TRABAC ACTIVATED CARBON USED AS ELECTRODE MATERIAL IN AQUEOUS SUPERCAPACITOR

Van Man Tran¹⁺, Dinh Tan Phat Pham¹, Huu Tru Nguyen², Van Hoang Nguyen¹, My Loan Phung Le¹,²

¹Faculty of Chemistry, HCMUS–VNUHCM
227 Nguyen Van Cu Street, Ward 4, District 5, Ho Chi Minh City, Vietnam

²Applied Physical Chemistry Laboratory, HCMUS–VNUHCM
227 Nguyen Van Cu Street, Ward 4, District 5, Ho Chi Minh City, Vietnam

*Email: tvman@hcmus.edu.vn

Received: 30 December 2016; Accepted for publication: 9 March 2017

ABSTRACT

Carbon materials i.e. activated carbon, carbon aerogel, carbon nanotubes (CNTs)… store a high electric power and a great stable cyclability when they are used as electrode materials in electrical double–layers capacitor (EDLC). In this work, activated carbon from coconut shells which was cooperatively provided by the Tra Bac Joint Stock Corporation–TRABACO was investigated as electrode materials in EDLC. Raw carbon material with large particle size was crushed and sieved to obtain a 43 µm grain size fraction for electrochemical characterization. The symmetric EDLC configuration based on Tra Bac carbon was tested in Swagelok–type cell using KOH electrolyte in the potential range 0–1 V. The CV curves indicated that charges can be stored enormously with a high reversibility and stability. The high performance of EDLC based carbon in KOH electrolyte could be further improved by variation of electrode composition. The rate capability of the material was also studied under different current ranges. In our best results, a specific capacitance of 20 F/g was obtained at the charge–discharge current of 1 A/g. Even at very high applied current range, the capacitance dropped slowly, less than fifteen percent.

Keywords: activated carbon, aqueous supercapacitors, cyclic voltammetry.

1. INTRODUCTION

Energy storage in batteries and capacitors is reliable for number of portable to large scale applications. The high appreciation of supercapacitor due to its long cycle life, stability, short time of charge/discharge as compared to those of batteries that is very promising for all needs of high power density. However, the current technology of practical supercapacitors limits at 10 Wh/kg so it can’t be used for long operation. Addition, the high cost of production is also a restriction for supercapacitors [1, 2].

Supercapacitors can be classified based on charge storage mechanism including a faradic and non–faradic process [1, 2]. The electrical double layered capacitors (EDLC) which is non–
faradaic one had been commercialized with carbon–based materials, such as activated carbon (AC hereafter), carbon aerogel, carbon nanotubes (CNTs)... [3, 4]. The high surface area of carbon materials enhances the specific capacitance of the supercapacitors. The high electric conductivity, chemical inert, electrochemical stability of carbon materials made it highly stability up to hundred thousand charge–discharge cycles with high power density [1, 2]. Besides, the low cost of the material is also a concern. Especially, AC is easily to fabricate, from different sources, i.e. coconut shell, paper, wood... follow a physical treatment (steam, heat, CO₂...) or chemical activation (with KOH, ZnCl₂, H₃PO₄...) especially characterized by highly porous structure and high specific surface area. Additional, the activation process applied to create functional groups on the surface which helps to enhance specific capacitance through pseudofaradaic process [5–8]. Compared to the faradic materials like RuO₂, NiO or conductive polymers with a high specific capacitance but a poor cycle–life, the carbonaceous materials still gains the interest due to its mentioned benefits.

In Vietnam, AC is widely used for absorption and treatment process to eliminate heavy metal ions, dyes, gases, smell in water, air or sol. And AC also meets all the demands adequate for batteries or supercapacitors production. However, a sequent treatment process (thermal and chemical) would be applied to the raw material to approach this high requirement.

Beside the electrode part, electrolyte is important factor for high energy and high power density applications [1, 5, 6]. The use of organic electrolyte increases operating potential up to 3 V but the specific capacitance and power density are lower than the aqueous supercapacitor [2, 4, 9].

In this paper, AC made from coconut shell through stream treatment at high temperature was used as material for symmetric EDLC in KOH, Li₂SO₄ and Na₂SO₄ electrolytes. The electrode composition was also investigated to obtain the highest capacitance of the capacitor.

2. MATERIALS AND METHODS

The AC was supplied by Tra Bac Joint Stock Corporation (TRABACO) with particle size 6×12 meshes (1.40–3.35 mm). The activating process can be found in [10]. Briefly, the coconut shell carbon was treated with high pressure steam at 850–950 °C for hours to create a desired porous network. All the chemicals used in this work were of reagent grade. Sodium sulfate Na₂SO₄ (> 99 %), lithium sulfate Li₂SO₄ (> 99 %), potassium hydroxide KOH (> 99 %) were supplied by Merck.

The original carbon material was then crushed and sifted to reduce particle size to 43 µm and heated at 80 °C to remove absorbed matter.

The morphology was investigated by SEM (JEOL JSM–7401F, Japan, Sai Gon Hitech Park). The nitrogen absorption–desorption isotherms were measured at –196 °C using a Micrometrics ASAP 2020 (Institute of Chemical Technology). The specific surface areas of the samples were determined from nitrogen adsorption data in relative pressure range from 0.05 to 0.2 using Brunauer–Emmett–Teller (BET) method. The total pore volume was obtained from the amount of gas adsorbed at the relative pressure 0.99. Pore–size distribution was calculated using Micrometrics software based on the Barrett–Joyner–Halenda (BJH) method. X–ray photoelectron spectroscopy (XPS) analyses were operated with an AXIS–NOVA (Kratos) X–ray photoelectron spectrometer using monochromated AlKα X–ray source (hv = 1486.6 eV) operated at 150 W under a base pressure of 2.6×10⁻⁹ Torr at Institute for Materials Chemistry and Engineering Kyushu University. All electrochemical measurements of material were
evaluated in 16–channel MPG–2 Battery Cycler (Biologic SA, France) of Applied Physical Chemistry Laboratory, VNUHCM–University of Science. For this purpose, the electrode made from AC with/without acetylene black carbon C65 (Cabot, USA) and polytetrafluoroethylene–PTFE (solution 60 wt%, Sigma–Aldrich) as binder. They were mixed thoroughly in ethanol and rolled into slices. The component percentage was investigated to optimize the capacitance of electrode.

Three electrodes cell include working electrode was electrode thin film pressed into Pt wire, Ti as counter electrode (CE) and the reference electrode (RE) was Ag/AgCl/KCl 3 M (E = 0.197 V vs. Li+/Li). The electrolyte solution of 1 M Na2SO4 and Li2SO4 (Merck, > 99%) was used. The cyclic voltammetry (CV) was performed in potential windows of –0.6 to 0.8 V vs. NHE and the specific capacitance was calculated from CV by formula (1) at scan rate 1 mV/s.

The symmetric EDLC was assembled with 6 mm diameter of two thin–film electrodes at the same weight pressed onto the stainless–steel surface as current collector. The two electrodes were separated by Whatman microfiber membrane soaked with 6 M KOH solution (Merck, > 99 %) or 1 M Na2SO4 and Li2SO4 solutions. The EDLC performance was investigated by CV and galvanostatic cycling (GCPL) at different charge–discharge rates to evaluate capacitance and cycling stability.

3. RESULTS AND DISCUSSION

The valuable parameters of AC for use in EDLC are specific surface area (SSA) and pore size distribution determining the specific capacitance [2, 9, 11]. The chemical composition of AC includes about 90 wt% of carbon amount and some of impurities or moisture with low content (Table 1). The specific surface area of AC reaches highly as 1000 m²/g, emphasizing the high porosity of carbon.

<table>
<thead>
<tr>
<th>Element</th>
<th>Percent wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>89.4</td>
</tr>
<tr>
<td>Cl</td>
<td>0.3</td>
</tr>
<tr>
<td>O</td>
<td>9.1</td>
</tr>
<tr>
<td>S</td>
<td>0.3</td>
</tr>
<tr>
<td>Si</td>
<td>0.9</td>
</tr>
</tbody>
</table>

Table 1. Chemical composition of AC.

Figure 1. SEM images of AC.
The high surface area of AC is importantly contributed to the EDLC capacitance. The particle size of AC was not in uniform distribution that cover a large range from 43 µm (sieve size) to few µm (Figure 1a, b) and the micropore of particles is also obviously seen (Figure 1c). The pore size was interested because it related to the ability of ions moving/diffusing from the electrolyte bulk to the surface and into the pore [8] and thus the selection of suitable electrolyte for supercapacitor. The analysis of pore size distribution (Figure 2) gives average pore diameter of 63.7 nm and 178.4 nm. As seen in Table 2, the distribution of the micropore area is nearly 99.7 % for the whole specific surface area.

**Table 2. Result of N₂ absorption analysis of AC.**

<table>
<thead>
<tr>
<th>External surface area (m²/g)</th>
<th>Micropore area (m²/g)</th>
<th>Total surface area (m²/g)</th>
<th>Micropore volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>29.7777</td>
<td>996.9555</td>
<td>1026.7332</td>
<td>0.386</td>
</tr>
</tbody>
</table>

**Figure 2.** Pore size distribution of AC.

In Figure 2, the cyclic voltammogram of AC in three–electrode system was typical for carbonaceous electrode. The electrode includes AC and PTFE at weight ratio 90:10. The electrode represents a slightly higher charge storage ability at negative potential round 0.2 V. The specific capacitance was calculated from the total charge stored by using following equation (1) with \( C \) (F/g), \( \Delta V \) (V) and \( m \) (g) was specific capacitance, potential window and weight of active material respectively with the unit given in brackets.

\[
C = \frac{1}{\Delta V \times m} \int Idt
\]  

(1)

The specific capacitances are almost similar when Li₂SO₄ or Na₂SO₄ solution was used, about 80 F/g (Figure 3). The value can be compared with other types of AC used in EDLC that specific capacitance of 75–300 F/g in aqueous electrolyte and 40–120 F/g in organic electrolyte [2, 4, 9, 12].
Figure 3. CV curves of AC electrode in different electrolytes at scan rate of 2 mV/s.

Figure 4. (a) CV curve of EDLC at scan rate of 1 mV/s and (b) variation of specific capacitance with scan rate in different electrolytes.

The symmetric EDLC with AC material (90:10) in two electrodes also represents the characteristic of surface charge distribution in the potential 0–1 V (Figure 4a). The charge/discharge have high reversibility that the CV curves exhibit a rectangle shape and did not change in many cycles. The specific capacitance of EDLC with electrolyte can be seen in Figure 4b that reduces about 4–5 times in comparing to these values measured in three–electrode system. This is coherent with equation (2) that a EDLC consists of two electrodes act as two capacitors contact in series [4] and the total capacitance reciprocal to the sum of the reciprocals of the component capacitances $C_a$ and $C_c$.

$$\frac{1}{C} = \frac{1}{C_a} + \frac{1}{C_c} \quad (2)$$

In KOH solution, the charge storage ability slightly enhanced at low potential. In addition, the CV curves exhibit mostly a symmetric rectangle shape, that is different with the one in Li$_2$SO$_4$ solution.

Qu et al. [11] investigated the relation between ion size and the capacitance and indicated that the capacitance increase with increasing ion radius $Li^+ < Na^+ < K^+$ and with the decreasing of solvated ion radius. However, the capacitance evolution is completely different in our case.
The specific capacitance in Li$_2$SO$_4$ solution is slightly higher than that in KOH. The higher scan rate, the more time needed for solvated ions to contact to and be distributed in the surface and in the pore of material. The specific capacitance is high at slow rate in Li$_2$SO$_4$ and KOH solution but slowed down rapidly at high scan rate. It could be explained by the large pore size of AC adapting for all solvated ions. The specific capacitance obtained in Li$_2$SO$_4$ is fairly to it in KOH solution, thus the neutral salt solution with low concentration and less corrosive is potentially used for EDLC. Although, the high concentration of salt solution can enlarge the potential window due to the increase of over potential to H$^+$ reduction or O$_2$ oxidation reaction. Sun et al. [13] reported the enlargement of oxidation potential of EDLC up to 1.6 V in 1 M Li$_2$SO$_4$ solution. Therefore, in our work, the operational potential in Li$_2$SO$_4$ and Na$_2$SO$_4$ solution was cut at 1 V and the concentration was 1 M to avoid the corrosion of stainless steel current collector and the decomposition of electrolyte at its surface.

The fast decrease of specific capacitance in KOH and Li$_2$SO$_4$ can be also explained by poor electric conductivity of the electrode. So, the electrical performance of electrodes was optimized by investigation of acetylene black C65 addition. The CV and constant current charge/discharge of different electrode compositions were performed in 6 M KOH solution.

![Graphs showing performance of EDLC with variation of electrode components in 6 M KOH (a–b). The percentage was AC: C65: PTFE. (a) CV curve at scan rate 50 mV/s and (b) plot of specific capacitance with scan rate. (c) CV curve of electrode with components at ratio (90:5:5) in 1 M Li$_2$SO$_4$ at scan rate 25 mV/s and (d) plot of specific capacitance with scan rate.](image)

The results in Figure 5a and 5b show that the conductivity of the electrode could be enhanced by adding C65 or decreasing PTFE percentage. The conductivity of AC is inversely...
proportional to the binder amount in electrode composition. The evolution was obviously seen with the addition of C65. The rectangle shape of CV was retained even at high scan rate and the current density also increased significantly. The electrode (90:5:5) give the highest specific capacitance and good cycling capacity as seen from CV curves. Moreover, the capacitance only slightly changed with the change of scan rate. The capacitance decrease of electrode (85:10:5) (10% C65) can be explained by the reduction of active material amount in electrode composition.

The electrode (90:5:5) also expose an excellent performance in charge/discharge measurement. The charge/discharge curve of EDLC (Figure 6) exhibited a linear relation between potential and charge/discharge time. However, the lower ionic conductivity and the configuration of solvated ions in the surface cause the high ohmic and distributed resistance in Li2SO4 solvent that given a large voltage drop δE. The specific capacitance was calculated using equation (1) with I become constant and ∫dt is replaced by charge/discharge time.

During cycling at different current rates (Figure 7a, b), the specific capacitance of the electrode (90:5:5) slightly decreased. At 1 A/g, the specific capacitance reaches 20 F/g. At four–time current, the specific capacitance dropped only by 15%, about 16.8 F/g. Event at 10 A/g, the specific capacitance still remained at 12.5 F/g. Furthermore, the specific capacitance retained 88% its initial value of 16.5 F/g after 10,000 continuous charge/discharge cycling.

The expected capacity results of the electrode (90:5:5) did not exhibit in Li2SO4 solution (Figure 5c, d). The ability of charge storage wasn’t enhanced with addition of C65. The specific capacitance at slow scan rate did not reach to value of original electrode. The highest was only 17 F/g and drop rapidly with increasing scan rate. This can be explained due to changing in porous structure of the electrode when adding C65 that decreasing in pore size and reduce the ability of large hydrated ions like Li+ or SO42– ions to reach the surface than small hydrated K+ or OH−. The specific capacitance reaches 14 F/g at current 1 A/g and well maintained after 100 cycles. Due to the small specific capacitance, the rate capacity was limited to 5 A/g with about 5 F/g retained capacitance (Figure 7a, b).
Figure 7. Performance of EDLC with electrode component at (90:5:5) in 6 M KOH (a–b) and in 1 M Li₂SO₄ (c–d). (a) and (c): Plot of specific capacitance with scan rate. (c) and (d): Evaluation of specific capacitance with cycle at 1 A/g.

4. CONCLUSIONS

The EDLC electrode made from Tra Bac coconut shell activated carbon exhibited a good capacitance, especially in KOH solution. The addition of acetylene black C65 enhanced capacitance due to improvement of electric conduction. The capacitance was 20 F/g at 1 A/g and 12.5 F/g at 10 A/g. The stable charge/discharge was verified that 88% the initial value was retained at 1 A/g after 10,000 cycles.

Na₂SO₄ and Li₂SO₄ could be used as electrolyte at low concentration beside KOH but the performance of EDLC in these electrolytes must be further improved. The further works will be focused on the decrease of particle sizes and the increase number of open pore and widen pore size.

Acknowledgments. This work was supported by Vietnam National University of Ho Chi Minh City and VNUHCM – University of Science through grant NVTX–2017 and HS2013–76–01.
REFERENCES


