electrolytes system showing a lower specific

capacitance than that observed in the present study from banana fiber carbon may be attributed to the increase in the internal resistance.^{21–22}

4. Conclusions

Carbons from banana fibers treated with KOH and ZnCl₂ as pore formers have been successfully prepared by the simple pyrolysis process. The activated carbon showed an enhancement in surface area of up to 30 times than the untreated one. Different particle structure, morphology, and surface area are greatly reflected in the high-rate long-cycle electrochemical performance. The specific capacitance of the carbon material treated with ZnCl₂ showed the best performance with a value of 74 F/g and 88% coulombic efficiency for 500 cycles at a high current of 500 mA/g. In addition to the excellent electrochemical properties of these activated carbons, it is worthwhile to mention that the source for carbon is a natural and renewable one and the synthesis and activation processes are eco-friendly. This study opens new avenues in the search for new carbon materials for EDLC applications because of the green processing, the cost associated with the precursor, and the simplicity in the activation process.

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References and Notes

- (1) Conway, B. E. *Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications*; Kluwer-Plenum Press: New York, 1999.
- (2) Frackowiak, E.; Beguin, F. *Carbon* **2002**, *40*, 1775.
- (3) Ahmadpour, A.; Do, D. D. *Carbon* **1996**, *34*, 471.
- (4) Lua, A. C.; Yang, T. J. *Colloid Interface Sci.* **2005**, *290*, 505.
- (5) Ahmadpour, A.; King, B. A.; Do, D. D. *Ind. Eng. Chem. Res.* **1998**, *37*, 1329.
- (6) Tanahashi, I. *J. Appl. Electrochem.* **2005**, *35*, 1067.
- (7) Guo, Y.; Qi, J.; Jiang, Y.; Yang, S.; Wang, Z.; Xu, H. *Mater. Chem. Phys.* **2003**, *80*, 704–709.
- (8) Wu, F. C.; Tseng, R. L.; Hu, C. C.; Wang, C. C. *J. Power Sources* **2004**, *138*, 351–359.
- (9) Kim, Y. J.; Lee, B. J.; Suezaki, H.; Chino, T.; Abe, Y.; Yanagiura, T.; Park, K. C.; Endo, M. *Carbon* **2006**, *44*, 1581–1616.
- (10) Stephan, A. M.; Kumar, T. P.; Ramesh, R.; Thomas, S.; Jeong, S. K.; Nahm, K. S. *Mater. Sci. Eng. A* **2006**, *430*, 132–137.
- (11) Ehrburger, P.; Addoun, A.; Addoun, F.; Donnet, J. B. *Fuel* **1986**, *65*, 1447.
- (12) Naoi, K.; Ogihara, N.; Igarashi, Y.; Kamakura, A.; Kusachi, Y.; Utsugi, K. *J. Electrochem. Soc.* **2005**, *152* A, 1047.
- (13) Liu, Y.; Xue, J. S.; Dahn, J. R. *Carbon* **1996**, *34*, 193–200.
- (14) de Levie, R. *Electrochim. Acta* **1963**, *8*, 751.
- (15) Hsieh, C.-T.; Teng, H. *Carbon* **2002**, *40*, 667.
- (16) Nian, Y.-R.; Teng, H. *J. Electrochem. Soc.* **2002**, *149*, A1008.
- (17) Lee, G. J.; Pyun, S. J. *Korean Electrochem. Soc.* **2006**, *9*, 10.
- (18) Zheng, J. P.; Cygan, P. J.; Jow, T. R. *J. Electrochem. Soc.* **1995**, *142*, 2699.
- (19) Subramanian, V.; Zhu, H. W.; Wei, B. Q. *Electrochem. Commun.* **2006**, *8*, 827.
- (20) Hulicova, D.; Yamashita, J.; Soneda, Y.; Hatori, H.; Kodama, M. *Chem. Mater* **2005**, *17*, 1241.
- (21) Mitani, S.; Lee, S. L.; Saito, K.; Yoon, S. H.; Korai, Y.; Mochida, I. *Carbon* **2005**, *43*, 2960.
- (22) Pell, W. G.; Conway, B. E.; Marincic, N. *J. Electroanal. Chem.* **2000**, *491*, 9–21.