Investigation of the Capacitive Properties of Activated Carbon Prepared from Corn Cob in Na$_2$SO$_4$ and K$_2$SO$_4$ Electrolytes

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Received: May 2, 2016    Revised: June 23, 2016    Accepted: June 26, 2016    Published: July 1, 2016

Abstract: Activated carbons (ACs) prepared from corn cob by KOH-activation were used as electrode materials in supercapacitor. SEM showed that the ACs consist of spherical shape particles that transformed to rod like structure as activation temperature increasing from 700 to 850 °C. FTIR studies indicated the presence of function groups on the ACs surfaces. Raman spectra showed that the disorder of ACs sample increase as activation temperature from 700 to 800 °C and decrease afterward. BET results revealed that the ACs have porous structure, contain mostly micropore with specific surface area in the range from 1496 to 2331 m$^2$ g$^{-1}$. The capacitance properties were investigated using cyclic voltammetry (CV) and galvanostatic cycling with potential limitation (GCPL). These electrodes show a specific capacitance as high as 225 F g$^{-1}$ in 0.5 M K$_2$SO$_4$ and 0.5 M Na$_2$SO$_4$ electrolytes. In charge-discharge test, about 90% of the initial specific capacitance is still retained after 500 cycles, indicating that the activated carbon prepared from corn cob could be used as supercapacitor electrode materials.

Keywords: Activated Carbon; Corn cob; Supercapacitor; Electrolyte

1. INTRODUCTION

Energy produced by renewable sources, such as wind and solar, are intermittent and have a large fluctuation in intensity. To overcome such obstacle, energy storage device based on the electrochemical reactions, electrochemical double layer capacitor (EDLC) is considered a practical solution [1,2]. The capacitance of an EDLC depends strongly on the specific surface area [3] of the electrode materials and electrolytes. Aqueous electrolyte solutions with the advantage of high conductivity, low resistance, and cost effective [4], have been often applied as electrolyte for EDLC despite its short operation voltage [5]. Taking economic efficiency into account, neutral solution is always chosen over acidic or basic solutions as it is more easily available, cheaper and less corrosive.

Corn is one of the top agricultural commodities in Vietnam, which leads to the huge quantity of the disposed by-product corn cob. Rich in cellulose and hemicellulose, corn cob is considered as prospective precursors for activated carbon production [6]. The conversion corn cob to activated carbon can be achieved through physical or chemical activation. Physical activation is conducted at elevated
temperature in the presence of oxidizing gases while chemical activation employed chemical agents at milder conditions [7,8]. In comparison to physical activation, chemical activation produces smaller pore size activated carbon and has advantages of less energy consumption and higher yield [9].

It is believed that the pore size distribution of carbon electrode and the size of solvated ions in the electrolytes must be in harmony in order to achieved optimum behavior [10,11]. In the present study, activated carbon prepared from corn cob using chemical activation was investigated its electrochemical performance in aqueous solutions of Na₂SO₄ and K₂SO₄. The as-prepared activated carbon shows a great promise to be utilized in supercapacitor.

2. EXPERIMENTAL

2.1. Preparation of AC sample

Corn cob (obtained from Dien Bien region, Vietnam), after washed and dried at 60°C, was grilled and sieved to particle size of 1-2 mm. It was then carbonized at 450 °C in 90 min under a constant flow rate of nitrogen (300 mL min⁻¹). The char sample was activated in KOH with a char:KOH ratio of 1:3 at preset temperature in the range of 700 - 850 °C in 90 min under nitrogen atmosphere (300 mL min⁻¹). The prepared carbon was neutralized by 0.1 M HCl solution then washed with hot distilled water, thereafter dried and stored in a desiccator ready for used. The samples were labeled as AC-700, AC-750, AC-800 and AC-850 according to activation temperature.

2.2. Physiochemical characterization of electrode materials

The prepared activated carbons were characterized by scanning electron microscopy, SEM (S4800-Hitachi). Surface functional groups were determined by Fourier Transform Infrared spectroscopy, FTIR (Nexus 670 FTIR-Nicolet). Structure of AC samples was evaluated by RAMAN spectroscopy (Raman Microscope- Renishaw). Pore texture and specific surface area were analyzed by BET method (Tri Star 3020-Micromeritics).

2.3. Electrode preparation and electrochemical measurements

The working electrodes were prepared by mixing 80 wt.% AC sample, 10 wt.% graphite and 10 wt.% polytetrafluoroethylene (PTFE) in ethanol. The mixture slurry was laminated onto aluminum foil and dried at 120 °C for 24h. Thereafter it was pressed under 10 MPa. The resulted electrode area is 1 × 1 cm².

The electrochemical performance of AC material electrodes was carried out by an electrochemical work station (Autolab PGSTAT302N-Metrohm) using a three-electrode system at ambient temperature with 0.5M Na₂SO₄ or 0.5M K₂SO₄ aqueous solution as the electrolyte. Pt wire and saturated calomel electrode (SCE) served as the counter and the reference electrodes, respectively. Cyclic voltametry (CV) measurements were conducted in the potential range of -1.0 ± 0.0 V vs. SCE at different sweep rates ranging from 2 to 50 mV s⁻¹. Galvanostatic cycling with potential limitation (GCPL) test was carried out at a constant current density in the range from 0.2 to 2.0 A g⁻¹.
3. RESULT AND DISCUSSION

3.1. Characterization

Fig.1 shows the SEM image of AC samples prepared at different activation temperature. It can be seen from the pictures that all the AC samples consist of spherical shaped particles aggregated together to form pieces or rods. At low activation temperature, the particles stack to develop big chunks and seem to lack porosity. The rods start to establish at 700 °C, longer at 750 °C and uniform rods with porous structure can be found at 850 °C. This may be due to the change in activation process. At temperature higher than 750 °C, except for the main carbon-hydroxide reaction (6KOH + 2C → K₂CO₃ + 2K + 3H₂), there are other reactions such as carbonate decomposition to produce CO₂ [12]. This CO₂ can also react with carbon by a different process (gas phase catalytic carbon gasification) producing CO, thus widening the pores and causing the change in ACs structure.

![Figure 1. SEM images of AC samples at different activation temperature](image)

Fig.2 shows the FTIR spectrum of the as-prepared samples. As can be seen in the figure, except for the absorption of O-H stretching of hydroxyl groups or adsorbed water at 3410 cm⁻¹, there are absorption at 1720, 1630, 1380, which could be assigned to the C=O vibration of carboxyl, lactonic or anhydride groups [13], C=C aromatic ring vibration [14] and C-H bending [15], respectively. The bands at 1060 cm⁻¹ is assigned to ring vibration in a large aromatic skeleton generally found in activated carbon [16]. The region between 700 and 1200 cm⁻¹ contains various bands related to aromatic, out of plane C-H bending with different degrees of substitution [17].
Figure 2. FTIR spectra of the AC samples

Figure 3. (a) Raman spectra of AC samples, (b) Typical Gaussian fitting for AC-700
Raman spectroscopy was performed to distinguish the order and disorder crystal structure of carbon materials, as showed in Fig. 3. The spectra of all AC samples have similar shape with two typical peaks at ~ 1350 cm\(^{-1}\) (disordered-induced peak, D band) and ~ 1580 cm\(^{-1}\) (intense tangential mode, G band) [18,19]. No significant difference was detected between the positions of the G bands. However, the D band positions shift to lower wave number as the activation temperature increases. The ratio of ID/IG value is generally used to describe the amorphous carbon and graphitized structure in the samples [20]. The greater the ID/IG value, the higher the level of disorder of AC material, and vice versa. Furthermore, ID/IG is inversely proportional to the crystalline size along basal plane (La) measured from XRD: 1/La = ID/IG [21]. Raman data was deconvoluted by employing Gaussian fitting method and the typical fitting of AC-700 sample is shown in Fig. 3b. It can be observed that the spectrum consists of as many as four bands: D4 (sp\(^3\) bonds or C-C and C=C stretching vibrations) at 1247 cm\(^{-1}\); D1 at 1345 cm\(^{-1}\); D3 (amorphous carbon) at 1541 cm\(^{-1}\) and G at 1591 cm\(^{-1}\) [22,23]. The fitting results along with ID/IG ratio and La were summarized in Table 1. ID/IG ratio of ACs increase from 1.43 to 1.81 as activation temperature elevated from 700 to 800 oC, then decrease to 1.60 at activation temperature 850 oC. According to Ref. [12], at activation temperature as high as 850 oC, there is additional reaction of CO\(_2\) and C. Compare to the main activation reaction between C and KOH, this one is more difficult to happen, therefore, amorphous activated carbon will react prior to graphitic carbon causing a lowering in the degree of disorder.

<table>
<thead>
<tr>
<th>Sample</th>
<th>ID (a.u)</th>
<th>IG (a.u)</th>
<th>ID/IG</th>
<th>La (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC-700</td>
<td>7350.9</td>
<td>5148.6</td>
<td>1.43</td>
<td>3.05</td>
</tr>
<tr>
<td>AC-750</td>
<td>5238.8</td>
<td>3143.6</td>
<td>1.67</td>
<td>2.61</td>
</tr>
<tr>
<td>AC-800</td>
<td>5563.1</td>
<td>3067.1</td>
<td>1.81</td>
<td>2.40</td>
</tr>
<tr>
<td>AC-850</td>
<td>6214.8</td>
<td>3889.9</td>
<td>1.60</td>
<td>2.72</td>
</tr>
</tbody>
</table>

The adsorption isotherm of N\(_2\) at 77K was used to deduce the surface characteristics of AC sample, as showed in Fig. 4. All isotherms belong to type I in the IUPAC classification, characteristic of microporous materials [24]. Beside, the knee of the isotherms is quite wide and it is increasing with the increase of activation temperature, indicating the presence of mesopore and the amount of mesopore enhance with temperature.
**Figure 4.** Adsorption isotherm of N\(_2\) at 77K of AC samples activated at different temperatures

**Table 2.** Porosity parameters of AC samples activated at different temperatures

<table>
<thead>
<tr>
<th>M(\text{Âreau} )</th>
<th>(S_{\text{BET}}) (m(^2)/g)</th>
<th>(S_{\text{mic}}) (m(^2)/g)</th>
<th>(S_{\text{ext}}) (m(^2)/g)</th>
<th>(V_{\text{mic}}) (cm(^3)/g)</th>
<th>(V_{\text{ext}}) (cm(^3)/g)</th>
<th>(V_{\text{tot}}) (cm(^3)/g)</th>
<th>(S_{\text{mic}}/S_{\text{BET}}) (%)</th>
<th>(V_{\text{mic}}/V_{\text{tot}}) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC-700</td>
<td>1496</td>
<td>1468</td>
<td>28</td>
<td>0.6470</td>
<td>0.0413</td>
<td>0.6883</td>
<td>98.1</td>
<td>94.0</td>
</tr>
<tr>
<td>AC-750</td>
<td>1752</td>
<td>1718</td>
<td>34</td>
<td>0.7696</td>
<td>0.0518</td>
<td>0.8214</td>
<td>98.1</td>
<td>93.7</td>
</tr>
<tr>
<td>AC-800</td>
<td>1740</td>
<td>1719</td>
<td>21</td>
<td>0.7374</td>
<td>0.0320</td>
<td>0.7694</td>
<td>98.8</td>
<td>95.8</td>
</tr>
<tr>
<td>AC-850</td>
<td>2331</td>
<td>2283</td>
<td>48</td>
<td>1.0413</td>
<td>0.0696</td>
<td>1.1109</td>
<td>97.9</td>
<td>93.7</td>
</tr>
</tbody>
</table>

Physical properties of ACs obtained from N\(_2\) adsorption, included specific surface area (\(S_{\text{BET}}\)), calculated by BET equation [25]; microporous surface area (\(S_{\text{mic}}\)), external surface area (\(S_{\text{ext}}\)) and micropore volume (\(V_{\text{mic}}\)), evaluated by the t-plot method [26]; mesopore volume (\(V_{\text{mes}}\)), estimated by the Barrett–Joyner–Halenda (BJH) method [27] and the total pore volume (\(V_{\text{tot}}\)), evaluated by the sum of microporous and mesoporous volumes were listed in Table 2. As can be seen from this table, all AC samples exhibit a developed specific surface area and high pore volumes (\(S_{\text{BET}}\) varies from 1496 to 2331 m\(^2\)/g\(^{-1}\), \(V_{\text{tot}}\) varies from 0.6883 to 1.1109 cm\(^3\)/g\(^{-1}\)), mostly contributed by micropore (\(S_{\text{mic}}\) and \(V_{\text{mic}}\) make up \(\sim 98\%\) of \(S_{\text{BET}}\) and \(\sim 94\%\) of \(V_{\text{tot}}\), respectively).

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*Canadian Chemical Transactions* Year 2016 | Volume 4 | Issue 3 | Page 302-315
Figure 5. Pore size distributions of AC samples activated at different temperatures

The pore size distributions (PSDs) of AC samples, calculated using density functional theory (DFT) [28] by assuming that the pores of the sample have slit shapes, are illustrate in Fig.5. The obtained results reveal pore width of all the AC samples are less than 6 nm, therefore Fig.5 only shows the PSDs in the range of 0.8 \( \div \) 6 nm. As can be seen from the figure, the AC samples have the appreciable amount of micropores and small amount of mesopores. The high activation temperature resulted in the increase of the amount of pore size bigger than 1.5 nm, except for AC-800 sample.

3.2. Electrochemical analysis

3.2.1. Cyclic voltametry test

Cyclic voltametry test were performed at different scan rate from 2 to 50 mV s\(^{-1}\) in two different electrolytes. The typical cyclic voltammograms of all ACs samples electrode in 0.5 M K\(_2\)SO\(_4\) and 0.5 M Na\(_2\)SO\(_4\) solution at can rate in the range from 2 mV s\(^{-1}\) to 30 mV s\(^{-1}\) are showed in Fig.6. Near symmetric and rectangular shape of all curves proves ideal electrochemical double-layer capacitor of AC materials. There are very small humps (at 2 mV s\(^{-1}\)) attributed to pseudofaradaic redox reactions related to the surface functionalities of the materials. The CV curves remain rectangular shape even at a scan rate up to
30 mV s\(^{-1}\), indicating a good capacitor behavior of the corn cob base activated carbon. It can be seen from Fig.6 that in two investigated solution, the rectangular shape of CV curves is distorted at elevated scan rate. This result can be explained by the diffusion of \(K^+\) or \(Na^+\) ions in the pores of AC materials, especially micropore. The diffusion rate is not entirely proportional to the scan rate.

**Figure 6.** Cyclic voltammograms of ACs sample electrodes in 0.5M \(K_2SO_4\) and 0.5 M \(Na_2SO_4\) at scan rates of 2 and 30 mV s\(^{-1}\)

The gravimetric capacitance, \(C_{CV}\), of ACs material electrodes was calculated from the CV curve using equation (1):

\[
C_{CV} = \frac{\sum |I|\Delta t}{2m\Delta V}
\]  

(1)

where \(\sum |I|\Delta t\) is the area of the current (A) against time (s) curve, \(m\) is the mass (g) of active material in the electrode, and \(\Delta V\) is the potential window (V).

The variation of \(C_{CV}\) of all AC samples in two investigated solution at different scan rates are presented in Fig.7. The following results can be obtained:

i) In both electrolytes, for all scan rates, the capacitance increases in order: AC-700 < AC-750 \(\approx\) AC-800 < AC-800. This result is in accordance with the increase of specific surface area in Table 2, AC-700 has
the smallest specific surface area (1496 m$^2$ g$^{-1}$). AC-750 and AC-800 have similar value (1752 and 1740 m$^2$ g$^{-1}$), and AC-850 has the highest value of all (2331 m$^2$ g$^{-1}$).

![Graph](image)

**Figure 7.** Capacitance variations of AC electrodes at different scan rates in
(a) 0.5M K$_2$SO$_4$ and (b) 0.5M Na$_2$SO$_4$ solutions

ii) Capacitance of all samples decreases with the increasing of scan rate. In K$_2$SO$_4$ electrolyte, capacitances of AC-700, AC-750, AC-800 and AC-850 at scan rate of 2 mV s$^{-1}$ are 163, 191, 194 and 208 F g$^{-1}$, respectively. These values drop to 45, 81, 101 and 110 F g$^{-1}$ at scan rate of 50 mV s$^{-1}$. In Na$_2$SO$_4$ electrolyte, capacitances at scan rate of 2 mV s$^{-1}$ are 145, 186, 188 and 195 F g$^{-1}$, sink to 47, 81, 94 and 110 F g$^{-1}$ at scan rate of 50 mV s$^{-1}$, correspondingly. The decrease of capacitance might be because at high scan rate, K$^+$ or Na$^+$ ions cannot access into the inner pores of AC materials, hence decrease the capacitance.

iii) Capacitance of all AC samples in K$_2$SO$_4$ electrolyte somewhat higher than in Na$_2$SO$_4$ electrolyte at scan rate lower than 10 mV s$^{-1}$. At higher scan rate, the capacitances of AC samples stay the same regardless of the electrolytes. This might be due to the hydrated ionic radius of K$^+$ (3.31 Å) is smaller than of Na$^+$ (3.58 Å) [29], therefore, at slow scan rate, the amount of K$^+$ ions can access to micropores is much higher than of Na$^+$ ions. Nevertheless, at fast scan rate, this difference is not so obvious.

3.2.2. Galvanostatic cycling with potential limitation

Charge/discharge cycling behavior of electrode materials are performed using Galvanostatic cycling with potential limitation (GCPL) and showed in Fig. 8. As showed in Fig.8, the voltage-time follows linear dependence and the charge-discharge curve is generally symmetric implying the typical capacitor behavior. Nevertheless, there is a little voltage drop at the beginning of the discharge curve, which is due to the internal resistance of the cell.

Fig. 9 presented the typical chronopotentiograms of AC-850 electrode at current densities range from 0.2 to 2.0 A g$^{-1}$ in potential window from -1.0 to 0 V vs. SCE. The curves retain a perfect linear and symmetrical triangle even at high current density, improving typical capacitive behavior of the material. The gravimetric capacitance from the chronopotentiograms, C$_{CP}$, was obtained by the following equation:

$$C_{CP} = \frac{Q}{\Delta V}$$
\[ C_{CP} = \frac{I_d \Delta t}{m \Delta V} \]

(2)

**Figure 8.** Galvanostatic charge-discharge curves of AC electrodes at current density 0.2 \( \text{A g}^{-1} \) in (a) 0.5 M \( \text{K}_2\text{SO}_4 \) solution, (b) 0.5 M \( \text{Na}_2\text{SO}_4 \) solution

**Figure 9.** Galvanostatic charge-discharge curves of AC-850 electrode at different current densities in 0.5 M \( \text{K}_2\text{SO}_4 \) solution

where \( I_d \) is the discharge current (A), \( m \) is the mass of active material in the electrode (g), \( \Delta t \) is the discharge time (s), and \( \Delta V \) is the potential interval (V).

The variation of \( C_{CP} \) of all the AC samples in two investigated solution at current density loading between 0.2 and 2.0 \( \text{A g}^{-1} \) are show in Fig.10. As can be seen from Fig.10, in current density range, the capacitance of AC samples increases in order: AC-700 < AC-750 < AC-800 < AC-850. In 0.5 M \( \text{K}_2\text{SO}_4 \) as well as in 0.5 M \( \text{Na}_2\text{SO}_4 \) electrolytes, capacitance of all AC samples decrease with the increasing in charge-discharge current density. In \( \text{K}_2\text{SO}_4 \) electrolyte, capacitance of AC-700, AC-750, AC-800 and AC-850 at current density of 0.2 \( \text{A g}^{-1} \) are 188, 209, 211 and 225 \( \text{F g}^{-1} \), respectively. These values drop to 90, 167, 180 and 186 \( \text{F g}^{-1} \) at current density of 2.0 \( \text{Ag}^{-1} \). In \( \text{Na}_2\text{SO}_4 \) electrolyte, capacitance at 0.2 \( \text{A g}^{-1} \) are 164, 203, 207 and 218 \( \text{F g}^{-1} \), fall to 78, 160, 175 and 183 \( \text{F g}^{-1} \) at 2.0 \( \text{Ag}^{-1} \), correspondingly.
Figure 10. Capacitance variations of AC electrodes at different current densities in (a) 0.5M K$_2$SO$_4$ and (b) 0.5M Na$_2$SO$_4$ solutions

It can also be seen from Fig.10 that the change in capacitance of the AC samples at different current densities is similar to the change at different scan rates. This result can confirm the findings by means of CV method and contribute to the specific surface area and diffusion of K$^+$ and Na$^+$ ions.

3.2.3. Charge and discharge test

The cycling stability of activated carbon from corn cob was carried out on AC-850 electrode in 0.5M K$_2$SO$_4$ electrolyte as it gave the highest capacitance. The charge/discharge cycling behavior of AC-850 electrode at constant density of 0.2 and 2.0 A g$^{-1}$ for 500 cycles is showed in Fig.11.

Figure 11. Cycle lives of AC-850 electrode in K$_2$SO$_4$ solution at current densities of 0.2 and 2.0 A g$^{-1}$ (the inserted image is several charge-discharge curves)

It can be seen from several cycles illustrated in the inserted image that the shape of the charge/discharge curves is in typical triangular shape with the same slope variation of charge and
discharge curves. This again indicates the double layer capacitance behavior of the electrode. The electrode exhibits excellent stability even at current density as high as 2.0 A g\(^{-1}\), about 90% of the initial capacitance is still retained after 500 cycles. This stability at high current density infers that this electrode material is suitable for fast charging application.

4. CONCLUSION

Activated carbon was successfully prepared from corn cob by chemical activation using KOH as activating agent and characterized by means of SEM, FTIR, Raman and BET. The as-prepared AC samples show a developed specific surface area of 2331 m\(^2\) g\(^{-1}\) with various function groups. Cyclic voltammetry and galvanostatic cycling with potential limitation results exhibit the ideal capacitive behavior of AC samples electrodes in K\(_2\)SO\(_4\) and Na\(_2\)SO\(_4\) electrolytes. The capacitance of AC-850 in K\(_2\)SO\(_4\) electrolyte is found to be 225 F g\(^{-1}\) at current density of 0.2 A g\(^{-1}\), 186 F g\(^{-1}\) at current density of 2 A g\(^{-1}\), and remains 90% of the initial value after 500 cycles. These results point out that the as-prepare activated carbon electrode is suitable for the EDLC supercapacitor.

REFERENCE


*The authors declare no conflict of interest*

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