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_2 activation at 750^0C. Electrochemical Impedance spectroscopy characterizations gave their Double layer Capacitances as $0.02Fg^{-1}$ and $0.17Fg^{-1}$ 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.

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. 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^3 at very low energy density[1]. 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[2].

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 [3]. About one gram of AC could have a surface area of $500m^2$ [4]. For example, a surface area range of between 446 to $1340m^2g^{-1}$ has been reported for Coconut shells [5]. A linear relationship between obtained capacitance and available surface area has also been observed [6,7].

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 [8]. 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 techniques 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 [9].

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, Rs, in series with the double-layer capacitance C_{dl} in parallel with a polarization resistance R_p fig.1 [8].
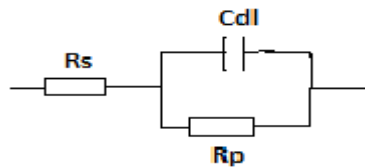

Fig. 1: Model of the electric double layer.

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

$$Z_{j\omega} = R_S + \frac{1}{1/R_p + j\omega C_{dl}}$$

3

Fig. 2 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 [10].

$$C_{dl} = Q^o \omega_{max}^{(1-n)}$$
4

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.

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

Evaluating the logarithm of the amplitude of eqn. 3 yields

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

5

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

$$\tau_1 = R_p C_{dl} \quad\quad\quad and \quad\quad\quad \tau_2 = \frac{R_s R_p C_{dl}}{R_s + R_p}$$

5b

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. 6[11].

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

6

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

The real and complex impedance values are obtained by 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. 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_2 activated Coconut shells and Rice husk. Petroleum residue tar served as binder for the Coconut shell powder, while the Rice husk was binderless. The precursors were procured from Sheda town of the Federal Capital Territory (FCT), Nigeria. The anode of the 'three -electrode' tetra-oxosulphate 1V (H_2S0_4) electrolyte cell was Graphite while $Ag/AgCl_2$ electrode served as reference.

Experimental methods:- The washed and dried precursors were pre-carbonised at 280^0C for 30 minutes, pulverized and sieved to 500microns. 75% by wt. of the coconut shells powder was homogenized with 25% of petroleum residue tar at 150^0C. Some quantities of the materials were subjected to $750kg/m^2$ for compacting to discs of approximately 25mm diameter in a compression mould. The weights of the formed discs were recorded. The carbonization method has been described elsewhere [12]. $C0_2$ activation was implemented at 750^0C for 60mins at an initial heating rate of 11^0Cmin^{-1}. 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 (Velleman PC10/8016) and Oscilloscope (LW2025B) is illustrated in fig. 2.
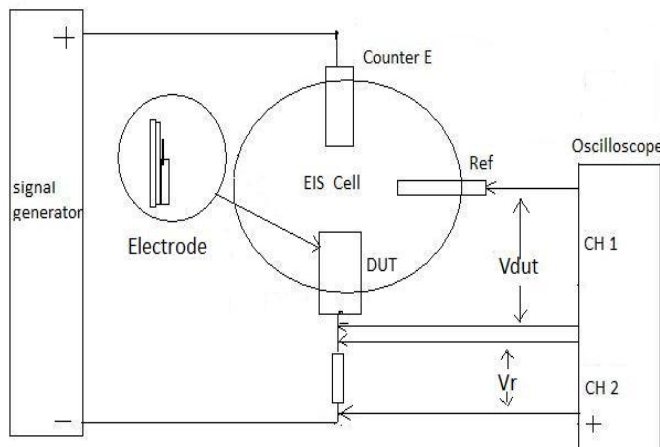

Fig.2 : Electrode characterisation experimental setup.

For each test, the function generator was used to scan the frequency range of $(0 - 1)$ MHz 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 $Ag/AgCl_2$ third electrode. The period time shifts (ΔT), 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. 5.
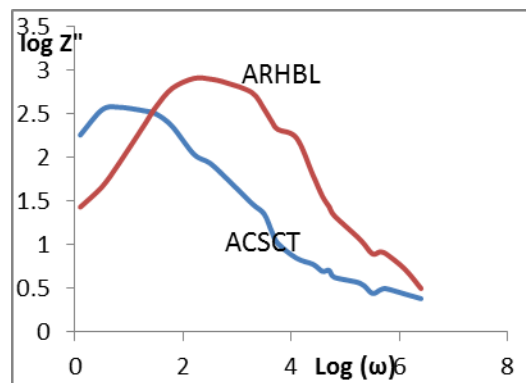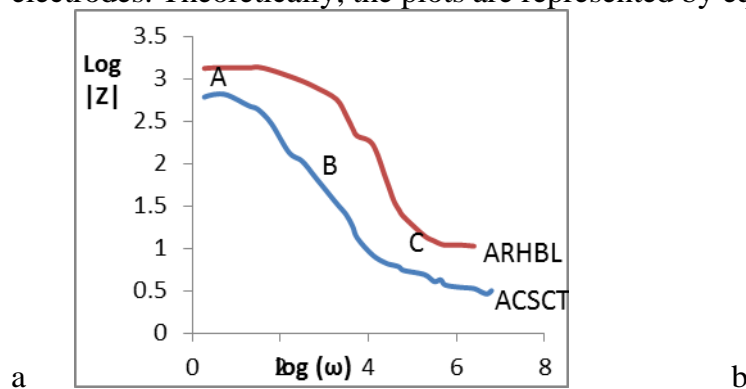

a

b

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 Rs + Rp 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 1327.4 Ω. Section B exhibits the complex frequency response of the capacitance. At high frequencies, the capacitance acts as a shunt across Rp, leaving only Rs in the circuit. For ARHBL the high frequency measured 10.9Ω constant impedance therefore represents the series resistance Rs. The polarization impedance represented by Rp 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. As the same electrolyte and cell was utilized for the two samples, observed difference in Rs was attributed to differences in contact resistance between the electrodes and their current collectors. This resistance was taken as the equivalent series resistance (ESR).

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 rises from low values at low frequencies, peaks at a certain value (ω_{max}) and drops linearly towards zero 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 ω_{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	Rs(Ω)	Rp(Ω).	(n)	ω_{max}(rad/s)	C_{dl}/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 (XRD) structural plots of the two electrodes taken by PANalytical X' Pert Pro unit are presented in figure 5.

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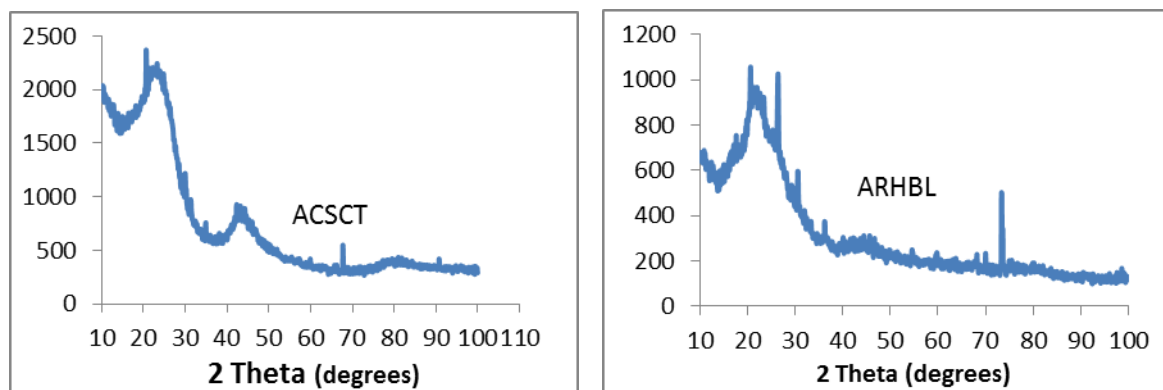
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Fig 5: XRD scan plots of ACSCT and ARHBL activated carbons.

Broad peaks corresponding to (002) and (100) planes characteristics of carbon structure appear in both XRD patterns between 15 and 35°. The sharp peaks that appear on the broad peaks are due to the presence of SiO_2 in the electrodes, which are commonly found on biomass raw materials. The peaks as expected are more pronounced in ARHBL since rice husk ash has been reported to contain up to eighty, (80) % silica content [13]. In fact, the XRD machine labeled the sample as 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.

References :-

[1] ELNA corporation, 2007: Capacitors principles and features. http://www.elna.co.jp/en.

[2] R. Kotz, A, M. Carlen : Principles and applications of electrochemical capacitors Electrochimica Acta 45 (2000) 2483–2498

[3] Chen J.H, Li W.Z, Wang D.Z, Yang S.X, Wen J.G, Ren Z.F. 2001: Electrochemical characterisation of carbon nanotubes as electrode in electrochemical double layer capacitor. PERGAMON Carbon 40(2002)1193 – 1197). Elsevier Science ltd.

[4] Grubs Tandy, 2009: Adsorption Isotherms, Methylene Blue on Activated Carbon Department of Chemistry, Unit 8271, Stetson University, Deland FL 32720.. wgrubbs@stetson.edu

[5] Farma R, M. Deraman, Awitrus E.T, I.A. Talib, R. Omar, J.G. Manjunatha, M.M. Ishak, N.H. Basri, B.N.M. Dolah. 2013: **Physical and electrochemical properties of supercapacitor electrodes derived from carbon nanotube and biomass carbon** International Journal of Electrochemical Science. 2013;8(1):257-273.

[6] Xu Ben, WU Feng, SU Yue Feng, CAO Gao-Ping, Chen Shi, Yang Yu-Sheng. 2007 : Preparation of Activated Carbon Nanotubes and their Electro – Chemical Capacitive Performance in Organic Electrolyte. School of Chemical Engineering and Environment, Beijing Institute of Technology, Beijing, China, 100081.

[7] Barbieri O, Hahn M, Herzog A, Kotz R, 2005 : Capacitance limits of high surface area activated carbons for Double Layer Capacitors. Elsevier Publishers, www.sciencedirect.com

[8] A Lasia, 1999: Electrochemical Impedance Spectroscopy and its Applications. Modern

Aspects of Electrochemistry. Kluwer Academic/Plenum Publishers, New York. Vol. 32, p. 143-248.

[9] B. V. Ratnakumar, M. C. Smart, S. Surampudi , 2008: Electrochemical Impedance Spectroscopy and its Applications to Lithium Ion Cells. Electrochemical Technologies Group, Jet Propulsion Laboratory, California Institute of Technology 4800 Oak Grove Drive, Pasadena, California 9 1 109.

[10] T.J. Katsube, N. Scromedia-Perez, 2003 : A method to determine electrode polarization characteristics. Current Research, 2003-H2. Canada.

[11] B.L Theraja, 1979: A Text-Book of Electrical Technology. 17[ths] revised EditionS.Chand & Company Ltd. Ram Nagar, New Delhi-110055.

[12] T.I. Imalerio, A. N. Amah, D.A. Onoja, A. A. Oberafo. 2013 : Nano pores surface area evaluation in palm kernel shells and masonia wood derived activated carbons. Conference proceedings, Nimacon 2013, T3 – 58. African University of Science and Technology,

[ ] Cleiton A, Nunes E, Mario C. Guerreiro, 2011: Estimation of Surface Area and Pore Volume of Activated Carbons by Methylene Blue and Iodine Numbers. Quim. Nova. Vol. XY. No. 1-5,200.

[13] Ram Prasad and Monika Pandey, 2012 :Rice Husk Ash as a Renewable Source for the Production of Value Added Silica Gel and its Application: An Overview . Bulletin of Chemical Reaction Engineering & Catalysis, x (x), 2012, xxx– xxx.

[8] Christian Lastoskie, Keith E. Gubbins, Nicholas Quirke 1993: Pore Size Distribution Analysis of Microporous Carbons: A Density Functional Theory Approach. Journal of Physical Chemistry, 1993. 97, 4786 – 4796

[10] Norwicki H, Barbara S, 2006 : Advanced Activated Carbon Test Method. New GRPD versus Classical Iodine number and BET surface area.

[11] Atkins P.W, 1999 : Physical Chemistry 6th Edition. Oxford University Press, Oxford 0X2 6DP.

[12] Abe I, Iwasaki S, 2001: Preparation of Activated Carbon by activation with Potassium Hydroxide from various raw materials. Journal of science and Industry, vol.75 No. 9 Page 437 – 440.

[13] Sudarvanto Y, Hartono S.B, Irawaty W, Hindarso H, Ismadji S, 2002 : High surface area activated carbon prepared from cassava peels by chemical activation. Biosource Technology, vol. 97, issue 5, March 2006, pages 734 – 739.

[14] Mohammad B.D, Maria M.I,Siti K.S, Mansur M.S, Awitrus E.T, 2010 : Biomass Carbon Electrode for Supercapacitor. University Kebangasaan Malaysia. www.sci.ui.ac.id/portal.id/wp-contact/uploads/ui-jakartal-penang.pdf

[15] Wang G, Zhang B, Yu Z, & Qu M. (2005): Manganese oxide/MWNTs composite electrodes for supercapacitors. *Solid State Ionics*, 176 (11-12) 1169–1174.

[16] Chen J.H, Li W.Z, Wang D.Z, Yang S.X, Wen J.G, Ren Z.F. 2001: Electrochemical characterisation of carbon nanotubes as electrode in electrochemical double layer capacitor. PERGAMON Carbon 40(2002)1193 – 1197). Elsevier Science ltd

[21] Ashwini Vittal Gopinath and Dale Russell, 2006 : An Inexpensive Field Portable Programmable Potentiostat. *The Chemical Educator,* Vol. 11, No. 1,

[22] V. Ruiz, C. Blanco, R. Santamaria, J.M. Ramos-Fernandez, M. Martinez-Escandell, A. Sepulveda-Escribano, F. Rodrguez-Reinoso. 2009: An activated carbon monolith as an electrode material for supercapacitors. Elsevier Carbon 47 (2009) 195-200.

[23] J.H. Chen, W.Z. Li, D.Z. Wang, S.X. Yang, J.G. Wen, Z.F. Ren. 2002 : Electrochemical characterisation of carbon nanotubes as electrode in electrochemical double-layer capacitors. Pergamon Carbon 40 (2002) 1193-1197

[1] A Lasia, 1999: Electrochemical Impedance Spectroscopy and its Applications. Modern Aspects of Electrochemistry. Kluwer Academic/Plenum Publishers, New York. Vol. 32, p. 143-248.

[2] B. V. Ratnakumar, M. C. Smart, S. Surampudi , 2008: Electrochemical Impedance Spectroscopy and its Applications to Lithium Ion Cells. Electrochemical Technologies Group, Jet Propulsion Laboratory, California Institute of Technology 4800 Oak Grove Drive, Pasadena, California 9 1 109.

[3] Ashwini Vittal Gopinath and Dale Russell, 2006 : An Inexpensive Field Portable Programmable Potentiostat. *The Chemical Educator,* Vol. 11, No. 1,

[4] V. Ruiz, C. Blanco, R. Santamaria, J.M. Ramos-Fernandez, M. Martinez-Escandell, A. Sepulveda-Escribano, F. Rodrguez-Reinoso. 2009: An activated carbon monolith as an electrode material for supercapacitors. Elsevier Carbon 47 (2009) 195-200.

[5] J.H. Chen, W.Z. Li, D.Z. Wang, S.X. Yang, J.G. Wen, Z.F. Ren. 2002 : Electrochemical characterisation of carbon nanotubes as electrode in electrochemical double-layer capacitors. Pergamon Carbon 40 (2002) 1193-1197.

[6]

[7] T.J. Katsube, N. Scromedia-Perez, 2003 : A method to determine electrode polarization characteristics. Current Research, 2003-H2. Canada.

[8] B.L Theraja, 1979: A Text-Book of Electrical Technology. 17th revised Edition. S.Chand & Company Ltd. Ram Nagar, New Delhi-110055.

[9] *E. Taer, M. Deraman1,, I. A. Talib, A. Awitdrus, S.A. Hashmi, A. A. Umar. 2011:* Preparation of a Highly Porous Binderless Activated Carbon Monolith from Rubber Wood Sawdust by a Multi-Step Activation Process for Application in Supercapacitors. *Int. J. Electrochem. Sci.,* 6 (2011) 3301 – 3315.

[10] Jean-Baptiste Jorcin, Mark E. Orazem, Nadine Pebere, benard Tribollet. 2005: CPE analysis by local electrochemical impedance spectroscopy. ELSEVIER Electrochimica Acta 51 (2006) 1473-1479.

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