

Preparation of Activated Carbon for Electric Double Layer Capacitors

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Mesophase activated carbon (MAC) was prepared from coal tar pitch derived Green Mesophase Powder (GMP) by chemical activation with potassium hydroxide (KOH). The influences of the activation temperature and the activation time on the pore properties were investigated. The trends of the parameters were also analyzed. By using the optimized parameters, the Brunauer-Emmett-Teller (BET) surface area of the obtained activated carbon reached 2838 m²/g and the pore volume was increased to 1.31 cm³/g. The adequacy of the trend for predicting the optimum values were verified effectively by the validation. The activated carbon electrode made from MAC showed an excellent electrostatic capacitance with 196F/g and 72F/cm³.

Keywords: Activated carbon, Electric car, Battery, Supercap

1. INTRODUCTION

An electrical double layer capacitor (EDLC) is an ultra-fast energy storage device utilizing electrical double layers formed by electrodes containing activated carbon and an electrolyte. The mechanism of charge and discharge is based on a simple adsorption and desorption phenomenon. Accordingly, compared with rechargeable batteries such as nickel metal hydride batteries and lithium-ion batteries, in which the mechanism of charge and discharge are based on electrochemical reactions, EDLC has advantageous characteristics of (1) being able to be electrically charged and discharged rapidly, (2) applicability in a wide temperature range, and (3) having a long cycle life. Conventional EDLCs, however, have a drawback of low energy density so that their main use has been generally limited to small-scale memory backup power supplies for cellular phones, and personal computers.

Recently, the activated carbon for EDLCs has been improved in increasing the energy density of the EDLC. As a result, EDLCs are now used in a wider range of applications such as backup power supplies for electrically controlled equipment in automobiles. Furthermore, large-scale EDLCs are now being developed as a supporting power supply for hybrid electrical vehicles (HEV) and fuel cell cars, and so the market for the EDLC is expected to get larger.

In order to manufacture activated carbon with a large surface area, chemical activation with potassium hydroxide (KOH) as the activation reagent has been widely used. The chemical activation of carbon materials has been investigated since the 1980s by many researchers, who obtained specific surface areas in the range 80 m² g⁻¹ to 3000 m² g⁻¹, depending on experimental conditions⁽¹⁻³⁾. The authors mentioned that the porosity of the activated carbon was significantly influenced by the carbon/KOH ratio and the activation temperature, but there is still not much evidence regarding which variable is the most significant and how these variables drive the activation.

This study has developed an activated carbon with a high electrostatic capacitance using an exclusively carbon material as the raw material, obtained by combining Green Mesophase Powder (GMP) with a special activation technique.

2. EXPERIMENTAL

2.1 Materials

GMP is a high-carbon-content and spherical material which can be easily graphitized due to its mesophase nature (see Figure 1). Differing from other conventional coal tar pitch derivatives, GMP is suitable to undergo activation and carbonization simultaneously. Some of the properties of GMP are shown in Table 1.

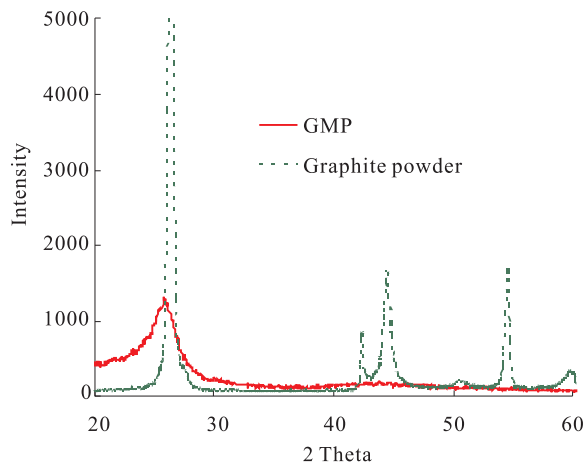


Fig.1. XRD patterns of GMP (solid line) and graphite powder (dashed line).

Table 1 Properties of green mesophase powder (GMP)

➤ Property	➤ Value
➤ Toluene insoluble	➤ >97%
➤ Quinoline insoluble	➤ >97%
➤ Volatile matter	➤ <10%
➤ Ash content	➤ <0.4%
➤ Average particle size (D50)	➤ 25±2μm

KOH flakes obtained from Liang-Kung Chemical Company were used as activating reagent in this article.

2.2 Activation of GMP

KOH was mixed uniformly with GMP in a certain ratio, and then the mixture was put into a rotary kiln. The kiln then was heated with a consecutive heating profile in a nitrogen atmosphere up to the designed temperature and held for various hours to achieve different extents of activation. After cooling, the carbons needed to be purged by steam for several hours to react with the metal potassium (K) formed during the activation reaction to water-soluble KOH. This step is generally called “deactivation”. Afterwards, the activated carbons were repeatedly washed in hot distilled water until the water reached pH~7.0 and then dried overnight at 70-130°C. To ensure particle size uniformity and the surface quality of any resulting activated carbon electrode, the carbon samples then underwent mechanical grinding to meet the designed particle size of less than 10μm. In this study, the activation temperature and the reaction time were chosen as variables in order to see how both the parameters drive the activation of GMP.

2.3 Characterization of activated carbon

The pore structures of the activated carbon were evaluated by measuring the nitrogen adsorption isotherm at 77.4 K (Micrometrics ASAP 2020 volumetric adsorption system). The specific surface area was calculated by using the Brunauer–Emmett–Teller (BET) equation. The mesopore size distribution was calculated from the N₂ adsorption isotherm by the Berret–Joyner–Halenda (BJH) method, and the total volume of pores was estimated using the cumulative volume of pore sizes from 1.70 nm to 300 nm.

MAC with a BET surface area of 2200 m²/g was chosen to evaluate the particle size effect in this report. Mechanical grinding was adopted for evaluating the size reduction technique. The particle size distribution of the ground carbons was obtained by a particle size analyzer and used to evaluate their influence on the surface quality of the electric double-layer capacitor (EDLC) electrode as well.

A complete characterization of the porous texture was made for the activated samples, which presented the highest values of BET specific surface area. For the purpose of comparison, a sample of commercial activated carbon made of nut shell (labeled as Carbon X) was also characterized.

2.4 Preparation of the electrode of EDLC

Electrode disks with 1.327cm² area were punched out from a 100 μm thick sheet of bound electrode material containing 50-75 wt.% of activated carbon, 15-30 wt.% of polyvinylidene difluoride (PVDF) as the binder. A dispersion mixture of 15% solid content in an organic solvent was strongly stirred until a smooth slurry was obtained. The slurry was coated by using a slit coating machine (Erichsen Coatmaster 510) on a 30μm aluminum foil (Japan Capacitor Company, JCC), and the achieved electrodes were dried at 150°C for 30 minutes in a regular oven and then for 8 hours in a vacuum oven. The EDLC cells were prepared by sandwiching two electrodes separated by a 25μm thick polypropylene (PP) based separator between two loaded nickel current collectors and were assembled in a glove box, the cells were then filled with electrolytic solution and hermetically sealed. The electrolytic solution used in this study was tetraethylammonium tetrafluoroborate (Et₄NBF₄) in Propylene Carbonate (PC) and provided by Aldrich. The electrostatic capacitance measurements were performed in a two-electrode arrangement by means of the cyclic voltammetry (CV) method (ACM field machine, Atlas), and the capacity was obtained from the area of the induced current-time (I-T) integration of CV scanning.

3. RESULTS AND DISCUSSION

3.1 Characterization of activated carbon

The BET surface area of the activated carbon is the most important property in the application of EDLC, in general, the larger surface area of activated carbon gives the higher capacity of electrode. Attempting to reach the optimized efficiency of activation, three ratios of carbon and potassium hydroxide (KOH/carbon) were chosen for the first approach. Figure 2 shows that the activated carbon with a BET surface area of 1530 m²/g in KOH/carbon with a ratio of 2.0 rose gradually to 2505 m²/g as the KOH/carbon ratio was increased to 3.0. This result also matches Ottawa's work⁽²⁾. Then, two activation times and temperatures were chosen as the activation parameters for the second approach. Three samples were produced using the same KOH/carbon ratio. After the activation, three samples (A-C) with BET surface areas larger than 2100 m²/g and pore volumes larger than 1.0 cm³/g were obtained, pore structures were listed in detail as Table 2. Figure 3 shows the N₂ adsorption isotherms of the three activated carbons, Samples A-C, and the commercial Carbon X. In Fig.3, the N₂ adsorption of the activated carbons shows that after the saturation pressure, for example Sample A, at P/P₀=0.41, adsorption does not occur significantly. This can be explained by the fact that there are a limited numbers of vacancies on the surface of the adsorbent. At high pressure a stage is reached when all the sites are occupied and further increase in pressure does not cause any difference in the adsorption process. Besides, the isotherms also indicate that the all the samples are essentially constituted by micropores which means that adsorption is limited to the completion of a single monolayer of adsorbate at the adsorbent surface. Therefore, adsorption of MAC and the Carbon X in this study all present the typical characteristics of Type I⁽⁴⁾. The isotherm in Fig.4 barely showed the hysteresis phenomenon in the adsorption/desorption cycle implying that the pores are essentially cylindrical ones, without a predominance of pores with funnel form or pores denominated ink-bottle.

Pore size distribution (PSD) is always linked to the ionic accessibility from the electrolyte to the electrode material, because the accessibility from electrolyte to the pore sites of activated carbon strongly depends on the microstructure. The activation process typically leads to the development of a porous network in the bulk of the carbon particles; micropores (< 2nm), mesopores (between 2 and 50 nm), and macropores (larger than 50 nm) are randomly created. Recent articles reveal that the content of mesopores will enhance their ionic accessibility, and that controlled porosity in the mesoporous range from 2 to 10 nm, which is about twice the solvated ion size, give the

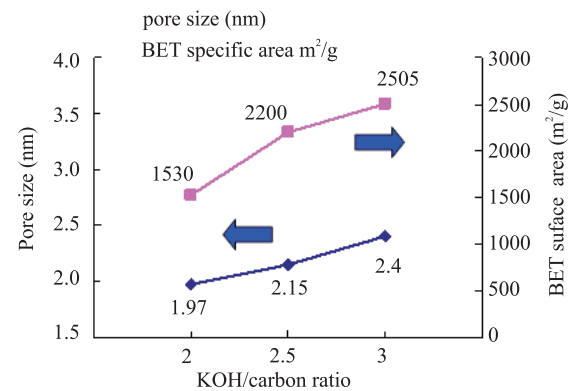


Fig.2. The BET surface area (—■—) and pore sizes (—◆—) of the various ratios of KOH/carbon.

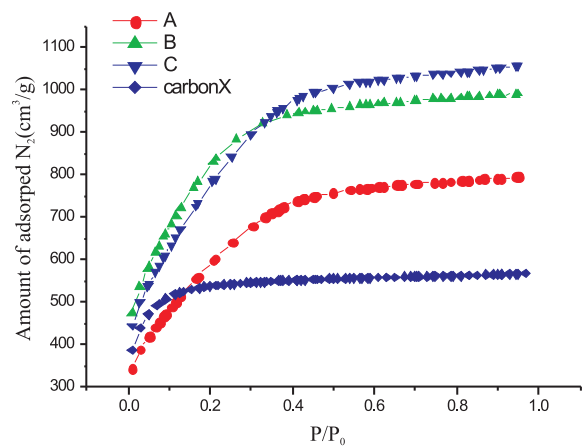


Fig.3. N₂ adsorption isotherms of activated carbons: —●— Sample A ; —▲— Sample B; —▼— Sample C; and —◆— Carbon X.

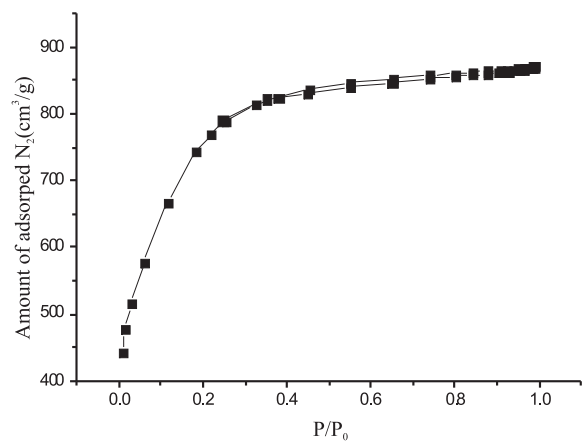


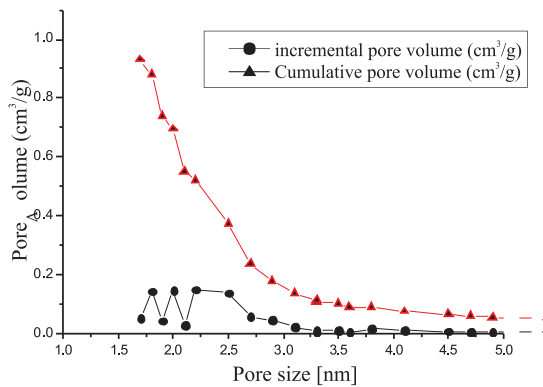
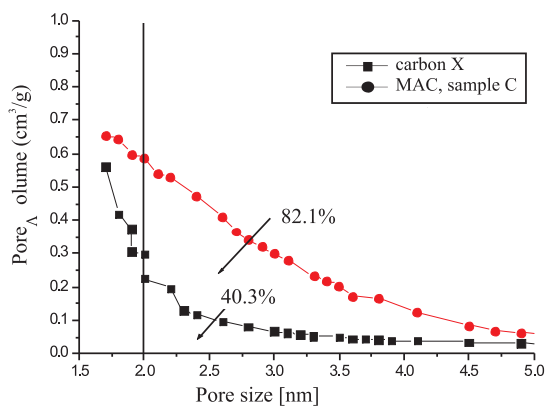
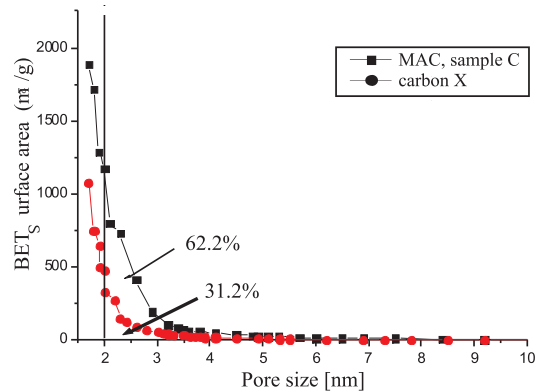
Fig.4. Adsorption/desorption cycle of MAC for Sample C.

optimum capacitance in the application of EDLC charge storage⁽⁵⁻⁷⁾. But there was a different work that showed that the micropores of less than 1nm will

Table 2 Pore structure of activated carbon (Samples A-C)

Sample	Activation temperature(°C)	Activation time(Hr)	BET surface area(m ² /g)	Pore volume(cm ³ /g)	Average pore size(nm)
A	900	2	2148	1.00	2.41
B	800	4	2800	1.07	2.27
C	900	4	2838	1.31	2.40

largely enhance the accessibility of ion between the interface, and some models had been proposed⁽⁸⁾. Figure 5 depicts the relationship between PSD and the pore volume of MAC showing that MAC has a narrow PSD and that most of the pores are in the size range of 2 to 2.5nm. The cumulative results of pore volume (Figure 6) and the BET surface area (Figure 7) also show that the MAC has higher portion of mesopores when compared with commercial Carbon X. In summary, based on the results above, it is indicated that activated carbon via the chemical activation method by using KOH has a narrow PSD and an average pore size of about 2.40nm. Further, the high portion of mesopore also implies that an electrode using MAC would have a higher capacitance than one using the commercial carbons.

**Fig.5.** Pore volume of activated carbon for Sample C.**Fig.6.** Pore volume accumulation of mesopores: MAC, Sample C (—●—); and commercial sample, Carbon X (—■—).**Fig.7.** BET surface area accumulation of mesopores: MAC, Sample C (—■—); and commercial sample, Carbon X (—●—).

Looking at the BET surface area results in detail, prolonging the activation time from 2 to 4 hours could significantly increase the BET surface area from 2148 to 2838 m²/g (Sample A, C). But Sample B which was made with the lower 800°C as the activation temperature could also produce activated carbon with a high BET surface area of 2800 m²/g, which is just slightly lower than Sample C. Therefore, in consideration of both BET surface area and energy saving concerns, taking 800°C as the reaction temperature, an activation time longer than 4 hours would also yield activated carbon with a BET surface area higher than 2800 m²/g. Ottawa⁽²⁾ using petroleum coke as the precursor also revealed the optimized activation temperature at 800°C. Pore size and pore volume are strongly dependent on the activation temperature and time. It was believed that a higher temperature would drive the overall activation faster and efficiently enlarge the pore structure. However, the cumulative result of pore volume shows that carbon using 800°C as the activation temperature have the larger portion of micropores than 900°C (Figure 8).

3.2 Effect of particle size reduction

The particle size of the MAC used in this work was originally about 30μm while the commercial products are in the range between 2~10μm. It is believed that the smaller the particle size of the carbon, the better the adhesion of carbon/foil and so the better the surface quality of the EDLC electrode.

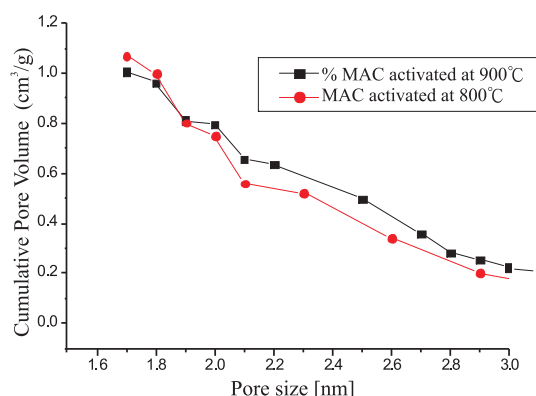


Fig.8. Cumulative pore volume of MAC activated at 900°C for Sample C (—■—); and at 800°C for Sample B (—●—).

By means of a mechanical grinding process, the MAC was successfully ground down to a particle size of $D_{50} = 0.91\mu\text{m}$ and $D_{50} = 7.0\mu\text{m}$ which are labeled as Sample D and Sample E, respectively. They were obtained by using the different grinding speeds and it shows that the higher the grinding speed, the smaller the particle size. Both samples were then placed under SEM observation, and the images are shown as Figs.9 (a)-(c). The SEM image of Sample D shows a flake-like shape which indicates that in high speed grinding, the carbon might be chopped from the center of the particle during the grinding process. However, the spherical shape produced by using a lower speed grinding parameter, suggests that the carbon surface of the MAC particle was being sliced, layer by layer, until the desired particle size was obtained. In this study, the slurry preparation using the MAC with particle size of $0.91\mu\text{m}$ had a serious particle aggregation and could barely be coated on the substrate. It was supposed that the smaller the particle size of the carbon, the stronger the interface interaction. This strongly implied that some surface treatment should be done before the slurry preparation. An electrode sample produced by using MAC with a particle size of $7.0\mu\text{m}$ shows a smooth and continuous surface in comparison with the sample made by the original carbons (Figure 10). This also indicated that carbon with a particle size of $7.0\mu\text{m}$ is suitable for making the electrodes of EDLC.

3.3 Electrostatic capacitance of the prepared electrodes.

Sample C and the commercial Carbon X were chosen for an evaluation of the capacitance of GMP activation. The two samples were prepared as carbon slurry using the same formulation, producing two $100\mu\text{m}$ electrodes by the method described above as experimental. The cyclic voltammety (CV) response of the cell of each sample was conducted between 0.0

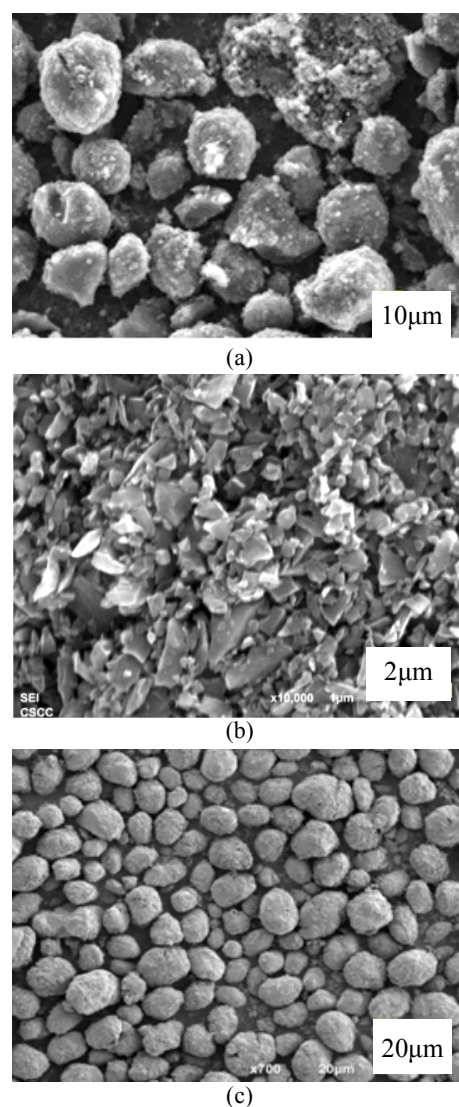


Fig.9. SEM images of: (a) original MAC; (b) Sample D, ground by means of high speed grinding; and (c) Sample E, ground by lower speed grinding.

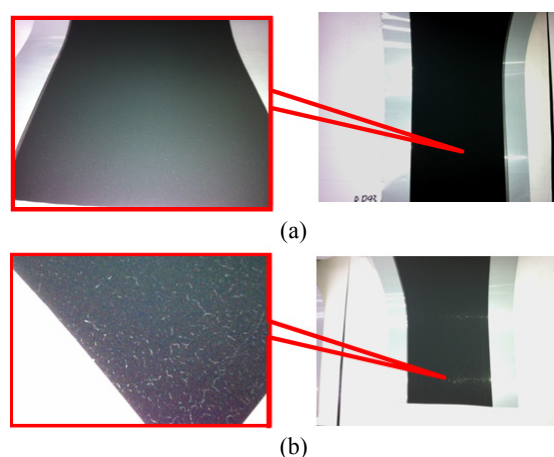


Fig.10. Surface feature of the electrode made by using: (a) ground carbon, and; (b) original carbon.

V and 1.0V at 10mV/s and the result is presented in Figure 11. The curves of both the MAC sample and the Carbon X sample are rectangular and symmetric to the zero horizontal axis with the weight specific capacitance of 196F/g and 90F/g (based on the activated carbon) and volumetric specific capacitance of 72F/cm³ and 60F/cm³ (based on carbon volume in the electrode), respectively. It shows that both MAC and Carbon X have excellent charge/discharge behavior, moreover, MAC has much larger specific capacitance. On the other hand, rolling is also a determining step for making high performance electrodes. Good rolling steps can make the overall carbon layer dense and create more routes for electron-transfer while charging and discharging. The electrode sample made from MAC under 1kg/cm roll pressing shows not only a more rectangular shape in CV scanning (Figure 12) but also a greater specific capacity retention after three consecutive scanning (Figure 13) than sample made from the Carbon X.

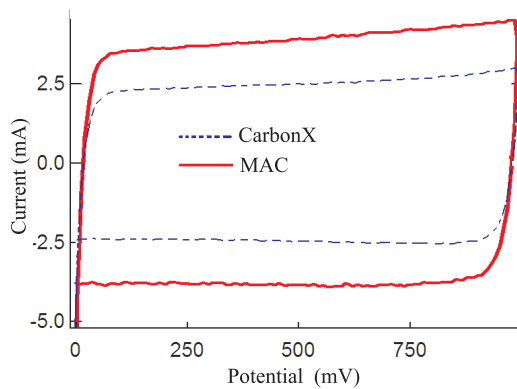


Fig.11. Cyclic Voltammetry scanning of MAC (solid line) and Carbon X (dashed line).

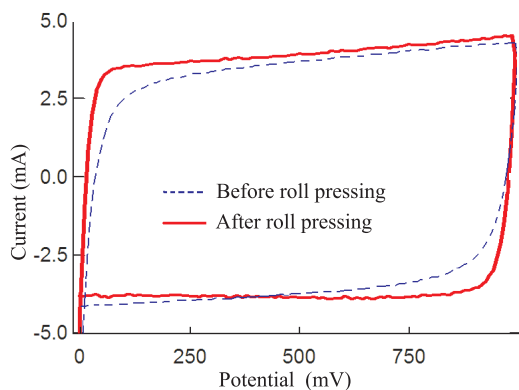


Fig.12. Cyclic voltammetry scanning of MAC: (a) with roll pressing (solid line), and; (b) without roll pressing (dashed line).

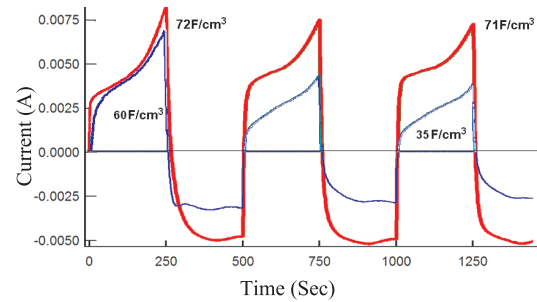


Fig.13. Electrostatic capacitance (current-time integration) of MAC and Carbon X after three consecutive CV scanings.

4. CONCLUSION

The chemical activation of the coal tar pitch derived GMP samples used in this work allows the conclusion that the developed process is appropriate for the production of MAC with high performance capacitance. Also the activated GMP produced presents high values of specific surface area, up to 2838 m²/g, high values of pore volumes, up to 1.31cm³/g. When these materials were compared with a commercial activated carbon and the electrode thereof, they presented excellent values in specific surface area, pore volumes and the specific capacitance of electrodes. These indicate that MAC is suitable for EDLC application. Moreover, the process developed and used in this article indicates the possibility of transforming the coal tar pitch to a product with higher commercial value.

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