

# Capacitance and Impedance Evaluations in Coconut Shells and Rice Husks Derived Activated Carbon Electrodes.

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## Abstract

Solid polarisable activated carbon electrodes have been prepared from Coconut shells and Rice husks. The preparation process involved precursor pre-carbonizations and conversion to solid carbon discs, inert environment carbonization and CO<sub>2</sub> activation at 750°C. Electrochemical Impedance spectroscopy characterizations gave their Double layer Capacitances as 0.02Fg<sup>-1</sup> and 0.17Fg<sup>-1</sup> respectively. The electrodes developed polarization impedances were 627.9Ω for the coconut shells and 1316.5Ω for the rice husks units. Their XRD scans showed that the electrodes were principally carbon and silica. The low polarization impedance of the coconut shell electrode was attributed to the activated petroleum residue tar binding material.

**Keywords:** Carbonization, Activation, Impedance spectroscopy, Polarization impedance, Double layer Capacitance

## 1.0 Introduction

Development of renewable energy resources has gained global attention in recent times. Such energy sources include solar, wind, hydropower, tidal wave, ocean thermal and geothermal. The periodic fluctuations of energy available from these sources makes the development of efficient and reliable storage systems imperative. Such storage systems with the capacity to receive and hold energy during peak hours of supply and deliver the stored energy for use at periods when the energy resource supply is low or completely off. Batteries and conventional dielectric capacitors have for a long time remained the main electrical energy storage devices. Intrinsically, batteries and low temperature fuel cells are typical low power devices and conventional capacitors may have a power density of 106 watts per dm<sup>3</sup> at very low energy density (Conway 1999). The need therefore arises for the development of storage devices that combine both high power capacity and high energy density. This necessity has been further strengthened by the high and fast energy storage and delivery requirements of recently emerging electric vehicles. Electric Double layer Capacitors (EDLC), also called Electrochemical Capacitors (EC) or Supercapacitors have been identified as intrinsically possessing these properties (Kotz and Carlen 2000).

In the EDLC, electric charges are stored by adhesion onto large surface areas of pores in polarisable solid electrodes. These electrodes are produced from high-surface-area Activated Carbons (AC), transition metal oxides, and electro-active polymers (Chen et al 2001). About one gram of AC could have a surface area of 500m<sup>2</sup>. For example, a surface area range of between 446 to 1340m<sup>2</sup>g<sup>-1</sup> has been reported for Coconut shells (Farma et al 2013). A linear relationship between obtained capacitance and available surface area has also been observed (Barbieri et al).

Capacitance and Impedance characterisation of the electrodes is commonly implemented with Electrochemical Impedance Spectroscopy (EIS). EIS studies the electrode's response to the application of a periodic small amplitude ac signal at different frequencies. These measurements are carried out at different ac frequencies and, thus, the name impedance spectroscopy. Analysis of the system response contains information about the interface, its structure and reactions taking place there (Lasia 1999). From the measured cell impedance in the form of real and imaginary components and phase angle, it is possible to examine and qualitatively determine several processes such as the electronic/ionic conduction in the electrode and electrolytes, interfacial charging either at the surface films or the double-layer, charge transfer processes and the mass transfer effects, if any. The time constants for these different processes being different, their features will show up at different frequencies in the EIS spectra. This technique is nondestructive since the polarization applied is low enough that linear polarization conditions (i.e., where the polarization increases linearly with current) are maintained and the rate equations are simplified accordingly (Ramakumar et al 2008).

In EIS modeling, an ideally polarizable electrode is taken as an ideal capacitor because there is no charge transfer across the electrolyte-electrode boundary. In this case the equivalent electrical model consists of the electrolyte resistance,  $R_s$ , in series with the double-layer capacitance  $C_{dl}$  in parallel with a polarization resistance  $R_p$  fig.1 (Lasia 1999).

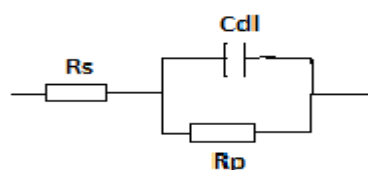


Fig. 1: Model of the electric double layer.

In this model,  $R_s$  represents the electrolyte and contact resistance between the electrode and current collector.  $R_p$  provides a value for the electrodes polarization resistance and  $C_{dl}$  represents the double layer capacitance. The total impedance of fig.2 may be expressed as

$$Z_{j\omega} = R_s + \frac{1}{\frac{1}{R_p} + j\omega C_{dl}} \quad (1)$$

Eqn. 1 assumes that the surface under investigation is homogenous. This is however never the case on porous solid electrodes. The lack of homogeneity which results in frequency dispersion at the surface is modeled with a constant phase element (CPE), such that the double layer capacitance of the porous surface is expressed as eqn.2.(Katsube and Scromedia-Perez 2003).

$$C_{dl} = Q^o \omega_{max}^{(1-n)} \quad (2)$$

Where  $n$  is a constant in the range  $0 \leq n \leq 1$ . It is determined by the negative drop rate of the complex impedance at high frequencies.

$Q^o = 1/|Z^n|$ , at  $\omega = 1.0 \text{ rads}^{-1}$  and  $\omega_{max}$  is the frequency at which the imaginary impedance is maximum.

Evaluating the logarithm of the amplitude of eqn. 1 yields

$$\log(|Z|) = \log(|R_s + R_p|) + \log(|1 + j\omega^1\tau_2|) - \log(|1 + j\omega^1\tau_1|). \quad (3)$$

Where  $\omega^1 = \omega^{(1-n)}$  and the Bode characteristics breakpoints  $\tau_1$  and  $\tau_2$  are at

$$\tau_1 = R_p C_{dl} \quad \text{and} \quad \tau_2 = \frac{R_s R_p C_{dl}}{R_s + R_p} \quad (3b)$$

Experimental plot and analysis of eqn.5 gives the values of  $R_s$ ,  $R_p$  and  $C_{dl}$  of the specific double layer.

In terms of phase, the impedance is as expressed in eqn. 4 (Theraja 1979).

$$|Z|_{j\omega} = |Z|(Cos\theta + jSin\theta) \quad (4)$$

Where  $\theta = 2\pi \frac{\Delta T}{T}$ ,  $\Delta T$  is experimentally measured time shift.

The real and complex impedance values are obtained through the use of this equation.

In this work, we join in the search for materials suitable for the preparation of high polarizable electrodes for electric double layer capacitors. The activated carbon electrodes were prepared from some local biomass precursors. Unfortunately however, there was no Potentiostat. Therefore, their EIS characterisation was implemented with a Digital Storage Oscilloscope and a Computer operated Function Generator.

### Materials and Methods:-

**Materials:** - The electrodes were prepared from inert air carbonized and CO<sub>2</sub> activated Coconut shells and Rice husk. The precursors were procured from Sheda town of the Federal Capital Territory (FCT), Nigeria. Petroleum residue tar served as binder for the Coconut shell powder, while the Rice husk was binderless. Compression machine utilized a compression mould designed with sample ejector and was constructed in Shesctco's central workshop. Carbonisation and Activation were carried out in a constructed stainless steel chamber that was inserted into a Muffle furnace. The chamber had external gas pipe connections. For the electrical characterisation, the anode of the 'three -electrode' tetra-oxosulphate 1V acid (H<sub>2</sub>SO<sub>4</sub>) electrolyte cell was Graphite while Ag/AgCl<sub>2</sub> electrode served as reference. Other equipment were a Digital Storage Oscilloscope (LW2025B), Computer operated Function Generator (Velleman PC10/8016) and X-Ray Diffractometer (PANalytical X' Pert Pro).

**Experimental methods:-** The washed and dried precursors were pre-carbonised at 280<sup>0</sup>C for 30 minutes, pulverized and sieved to 200microns. 75% by wt. of the coconut shells powder was homogenized with 25% of petroleum residue tar at 150<sup>0</sup>C. The Rice Husk was compressed without a binder. Some quantities of the materials were subjected to 750kg/m<sup>2</sup> for compacting to discs of approximately 25mm diameter in the compression mould. The weights of the formed discs were recorded. The carbonization method has been described elsewhere (Imalerio et al 2014). CO<sub>2</sub> activation was implemented at 750<sup>0</sup>C for 60mins at a heating rate of approximately 11<sup>0</sup>Cmin<sup>-1</sup>. After taking their weights, the formed activated carbon electrodes were pressed on partially acid etched aluminum foils that served as current collectors. The mounted electrodes and current collectors were supported by epoxy resin on glass slides. The two electrodes from the Coconut shells and Rice husk were labeled as ACSCT and ARHBL respectively.

The electrochemical characterisation setup comprising the three electrode cell, Function Generator and Oscilloscope is illustrated in fig. 2.

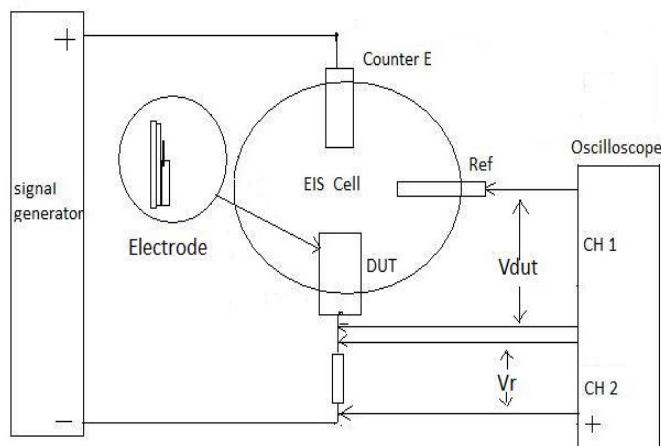


Fig.2 : Electrode characterisation experimental setup.

For each test, the function generator was used to scan the frequency range of (1.0M – 1.0)Hz at 1.02Vrms. Channel 2 of the oscilloscope measured the voltage drop across the 10.1Ω standard resistor ( $V_R$ ), while Channel 1 measured that across the electrode under test ( $V_{DUT}$ ). This was referenced to the Ag/AgCl<sub>2</sub> third electrode. The period time shifts ( $\Delta T$ ), reactance introduced between the two waveforms were also recorded at each frequency.

**Results and Discussions:** - Fig.3a shows the total Bode Impedance plots of the tested electrodes. Theoretically, the plots are represented by eqn. 3.

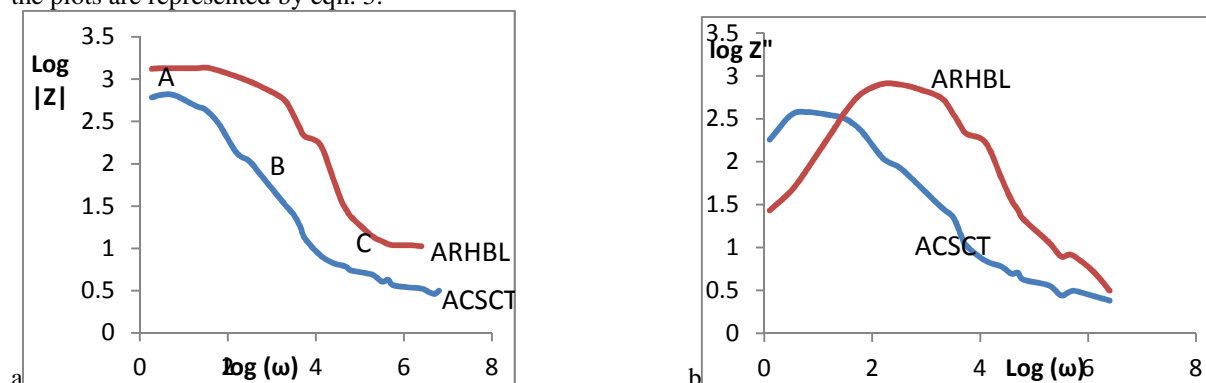


Fig: 3 Total Bode Impedance and Imaginary impedance plots of ACSCT and ARHBL.

For the purpose of analysis, the plot is divided into sections A, B and C. At low frequencies (section A), capacitance is considered open circuit. The constant impedance in this range represents  $R_s + R_p$  fig.1. Also when viewed from eqn.5, when  $\omega \ll 1$ , the last two terms equals zero. The ARHBL gave maximum impedance at this low frequency as 1327.4Ω while ACSCT gave 627.9Ω. Section B exhibits the complex frequency response of the capacitance. At high frequencies (section C), the capacitance acts as a shunt across  $R_p$ , leaving only  $R_s$  in the circuit. For ARHBL the high frequency measured 10.9Ω constant impedance therefore represents the series resistance  $R_s$ . The polarization impedance represented by  $R_p$  is thus 1316.5Ω. These values are also derivable from the complex Nyquist plot of fig. 4b in which the semicircle intercepts on the real axis defines the impedances.

The computed Series and Polarization resistances of the two electrodes from the Bode impedance plot fig.3 is presented in Table 1. Biomass activated carbon electrodes exhibit high impedances, this is evident in the ARHBL. This explains why when used in preparing electrodes, graphite powder or carbon nanotubes are usually added to biomass activated carbons to improve on their conductivity. The mixture of coal tar pitch and coconut shells powder in the ACSCT exhibited some form of electrical conductivity after activation. This was attributed to coal tar pitch mesophase conductivity. This explains the lower impedances recorded for the ACSCT. Also as the same electrolyte and cell was utilized for the two samples, observed difference in  $R_s$  was attributed to differences in contact resistance between the electrodes and their current collectors.

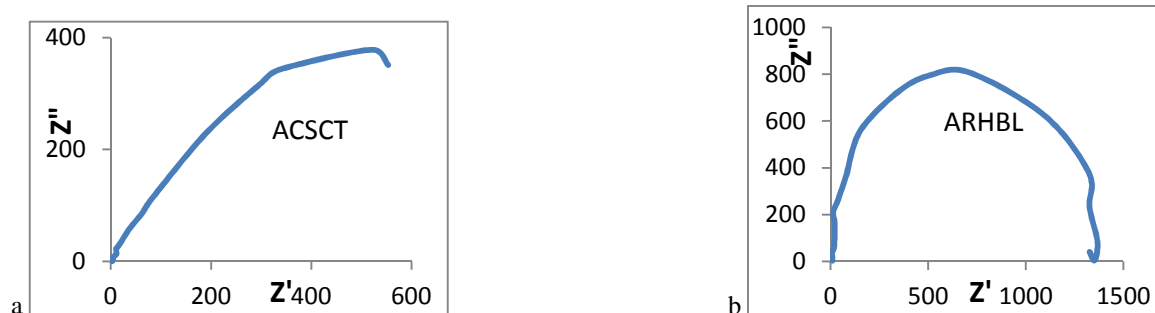


Fig.4: Complex Nyquist plots of ARHBL and ACSCT electrodes.

Plot of the imaginary impedance as function of frequency is presented in fig.3b. The complex impedances rise from low values at low frequencies, peak at a certain value ( $\omega_{max}$ ) and drop linearly at higher frequencies. Gradients of the linearly decreasing segments of the two traces gave CPE element  $n = 0.7$  for ARHBL and  $0.97$  for ACSCT. The computed results for the two electrodes are given in Table 1. With the CPE constants and  $\omega_{max}$  determined, the capacitances were evaluated with eqn. 4.

The complex plane Nyquist plots of the two samples are presented in fig. 4a,b. EIS analysis commonly employs Nyquist plots. The presence of CPE element is indicated by the plots. While fig.4a suggests the presence of faradaic reaction and shallow pores, fig.4b indicates the presence of a fractal surface with deep pores [8]. This corresponds with the measured specific capacitances (Table 1). The capacitance of the deep pores rice husk, is clearly higher than that of the coconut shells.

Table 1:- Rice Husk and Coconut Shells Activated Carbon Electrodes EIS derived parameters.

Electrode	$R_s(\Omega)$	$R_p(\Omega)$	(n)	$\omega_{max}(\text{rad/s})$	$C_{dl}/\text{g(F)}$
ARHBL	10.9	1316.5	0.97	123.3	0.17
ACSCT	3.0	627.9	0.70	6.31	0.02

X-Ray Diffractometer powder plots of the two electrodes are presented in figure 5.

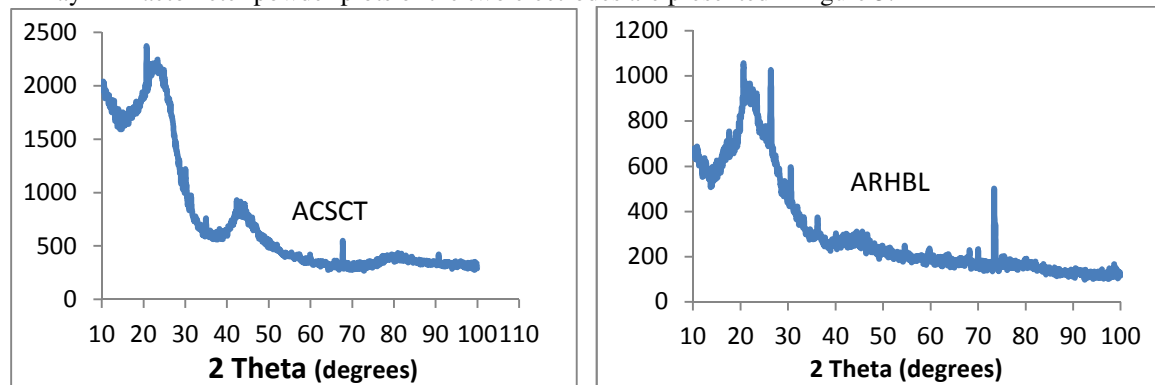


Fig 5: XRD scan plots of ACSCT and ARHBL activated carbons.

Broad peaks corresponding to (002) and (100) planes characteristics of carbon structure appear in both XRD patterns between  $15$  and  $35^\circ$ . The sharp peaks that appear on the broad peaks are due to the presence of  $\text{SiO}_2$  in the electrodes, which are commonly found on biomass raw materials (Taer et al 2011). The peaks as expected are more pronounced in ARHBL since rice husk ash has been reported to contain up to eighty, (80) % silica content (Prasad and Pandey 2012). In fact, the XRD machine labeled the sample as  $\text{SiO}_2$ .

## Conclusions

The fairly high capacitances obtained for the two electrodes are indicative of the materials suitability for the preparation of electrodes for high energy storage electric double layer capacitors. The work has also demonstrated that with a properly configured electrochemical cell, the combination of a standard resistor, digital storage oscilloscope and function generator can be used to acquire data for electrochemical impedance spectroscopy. Detailed implementation of the data analysis procedures is however a basic requirement. With further improvement in the electrodes preparation methods and cell configuration, it may be possible to improve on the parameters obtained for the utilized precursor materials.

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