# Mesoporous Carbon Derived from Wastes as an Electrode Material for Electric Double Layer Capacitors.

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## Abstract

Carbon of different form have been extensively used in variety of electrochemical systems such as batteries and electric double layer capacitors (EDLCs). In the present days EDLCs are widely employed for practical applications as high power devices since they possess large capacitances, high energy density and long cycling life. The intention of using mesoporous carbon in EDLC development is attributed to the recognized fact that the layer surface area that an EDLC can provide for adsorption of electrolyte on the electrode material and there by resulting in the storage of more energy in EDLC. The purpose of this investigation is to employ mesoporous activated carbon (MAC) prepared by chemical activation to understand the influence of porosity and specific capacitance. The study is also focused by modifying the surface properties of the carbon matrices by increasing and decreasing the functional group density.. The specific capacitance values obtained through cyclic voltammetry and the symmetric curves obtained from chronopotentiometry or charge/discharge techniques suggested that this material can be well employed for the manufacture of EDLC. Among the different conditions studied, the carbon matrix prepared at 900 C followed by oxidation proved to be the best material and is highly suitable for EDLCs. The imparted functional group and surface morphology of the carbon matrices were observed by FT-IR and scanning electron microscopy techniques.

**Key words** : Activated carbon; Electrodes; Electrochemical properties; Heat treatment.

## 1. Introduction

Electric double layer capacitors (EDLC) are widely employed in the present days for practical applications as high power devices since they possess large capacitance, high energy density and long cycling life. The EDLC device stores electricity physically and lacks chemical reactions found in rechargeable batteries during charging and discharging. Therefore EDLC has remarkably long cycle life and high power density than the rechargeable battery. For this purpose material such as activated carbon, carbon aero gel, silica gel, polyaniline-implanted carbon, metal supported carbon, carbon nanotubes are currently under use (Chensha et al., 2004; Jong and Park, 2002). Among the available materials activated carbons are extensively used due to the trend of increasing portable electric devices and the demand for global environmental conservation that requires the development of high energy density capacitors and batteries ( Hal-Bon et al, 2000). The intension of using activated carbon for EDLC is attributed to the recognized fact that the surface area available provides the adsorption of electrolyte on the carbon electrode and there by resulting in the storage of more energy

(Hsisheng et al., 2001; Liu and Osaka, 1996; Liu and Osaka, 1997). In this type of materials the charges gets accumulated at the electrode/electrolyte interface mainly due to the electrostatic force of attraction and the capacitance is subjective to its effective surface area (Satoshi et al., 2004). Although the total surface area is the prime concern for the electrode material, other aspect of surface physics and surface chemistry can be critical for the electrode performance towards a huge charge storage ( Kierzek et al., 2004). The specific capacitance of an activated carbon is also dependent on many characteristic properties such as ions dimensions, dielectric constant, solvating power, viscosity, conductivity of the carbon composite, blockage of carbon pores by the binder, thickness of the composite and the separators etc. In addition, the oxygen containing functional groups in carbon materials have also been reported to be one of the important surface group that affect the capacitance properties. Due to these factors the charge accumulated in a unit mass of porous material varies from one carbon to the other.

The preparation of EDLC so far have been derived from precursors such as coconut shell, coal etc. either by physical or chemical activation with well developed micro porosity and sufficient surface area (Wenming, et al., 2002). Since there are not many reports available on the capacitance behavior using mesopores carbon (MAC), the current investigation is focused on the evaluation of mesopores activated carbon prepared from rice husk by two-stage process. The relation between porosity and specific capacitance is also studied. Capacitance characteristics were evaluated by cyclic voltammetry and chronopotentiometry techniques. The contribution of functional group intensity towards capacitance were also studied.

## 2. Experimental methods

### 2.1. Preparation of porous carbons

Porous carbons were prepared by two different steps: precarbonization and chemical activation. The preparation of the carbon material is discussed in detail by the authors in our previous reports (Kennedy et al., 2005). Briefly, the raw material rice husk was heated to $400^0C$ for about 4 hours under $N_2$ atmosphere followed by cooling to room temperature to yield precarbonised carbon (PCC). This precarbonised carbon was then subjected to chemical activation. In the chemical activation process 50g of the precarbonised carbon was agitated with 250 g of aqueous solution containing 85% $H_3PO_4$ by weight. The ratio of chemical activating agent / precarbonised carbon was fixed at 4.2. The chemical activant and precarbonised carbon was homogeneously mixed at $85^0C$ for 4 hours. After mixing the precarbonised carbon slurry was dried under vacuum at $110^0C$ for 24 hours. The resulted samples were then activated in a vertical cylindrical furnace under $N_2$ atmosphere at three different temperatures 700, 800 and $900^0C$ using a microprocessor controlled temperature programmer and maintained at that constant temperature for one hour before cooling. After cooling the activated carbon was washed successively several times with hot water until the pH becomes neutral and finally with cold water to remove the excess phosphorous compounds. The washed sample was dried at $110^0C$ to get the final product. The samples heated at activation temperatures 700, 800 and $900^0C$ were labeled as C700, C800 and C900.

## 2.2. Surface modification of porous carbons

The surface functional group of the porous carbon was modified by subjecting the material at oxidizing and reducing atmospheres. The surface functional group intensity was varied only for the plain activated carbon C900 that possessed maximum surface area comparatively. The functional groups was increased by refluxing C900 with 4N nitric acid ($HNO_3$) at about 150°C for 10 hours in a round bottom flask fitted with Liebig condenser, followed by filtering and washing with distilled water continuously until it attains neutral pH. The sample was, then dried in an oven for 5 hours and was labeled OC900. Similarly the functional group intensity was reduced for C900 by refluxing the carbon with a mixture of diethyl ether and lithium aluminum anhydride in a round bottom flask, fitted with Leibig condenser at about 50°C for 10 hours. This carbon was then filtered and washed with distilled water followed by oven drying for 5 hours and labeled as RC900.

## 2.3. Surface area analysis

The $N_2$ adsorption – desorption isotherms of the activated carbons were measured using an automatic adsorption instrument (Quantachrome Corp. Autosorb 1C surface area analyzer) for the determination of surface area and the total pore volumes. Prior to the measurements the carbon samples were degassed at $150^0$C for overnight. The nitrogen adsorption – desorption data were recorded at 77K. The total surface areas were calculated using the BET model that is widely used for determining the specific surface area. In addition, the t-plot method was applied to calculate the micropore volume and external surface area (mesoporous surface area). The total pore volume was estimated to be the liquid volume of adsorbate at a relative pressure of 0.99. All surface area measurements were calculated from the nitrogen adsorption isotherms by assuming the area of the nitrogen molecule to be $0.162nm^2$.

## 2.4. Preparation of carbon electrodes and construction of test capacitors

Approximately 0.3g of plain and surface modified mesoporous activated carbon samples were ground into fine powder and were made in the form of pellets of dimension 1.8× 13.5 mm using PTFE paste as the binder at a high compression pressure of 2 MPa. All electrochemical measurements were carried out in a two-electrode coin-type cell (capacitor) in which a separator soaked in 1M $H_2SO_4$ solution was sandwiched between the two carbon electrodes. Stainless steel leads were fixed to the outer face of the pellet using conducting silver paste to ensure ohmic contact. For cyclicvoltammetry (CV), one electrode of the cell was used as the working electrode while another electrode was used as the counter and reference electrode (Chien and Hsisheng, 2002). The electrochemical property of the plain, oxidized and reduced carbons were performed using CHI: 605A electrochemical analyzer (USA). The potential scan rates were ranging from $1mVs^{-1}$ to 100 $mVs^{-1}$ within a potential window of +6 to -6V. The capacitance of the carbon electrode was calculated by integrating the area of voltammograms in the potential range applied as given in the equation

$$C = \int idt / dv \qquad (1)$$

Where,' C' is the capacitance in mF/g, 'i ' is the current in mA and v is the voltage.

The galvanostatic charge-discharge measurement is recognized as a typical test in evaluating the capacitive performance of the electrode material for capacitors and the typical chronopotentiograms were performed at a current value of 1mA. The capacitance was calculated using the equation (2).

$$C = 2it / w\Delta v \tag{2}$$

where 'C' is the capacitance, 'i' is the discharge current, 'w' is the weight of the electrode, '$\Delta v$' is the potential difference in discharge.

### 2.5. FT-IR spectroscopy

Perkin Elmer Infrared spectrophotometer was used for the determination of functional groups of plain, surface groups modified carbon samples. The carbon samples were mixed with spectroscopic grade KBr and made in the form of pellets at a pressure of about 1MPa. The pellets were about 10mm in diameter and 1mm thickness. The samples were scanned in the spectral range 400 - 4000 cm$^{-1}$.

### 2.4. Scanning Electron Microscope (SEM)

The surface morphology of mesoporous activated carbon C900 sample were determined using Leo-Joel scanning electron microscope at the desired magnification. The carbon samples were coated with gold using a gold sputtering device for the clear visibility of the surface morphology.

## 3. Results and Discussion

The surface area and pore volume parameters of the prepared plain MAC carbon are shown in Table 1. The electrochemical properties of the fabricated activated carbon capacitors were studied by cyclic voltammetry. The cyclic voltammograms at 1mVs$^{-1}$ scan rates for MAC900 is shown in Fig. 1.

**Table 1. Surface area and pore volume parameters of the porous carbons.**

| Sample | $S_{BET}$ (m$^2$g$^{-1}$) | $S_{mic}$ (m$^2$g$^{-1}$) | $S_{meso}$ (m$^2$g$^{-1}$) | Average pore diameter ( A$^{\circ}$) | $V_{meso}/V_{tot}$ (%) | Pore volume (cm$^3$g$^{-1}$) |
|---|---|---|---|---|---|---|
| C700 | 344.7 | 202.7 | 142.0 | 38.82 | 66.78 | 0.345 |
| C800 | 379.4 | 214.6 | 164.8 | 39.36 | 68.41 | 0.373 |
| C900 | 438.9 | 214.9 | 224.0 | 35.28 | 69.33 | 0.387 |
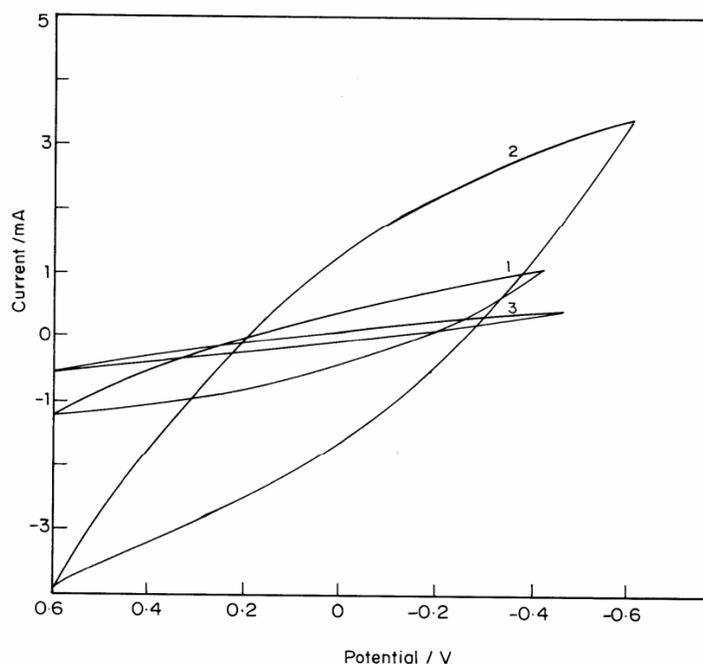
**Figure 1. Cyclic voltammograms of a) C900 b) OC900 c) RC900 swept at 1mVs[-1].**

The data demonstrated that the electrodes were stable with in potential range employed and the peaks due to Faradic current were not observed for the systems. For all the MAC's studied at varied sweep rates, rectangular shaped voltammograms were not observed. Instead all the voltammograms were found to be tilted. This indicates there is a hindrance to the motion of the ions in the pores and signifies that at all these potential sweep rates, the ohmic resistances for electrolyte motions in carbon pores has affected the double layer formation mechanism and the charge stored has been recognized to be distributed. The increase in the induced current with the sweep rate would have intensified the potential difference between the mouth and the bottom of the pores and thus resulted in the delayed current response as shown by the tilted voltammograms (Kim et al., 2004; Hsin et al., 2005). The voltammograms also revealed that the induced current increased with the activation temperature of the carbon materials. The voltammery curves obtained were smooth and suggested that the electric charge is stored in the electric double layer at the interface between the polarizable electrode and the electrolytes in spite of its totally solid state structure (Haichao et al., 2004). No redox is observed in the sweep region and cyclic voltammograms was unchanged on repeated runs. The lack of any peak proves to be a pure electrostatic attraction in the capacitance behavior. This behavior suggests that the EDLC cell of the MAC electrodes shows good capacitor performance (Hal-Bon et al., 2000).

The specific capacitances of the carbon samples as a function of sweep rate are shown in the Table 2 - 4 and found that the specific capacitance decreases gradually with increasing potential sweep rate. The ions that are large than the pore size may block the entrances of the micropores that leads to the reduction in the specific capacitance. The capacitance of the cells prepared using the carbon, activated at 900°C performed

better than those activated at 700 and 800°C. The large drop in capacitance at low activation temperature is due to the occurrence of more internal resistance within the carbon matrices ( Chan, 2005).

Table 2. Capacitance of the C900 series activated porous carbon of different scan rates.

| Sample | Capacitance (mFg$^{-1}$) | | | | | |
|---|---|---|---|---|---|---|
| | 1 mVs$^{-1}$ | 10 mVs$^{-1}$ | 25 mVs$^{-1}$ | 50 mVs$^{-1}$ | 75 mVs$^{-1}$ | 100 mVs$^{-1}$ |
| **C700** | 488.9 | 42 | 15.7 | 5.4 | 3.7 | 3.0 |
| **C800** | 1730 | 131.3 | 41.5 | 25.9 | 13 | 6.3 |
| **C900** | 2620 | 524 | 35 | 27.9 | 20.5 | 8.8 |
| **OC900** | 3420 | 907 | 170 | 85.7 | 49.7 | 38.2 |
| **RC900** | 1200 | 26.8 | 24.5 | 14.4 | 9.5 | 8.7 |

Fig. 2 shows the specific capacitance results plotted against the BET surface area for the plain activated carbons. The capacitance of plain MACs had almost a linear increase with BET surface area having regression value 0.94. The deviation of linearity was observed when the specific capacitance values were plotted against the micropore surface area of the carbons Fig. 3. This leads to the conclusion that in addition to the BET surface area, the pore volume and pore size distributions are the crucial parameters in developing EDLC electrode materials. Although the micropore surface area became constant with increase in the activation temperature from 800 to 900$^{0}$C, the capacitance never attained a constant value. This could be attributed to the fact that at higher activation temperatures the increase in mesoporosity of the carbon material would have enhanced the feasibility of the electrolyte ions to migrate deep into the micropores of the carbon material to form electric double layer. This observation suggests that the specific capacitance not only depends upon the total surface area but also depends on the mesopore surface area as shown in Fig. 4 and emphasizes that the mesopore of the carbon matrix plays a dominant role towards the EDLC (Kierzek et al., 2004; Emmenegger et al., 2003). The surface morphology of mesoporous activated carbon C900 samples is shown in Fig. 5.

Other than surface area and pore size distribution some other factors may also play an important role towards charge/discharge capacitance. In this context we also focused our study by modifying the intensity of the functional groups present on MAC's. The main functional group that is present in the plain MAC's is composed of carbon-carbon (C-C) and carbon-hydrogen (C-H)  and  carbon-oxygen double bond C=O (Kennedy et al., 2004). In addition to these the other components like Si and P may be present as impurities in the material that were incorporated during the preparation process of the material and can enhance the electrochemical properties. The FTIR spectrums of C900 series  carbon materials are shown in Fig. 6.
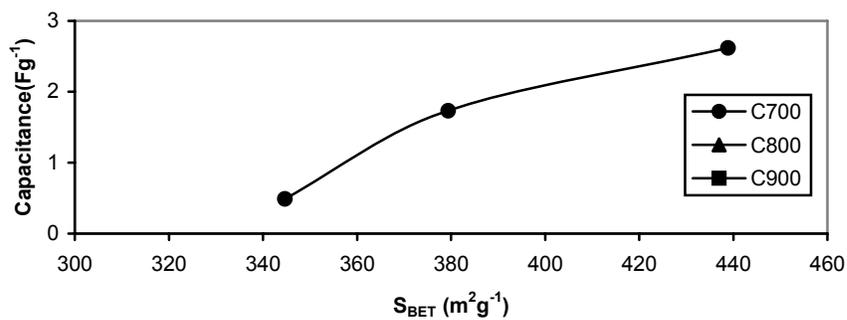
**Figure 2. Variation of capacitance with BET surface area at different activation temperatures of MACs**
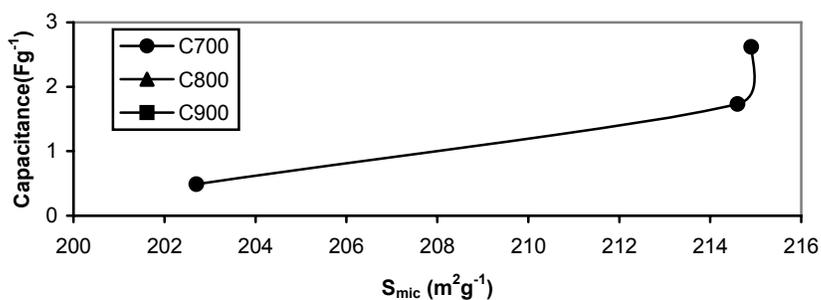


**Figure 3. Variation of capacitance with micropore surface area at different activation temperatures of MACs**
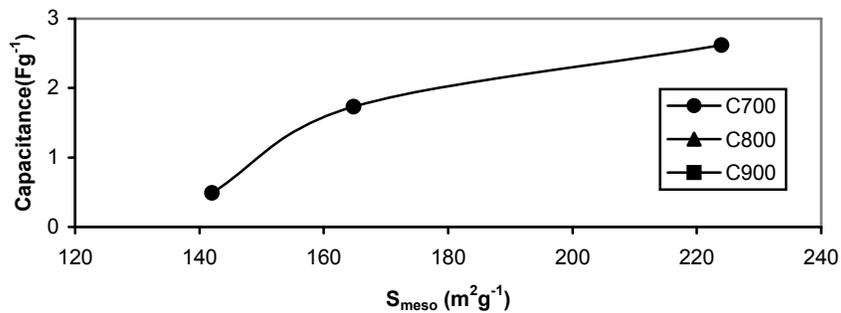


**Figure. 4. Variation of capacitance with mesopore surface area at different activation temperatures of MACs**

Introducing more functional groups on the matrices using acid treatment can increase the capacitance values. In this work we found that the intensities of the functional groups increased comparatively than that of the plain MAC's. On the other hand Lithium anhydride employed as a reducing agent, reduced the surface functional groups remarkably. The specific capacitance values of the plain MAC, surface oxidized and reduced samples are shown in Table 2. The result revealed that the order of the specific capacitance obtained were of the order OC900 > C900 > RC900 among the C900 carbon series. The increase and decrease in the specific capacitance values compared to the plain MAC's is attributed to the difference in structure and surface properties of the modified carbons. This modification is well evidenced through FT IR technique. The FT IR spectra shown in Fig. 6 confirms the presence of the increased content of C=O functional group that is assigned to carbonyl and carboxyl at about $1700 cm^{-1}$. The increased intensity of carbonyl and carboxyl groups are believed to be the key species promoting the capacitive performance of the carbons as good capacitors (Masashi et al., 1996). The peak at $1590 cm^{-1}$ reflect the vibration of carbocyclic plane of the MAC's and becomes more sharper for the oxidized carbon, due to the quite removal of amorphous carbonaceous matter. The increase in functional group intensity leads to the increase in the polarizability of the carbon matrix and thereby converting it into polarizable matrices. These functional groups present on the surface of the carbon matrices can attract the solvated electrolyte ions due to electrostatic force of attraction between the carbon surface and the solvent ions. Therefore as the functional group increases the charge density increases, and as the charge density increases the electric double layer capacitance increases. One more additional fact is that during the preparation of oxidized MAC's the surface is imported with more oxygen groups and would make the carbon surface a hydrophilic. This hydrophilicity increases the wettability of the carbon due to electrolyte and resulting in the significant increase in the building up of the charges. The enhancement in the capacitance is therefore partially attributed to the improvement in wettability of the electrode material, resulting in a higher usable surface area and a lower internal resistance. One interesting fact observed for all the reduced carbons is that the specific capacitances dropped to a lower value than the plain MACs. This confirms that the functional groups play a major role in importing or enhancing the specific capacitance of the polarizable electrode (Mitsuhiro et al., 1996).

The galvanostatic charge /discharge measurement is also recognized as a typical test in evaluating the capacitive performance of electrode materials for capacitors and typical chronopotentiogram of the sample C900 capacitors at 1 mA is shown in the Fig. 7. The calculated capacitances estimated using these curves were 150, 1.85 and $0.90 mFg^{-1}$ for C900, OC900 and RC900 capacitor cells respectively. The symmetry and very quick charge/discharge characteristics and almost constant slope of these curves support that the electrode has high electrochemical reversibility and excellent capacitance characteristics. This suggests that the capacitance was almost stable throughout the cycles and there was no decay in the specific capacitance was observed. All the studies signify that the carbon materials are best suited for EDLC application (Masaya et al., 2004; Chi-Chang and Chen-Ching, 2002).
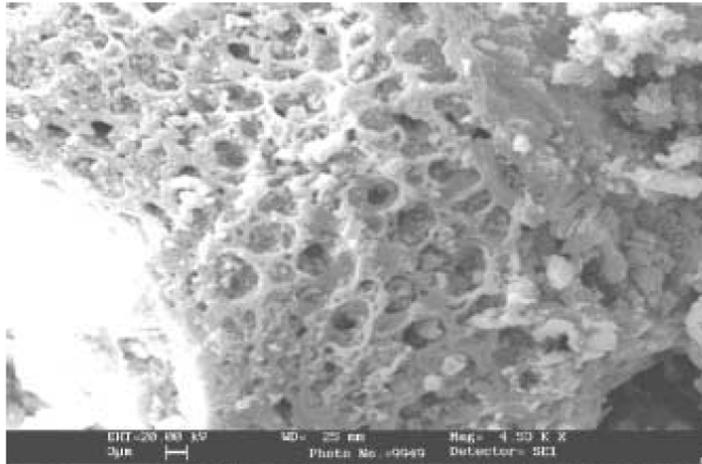
**Figure 5. Scanning electron micrograph of C900 sample.**
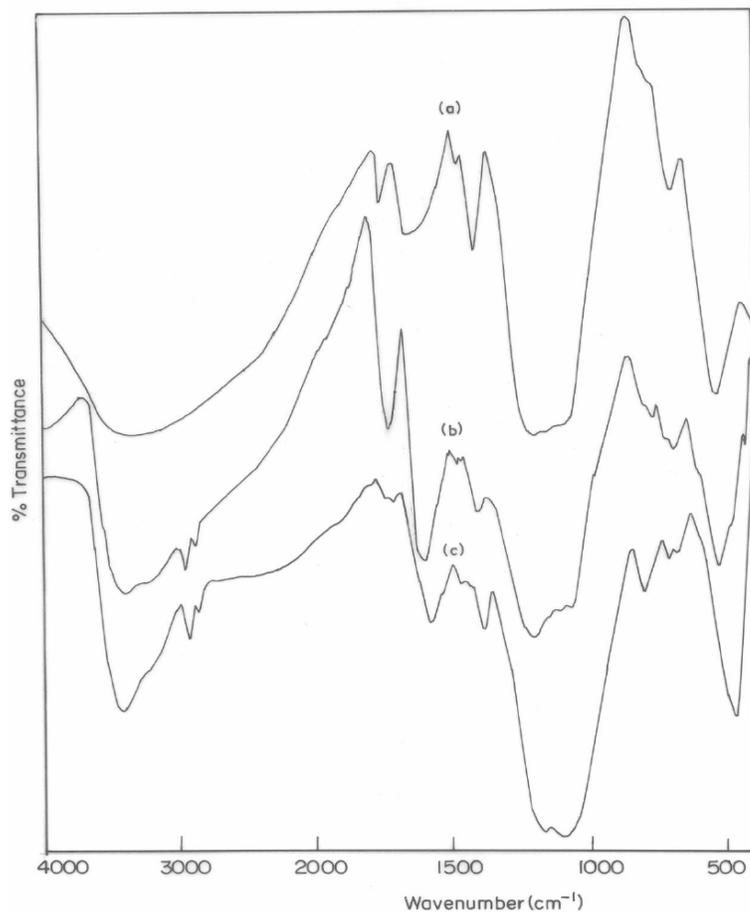


**Figure 6. FT-IR spectrum of a) C900 b)OC900 and c)RC900**
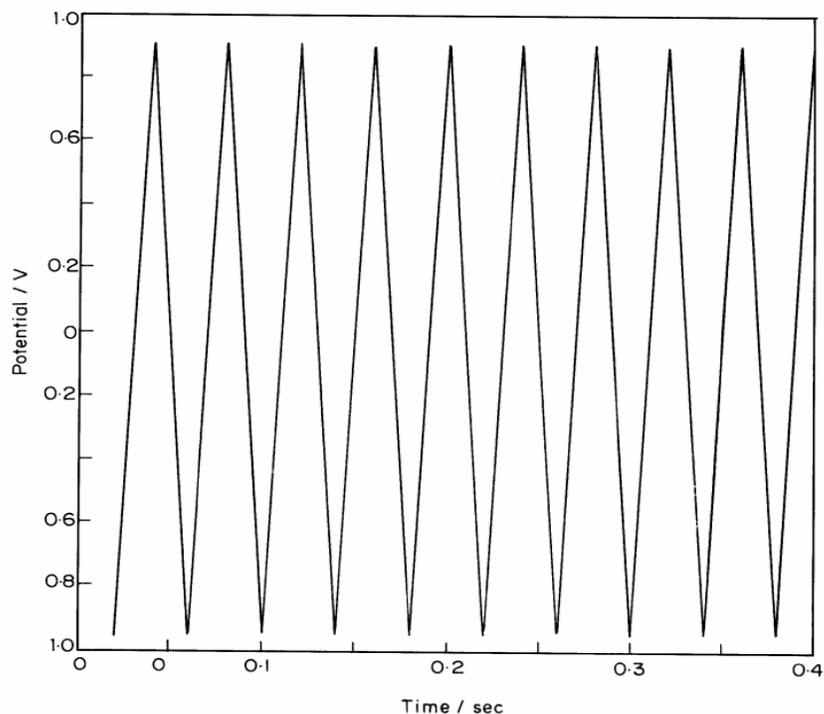
**Figure 7. Chronopotentiogram of mesoporous C900 sample**

## 4. Conclusions

The capacitance of porous carbon prepared at three different temperatures was measured and the capacitance of C900 was higher than C700 and C800 due to increased mesopore surface area content. Other than surface area and pore size distribution, the surface modification of the carbon matrices resulted in a change in the capacitance values. The oxidized carbons showed higher capacitance values than the plain and surface reduced carbons. The enhancement in the capacitance is thus partially attributed to the improvement in wettability of the electrodes leading to higher usable surface area and low internal resistance. All the results suggest that the functional groups play a major role in the development of EDLCs. The symmetric curve and quick charge/discharge characteristics enables these carbon materials to be employed as a capacitors. The columbic efficiency of about 99.5% for 100 cycles suggest that the capacitors possess excellent cycle stability and can perform as a very good EDLCs.

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