

Synthesis of activated carbon from black liquor for the application of supercapacitor

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Abstract

In this present study, the black liquor carbonization has been investigated by hydrothermal process. The activated carbon from the carbonization of black liquor (AC-BL) and biomass based activated carbon from citrus sinensis flavedos (AC-OP) has been investigated for the suitability in supercapacitor application. The study have analysed in electrochemical measurement of both AC-BL and AC-OP in electrochemical station. The role of stable hydroxyl molecules on the surface of carbon material has been observed and its effective conductivity is studied. The superior performance of AC-OP derived nano porous carbon has fast ionic and electronic diffusion of the electrolyte in and out of the pores during charging and discharging due to high surface area. AC-BL exhibited with an EDLC mechanism, but AC-OP shows the pseudo capacitance property. The porous structure and oxygen doping characteristics in AC-BL can influence the potential electrode material for applications in the field of supercapacitors. With the help of this movement, electronic conductivity of the AC-BL has been increased. In general, electrochemical stability of the EDLC is far better than pseudo capacitor. From the EIS analysis, ESR value is very small for AC-BL (60 Ω), when compared to AC-OP (155 Ω). To conclude that the EIS results of low conductivity by AC-BL has potential to be future supercapacitor with enhanced treatment in carbonization techniques.

Introduction

Activated carbon, also called as activated charcoal, is a type of carbon handled to have little, low-volume pores that expansion the surface area and it is accessible for adsorption or chemical reactions. Because of its high level of micro porosity, carbon has a surface area more than 3,000 m^2/g as dictated by gas adsorption [1-4]. Activated carbon (AC) is usually derived from charcoal and it is referred as activated coal [5, 6]. From the available carbonaceous materials, AC is the capable candidate for supercapacitor, owing to the high specific surface area and low-cost. Although in AC, a greater number of carbon atoms cannot be contacted with the electrolyte which directed the ineffectiveness of carbon atoms. Similarly, the electrical conductivity of AC restricted the application in high power density devices [6-9]. Initially activated carbons from biomass are produced from bamboo, coir, lignite, rice husk, coconut shell carbon, coconut tree sawdust carbon and from agricultural by-products, peels of banana [7] and orange [8]. Black liquor is a by-product from kraft pulping process which is directly used as a liquid fuel with the substituent. While burning black liquor can emit pollutants such as CO_2 and SO_2 . There is recent development in production of activated carbon from black liquor [10]. In this development, the different methods used for the production of activated carbon are hydrothermal, pyrolysis and hydrodeoxygenation process [10-14].

By removal of colour and impurities, Lignin and cellulose substitutions of the black liquor can convert into carbonization material. In carbonization process, organic compounds converted into saturated carbons as carbon compounds. The process of carbon bonds at high pressure and temperature under closed system at 160 - 300°C can produces activated carbon from the sources of rice husk, cotton seed and coconut shell [11-14].

Kyle McGaughy et al [15] conducted hydrothermal carbonization of food waste at 200, 230 and 260°C for 30 min. They found that fixed carbon content has increased from 18.8 to 22.4 with increase in temperature. The product hydrochar is mainly used as solid fuel and carbon storage.

Suteerawattananda et al [16] conducted hydrothermal carbonization on rice husk at 180 – 250°C and 12-42 bar. He found that fixed carbon percentage has doubled by increasing the temperature. XRF analysis shows that reduce in alkali and alkali earth materials have decreased. Fernandez ME et al [17] conducted hydrothermal on orange peel. The hydrochar was chemically activated with phosphoric acid. The characteristic shows that it adsorbs three pharmaceuticals diclofenac sodium, salicylic acid and flurbiprofen. Kyle McGaughy et al [15] conducted hydrothermal on paper mill sludge at 180, 220 and 260 °C. The hydrochar produced will have same combustion indices as that of the coal. It is used to be a solid fuel. Similarly, M. Toufiq Reza et al[18] conducted hydrothermal on wheat straw at 180- 260°C for 2-8 hr. Up to a temperature of about 220°C the digestate contains primarily cellulose and lignin. After reaching a temperature of 260°C the cellulose is completely converted to carbon and lignin rich hydrocarbon.

Hydrothermal carbonization on sugarcane bagasse carried out by wet torrefaction by Wei-Hsin Chen et al in which this has carried by water or dil. sulphuric acid [19]. The bagasse has higher heating value raises up to 20.3%. Microwaves are used to raise the temperature of solution and maintain the temperature. Microwave treatment on the samples, offered a greater number of active sites which further expected to provide more channels for speedy ion transport and enhance the electrolyte diffusion into the electrodes [6-8]. Additionally, this microwave approach highly influenced the electrochemical performances of the material [20]. When compared to the normal samples, the microwave annealed samples exhibited a good value of specific capacitance and small equivalent resistances [21].The calorific value of biomass can be calculated.

Lee et al processed hydrothermal carbonization on leather waste at a temperature of 180-200°C[22]. The temperature gives good yield, higher heating value and high quality of solid fuel. The produced hydrochar has lower sulphur content which is a pollution free energy source. It reduces the pollution due to leather waste. Elaigwu et al studied hydrothermal carbonization on rapeseed husk at 150-200°C[23]. The microwave heating is carried out at with the help of water. When the residence time and temperature increases, the yield gets decreased. The energy quality of produced hydrochar gets increased. The process is zigzag for a time of about 20 min. Further increase in residence time the process gets steady.

Table 1. Properties of black liquor[10, 24]:

PARAMETERS	VALUE
pH	13-14
Colour intensity	3100
BOD	5100 ppm
COD	12245 ppm
TDS	402.68 ppm
Total phenol	38.54 %
Sulphate	1762 %
Cd	0.06 %
Cr	0.22 %
Cu	0.10 %
Fe	3.99 %
C	30.7 %
H	3.7 %
O	35.9 %
S	5.7 %
Organic materials	61.8 %
Inorganic materials	38.1 %
Carbon content	36.3 %
Sodium content	18.6 %
Coke content	52.5 %
Ash content	42.9 %

The treatment of activated carbon is used for the removal of such impurities over surface atoms to washout. The Environmental application of activated carbon is used for ground water remediation, drinking water filtration, air purification and in medical applications [24-26]. However, majority of activated carbon is used as solid fuel, membrane and electrodes.

In this work, the carbon is extracted biomass (*Citrus sinensis* flavedos) and black liquor, which is the source material for the electrodes used in supercapacitor. The carbon is then activated using activating agents like Sulphuric acid. The stability of carbon of the samples are analysed using TGA and FTIR. By using Cyclic Voltammetry, Galvanostatic Charge Discharge measurement (GCD) and Electrochemical

Impedance Spectroscopy (EIS), electrochemical measurements for the application of super-capacitor were investigated.

Experimental Setup

Black Liquor is base in nature. The pH value of the black liquor is 14. It is above the pH level of 7. Black liquor is neutralized by adding the dil. H_2SO_4 . Due to the addition of acid the lignin separation takes place. The black liquor is changed to dark brown colour. The colour is changed due to the precipitate present in the black liquor. After that, the filtration process is carried out by using filter paper. The lignin is separated from the black liquor in filtration process.

Carbonization is the process of conversion of dead or live organic matter into carbon product. It converts organic matter to carbon residue by destructive distillation. Hydrothermal process takes place mainly at 180 to 300°C. The carbon bonds present in the materials gets destructed and residue carbon is obtained as product. The filtered product is taken in Teflon lined reactor. The hydrothermal reactor is placed inside the furnace at a temperature of 200°C for about 24 hrs. In this process, the carbon-carbon bond present in black liquor starts to break due to pressure and temperature developed inside the reactor. The black liquor is taken outside after 24hrs from the furnace. The carbonized black liquor converts into solid state by drying process named as AC-BL. The AC-BL is kept inside the hot air oven for drying process at a temperature of 150°C for about 4hrs. After completing the process, the AC-BL is converted into activated carbon and it is stable in nature. It is further analysed to find its properties.

Fresh orange peels (*Citrus sinensis flavedos*), named as AC-OP, were purchased from local shop and sliced with appropriate dimensions for simple activation. The pre-carbonized orange peel was grinded and sieved with particle less than 1 mm. These samples were carbonized at 600°C in muffle furnace in nitrogen gas environment, at a constant flow rate of 1 litre per minute for a period of 3 hrs. This material is kept overnight under CO_2 atmosphere. The collected carbon was grounded into powder and rinsed with 1 M of H_2SO_4 named as AC-OP. Then the samples were dried at 60°C for 24 hrs. Finally, the chemically activated carbon is neutralized to 7 pH after washing with deionized water.

Hydrothermal reactor consists of Teflon lined 100 ml capacity stainless steel cylindrical system. It can work under autogenic pressure and with maximum temperature of 210°C. The Teflon lining has 4 mm thickness. Figure 01 shows the pictorial representation of hydrothermal reactor.

The Perkin-Elmer spectrum one FTIR was used to analyze the activated carbon for both AC-OP and AC-BL. Drops of liquid samples are placed between two plates of salts made of potassium chloride or sodium hydroxide without any air-lock. The wave-length between 400 and 4000 cm^{-1} is fixed and data are interpreted for all the liquid samples. This technique is used widely for studying the infrared spectrum for liquids, gas or solids. During FTIR analyses mainly four different groups were studied due to the presence in the samples.

Thermogravimetric analyses (TGA) were performed for two samples for each AC composition using a model TGA Q 500 V2010 Build 36 TA Instrument System. After drying at 60°C, the AC was placed inside a cylindrical steel mold with 5.5 mm in diameter and 10 mm in length. The mass variation as a function of temperature was carried out in air at a heating rate of 10°C/min from RT to 800°C. Its design integrates a thermobalance engineered for maximum baseline flatness and high sensitivity, with the power and flexibility of an infrared furnace, and a proven horizontal purge gas system.

Electrochemical properties were measured by cyclic voltammetry using OriginLab electrochemical workstation at room temperature (25°C). The graphite rod is considered as the working electrode. To prepare the working electrode, the samples are mixed with the rubber solution and made slurry. Then the slurry is coated on graphite rod. A Pt wire and Ag/AgCl electrode are used as counter and reference electrodes, respectively. Cyclic voltammetry is recorded in 0.5 M H₂SO₄ aqueous solution at a scan rate of 30 mVs⁻¹. For analysing the performance of supercapacitor, the electrode is prepared as reported in the previous study. An equivalent series resistance and charge transfer resistance of the AC-BL and AC-OP samples are measured by using electrochemical impedance spectroscopy.

Results And Discussion

The carbonization of black liquor is carried in Teflon lined hydrothermal reactor and Orange peel has been carbonized directly in the muffle furnace. The carbonization of activated carbon as AC-BL is represented in Figure 2. The carbonized materials are dried to hold less than 2 wt moisture before subjected to activation with 0.5 M H₂SO₄.

The wavelength of 1614 cm⁻¹ indicates the carbonyl structure either -(CO)H or -(CO)-. The aldehydes or ketones implies at 2923 cm⁻¹ which show a broader spectrum indication. At this broadband wavelength of 2730 and 1710 cm⁻¹ shows the formation of carbonyl acids that was due to the hydroxyl bond over the carbon atom. The FTIR result in Figure 3 and 4 shows that wavelength from 3010 to 2800 cm⁻¹ has a broad intensity. This more widespread intensity denotes the presence of a high concentration of carbon.

The C-O bond of lignocellulose breaks at low enthalpy by leaving aldehyde or acid or alcohol, or by leaving all others. The intensity in the sample at 1614, 1578 and 1514 cm⁻¹ indicates aromatic/cyclic compounds with hydroxyl or carbonyl group. Also, there is arene compounds formation from the coupling of α -carbon radical and carbonyl group are either formed from ester dissociation or phenolic compounds. The aromatic/cyclic compounds, as indicated in the wavelength of 1058 cm⁻¹, confirmed the presence of β -hydroxyl carbonyl compounds. Table 2 reports the band assignment in AC-BL and AC-OP.

Table 2. Wavenumber observed in activated carbon in FTIR on transmission mode on both AC-BL and AC-OP

Absorption Range (cm ⁻¹)	Appearance	Group	Compound Class
3430	Strong	-CH ₂ -	Hydrocarbon
2923	Strong	-CH ₂ -	Hydrocarbon
2853	Strong	-CH ₂ -	Hydrocarbon
1614	Strong	C=O Stretching	Aldehyde
1578	Medium	C=O Stretching	Aldehyde or Ketone
1467	Weak	C-H Bending	Alkane
1378	Weak	C-H Bending	Aldehyde
1212	Strong	C-O Stretching	Alkyl aryl Ether
1133	Strong	C-O Stretching	Aliphatic Ether
1090	Strong	C-O Stretching	Aliphatic Ether

TGA is an instrument used to conduct the chemical properties like thermal decomposition, chemisorption and solid-gas reaction and physical properties like phase transition, absorption, adsorption and desorption. TGA can be used for materials characterization through analysis of characteristic decomposition patterns. In TGA the composition and thermal stability of the material can be exhibits weight loss due to decomposition, dehydration and oxidation. Figure 6 show the AC-OP in TGA investigation. Here, the sample is heated in an environment. The weight loss in the sample have drastically declined to 90 wt% until 70°C and, further increase in temperature show a linear decrease manner from 90 to 80 wt% from 70 to 700°C. Similarly, Figure 7 shows the multistage decomposition in the sample AC-BL observed at 100 and 150°C in TGA graph.

The weight losses in TGA result indicate that this might be due to different processes such as decomposition, evaporation, reduction and desorption. First phase at 100°C the respective weight loss in TGA can be appeared as water evaporation and desorption of the hydroxyl compounds. Second phase at 150°C the respective of weight loss might be the decomposition of alkaloids and desorption of allyl and cyclic hydrocarbon. By interpreting with FTIR and TGA, it is proved that alkaloids are present over the surface of the AC-BL sample.

Electrochemical Measurements:

To perform an electrochemical analysis, either 2 electrode or 3 electrode system is preferred. Here, the steps involved for working electrode preparation is discussed. To estimate the electrochemical performance, electrode should be prepared using the samples, mixed with rubber solution in the proportionate ratio of 60:40. The prepared mixture looked like slurry and it was coated on graphite pencil rod using brush. Finally, it was dried at room temperature for the required duration. The amount of

material coated on the lead is 0.1 g, approximately. The electrolyte for the analysis process chosen was 1 M H₂SO₄. The electrochemical analysis was tested in the potential window of -1 to 1 V. CV, GCD and EIS analysis are carried out in electrochemical workstation (Orignalys, France).

From the three electrode system, CV results of the samples using 0.5 M H₂SO₄ solution as an electrolyte is shown in Fig. with the range of -1 to +1 V. For an ideal supercapacitor, CV curve with rectangular nature is important. AC-BL exhibited an EDLC mechanism and AC-OP showed the pseudo capacitance. There dox peaks movement of the sample AC-OP is observed at the positive voltage, due to the samples obtained from the activation of orange peels. With the help of this movement, electronic conductivity of the sample is getting increased. In general, electrochemical stability of the EDLC is far better than pseudo capacitor. Owing to, electrochemical property of microwave treated material, it exhibited high electrochemical performance.

In GCD, during the charging/discharging process, the presence of meso-pores smoothens the progress of the rapid transport of ions and migration of ions. GCD curves of AC-BL and AC-OP is shown in Figure 8 with a potential range of -0.45 V to +0.7 V and +0.3 V to 0.45 V at current density of 0.05 A g⁻¹. It is observed that, the specific capacitance of 89.28 and 133.92 F g⁻¹ obtained from GCD spectra for AC-BL and AC-OP respectively. From the GCD curves it was observed that, AC-OP exhibited low potential window. At the same time, the voltage drop is very less for AC-OP, when compared to AC-BL. AC-BL exhibited near triangular GCD curves, with EDLC and a little bit of pseudocapacitive effect.

Impedance spectra of AC-BL and AC-OP are shown in Figure 9. In the high frequency zone, EIS curve is intercepted with the real axis ascribed to equivalent series resistance (ESR). From the EIS analysis, ESR value is very small for AC-BL (60 Ω), when compared to AC-OP (155 Ω). Similarly, the charge transfer resistance of 40 Ω and 19 Ω is observed for AC-BL and AC-OP. Increased R_{ct} for AC-BL is due to the poor conductivity of electrode and an electrolyte used. AC-OP exhibited closer to Warburg resistance in the low frequency zone suggested the level of ion diffusion.

Conclusion

The role of stable hydroxyl molecules on the surface of carbon material has been observed and its effective conductivity is studied. The superior performance of AC-OP derived nano porous carbon has fast ionic and electronic diffusion of the electrolyte in and out of the pores during charging and discharging due to high surface area. AC-BL exhibited with an EDLC mechanism, but AC-OP shows the pseudo capacitance property. The porous structure and oxygen doping characteristics in AC-BL can influence the potential electrode material for applications in the field of supercapacitors. With the help of this movement, electronic conductivity of the AC-BL has been increased. In general, electrochemical stability of the EDLC is far better than pseudo capacitor. From the EIS analysis, ESR value is very small for AC-BL (60 Ω), when compared to AC-OP (155 Ω). To conclude that the EIS results of low conductivity by AC-BL has potential to be future supercapacitor with enhanced treatment in carbonization techniques.

Declarations

ACKNOWLEDGEMENT

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Tables

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1378	Weak	C-H Bending	Aldehyde
1212	Strong	C-O Stretching	Alkyl aryl Ether
1133	Strong	C-O Stretching	Aliphatic Ether
1090	Strong	C-O Stretching	Aliphatic Ether

Figures



Figure 1

Hydrothermal reactor used for carbonization of black liquor

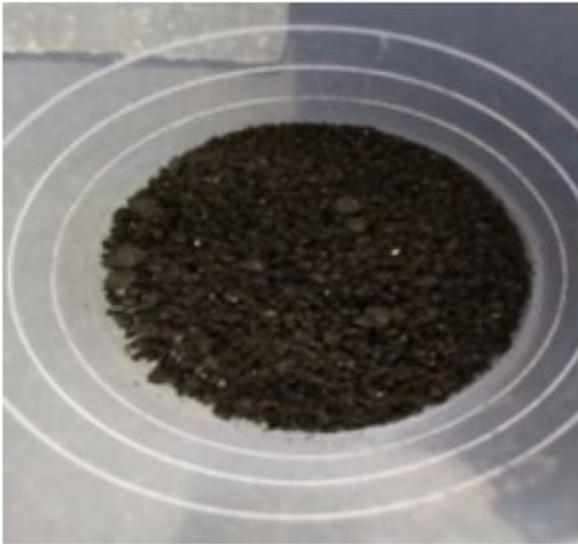


Figure 2

Carbonization in hydrothermal synthesis of AC-BL

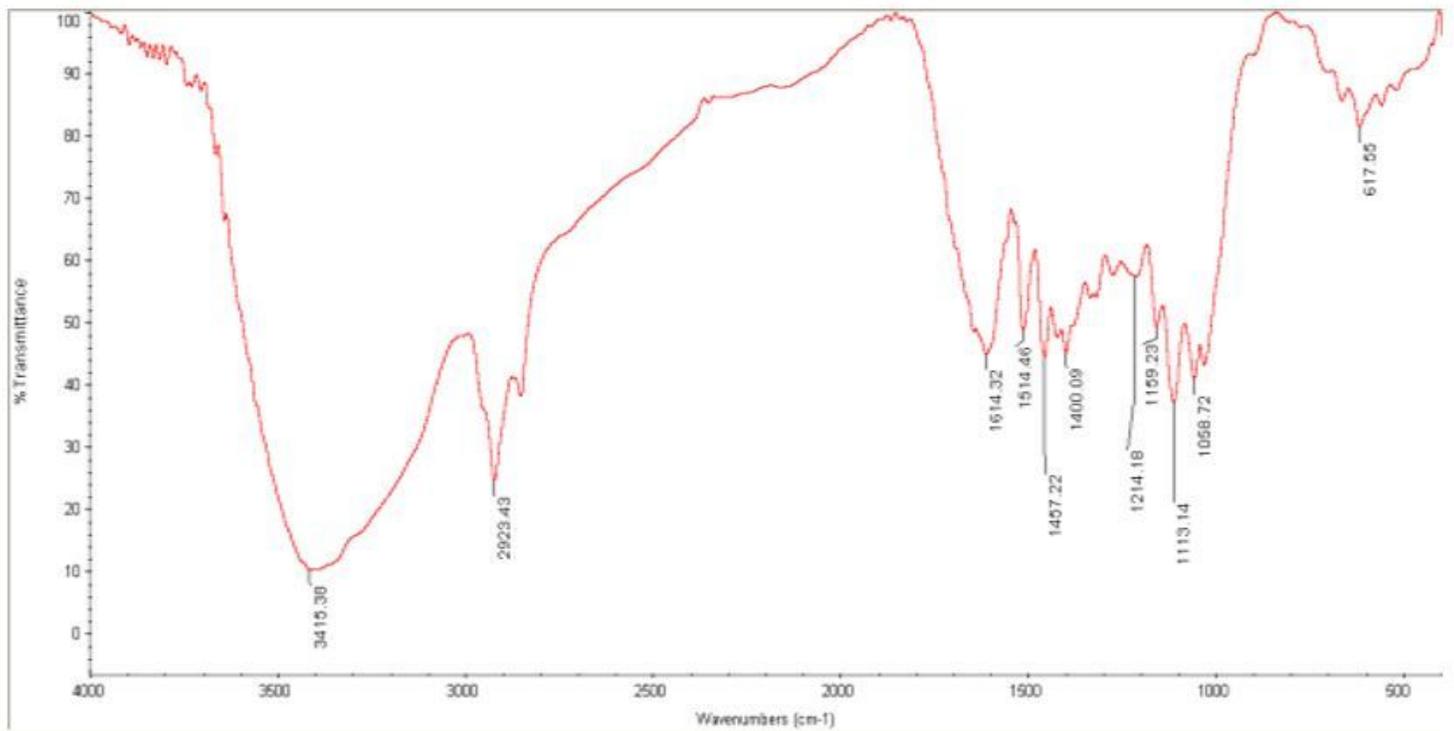


Figure 3

FTIR spectrum identification for AC-BL

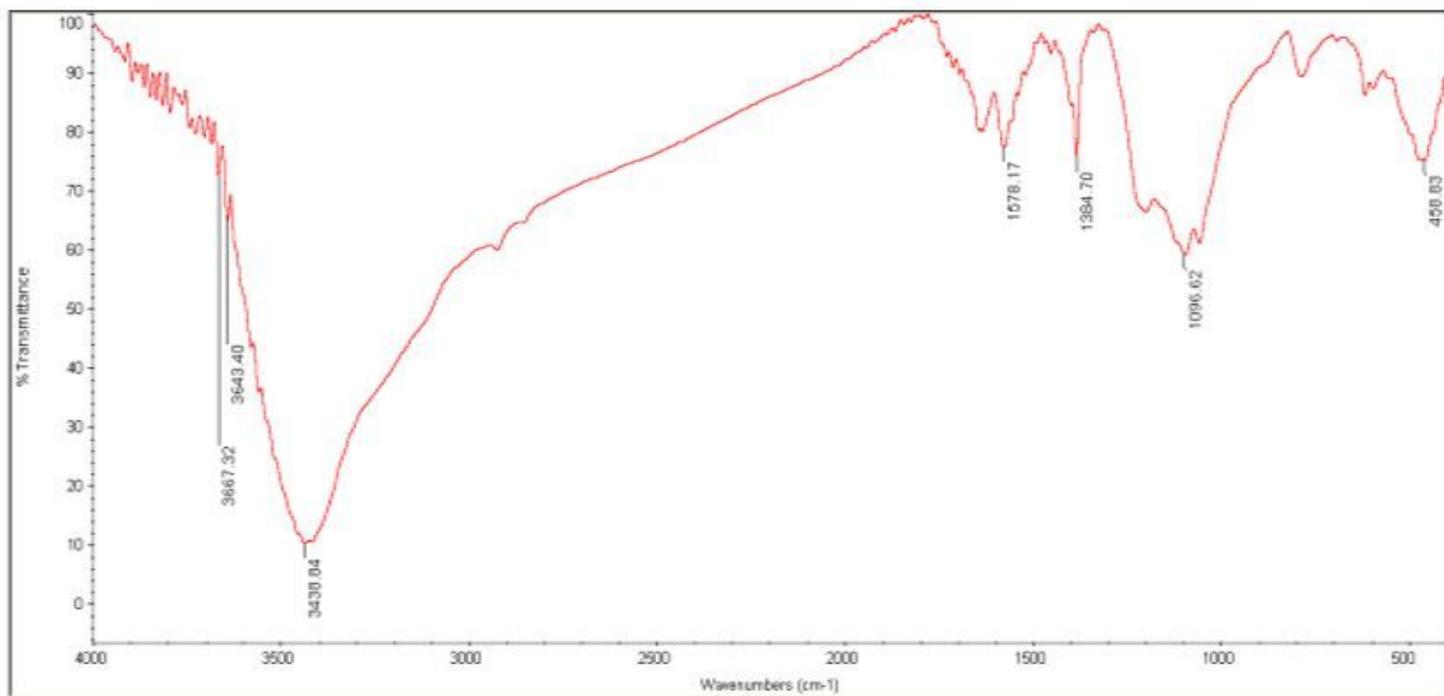


Figure 4

FTIR spectrum identification for AC-OP

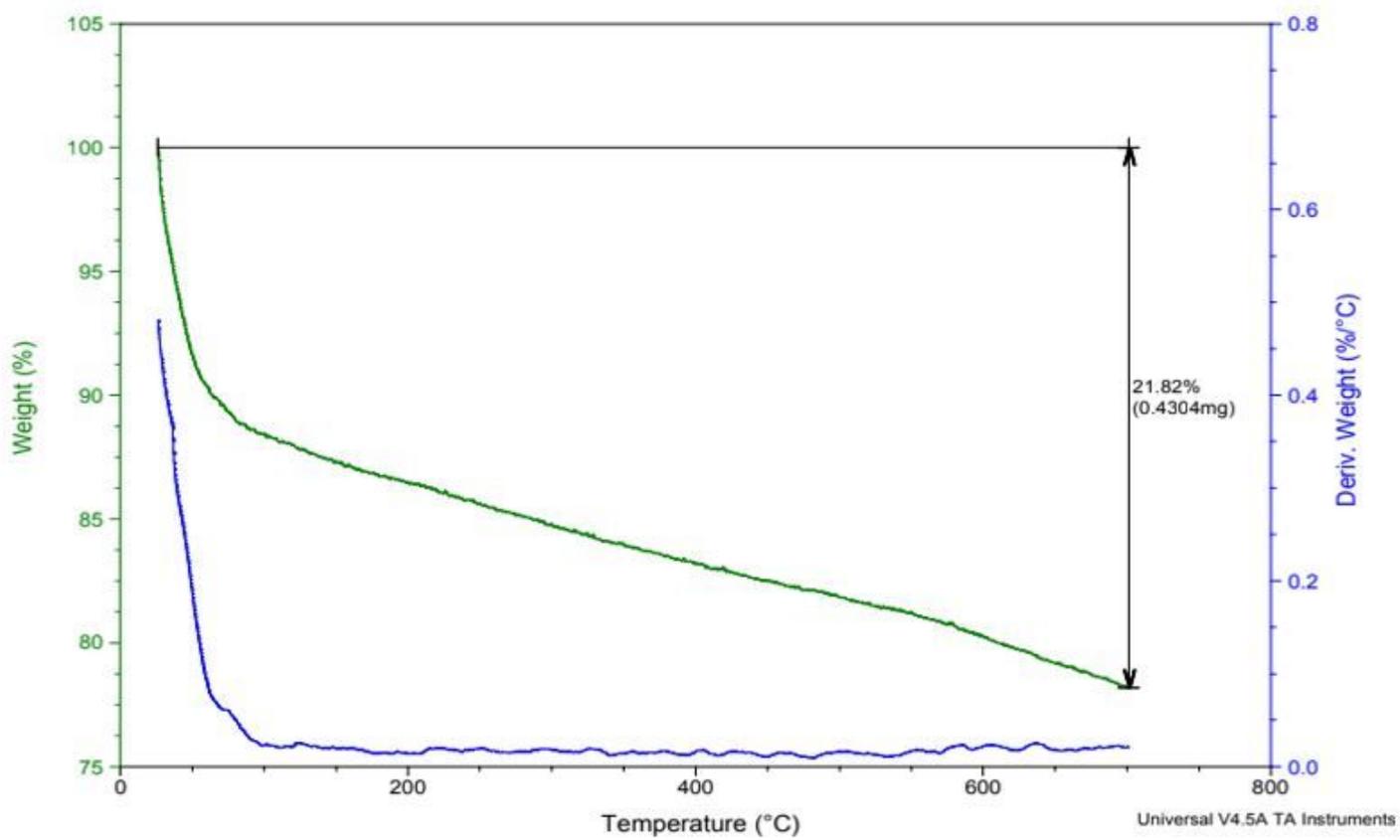


Figure 5

TGA data of AC-OP

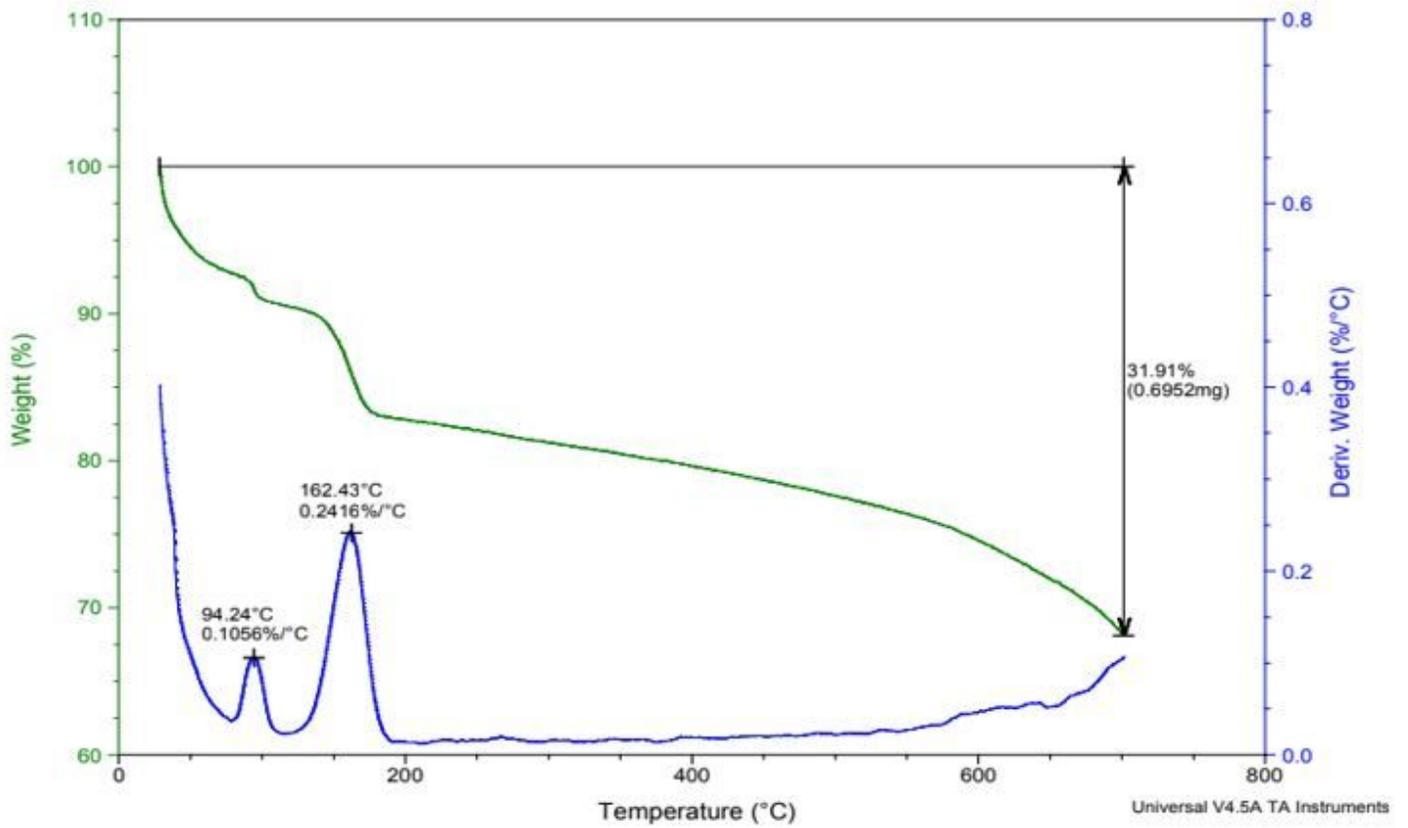


Figure 6

TGA data of AC-BL

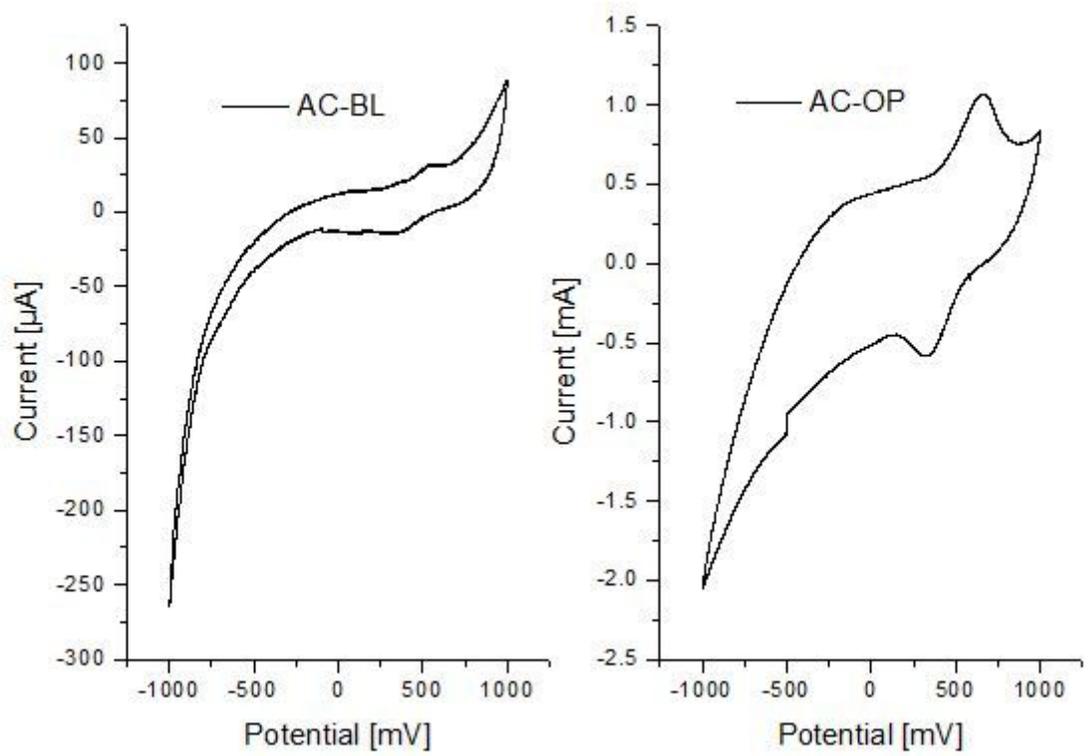


Figure 7

Cycle Voltametric curves of as prepared AC-OP and AC-BL samples at a scan rate of 30 mVs⁻¹

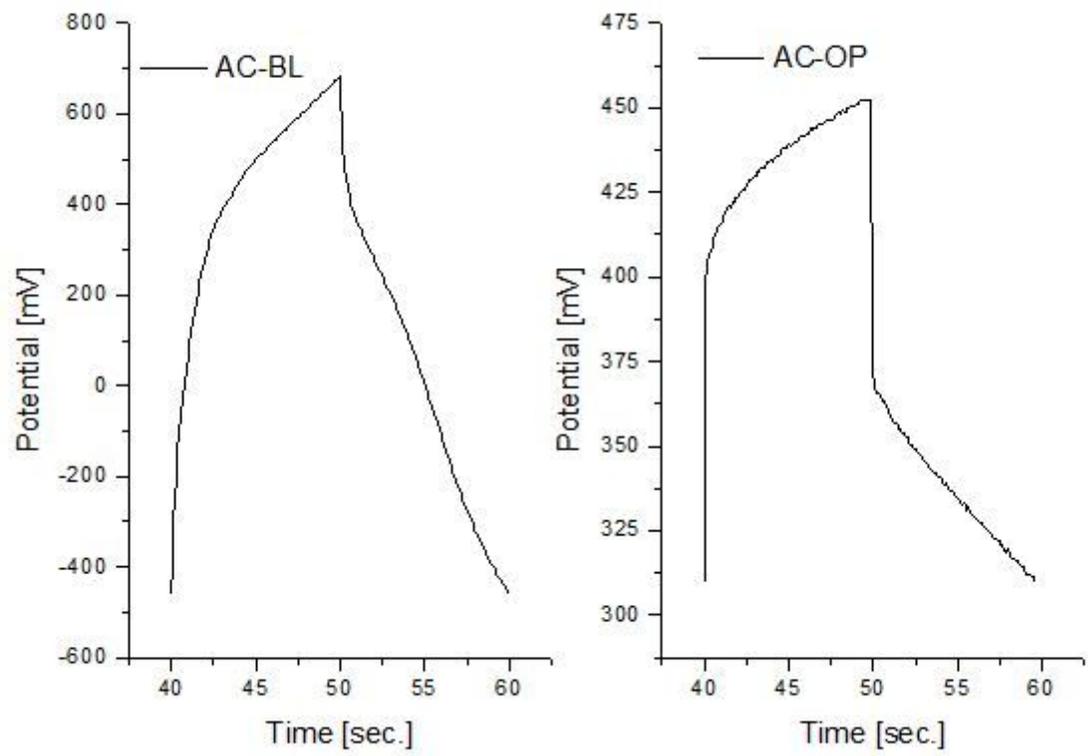


Figure 8

Galvanostatic Charge and Discharge spectra of sample AC-OP and AC-BL

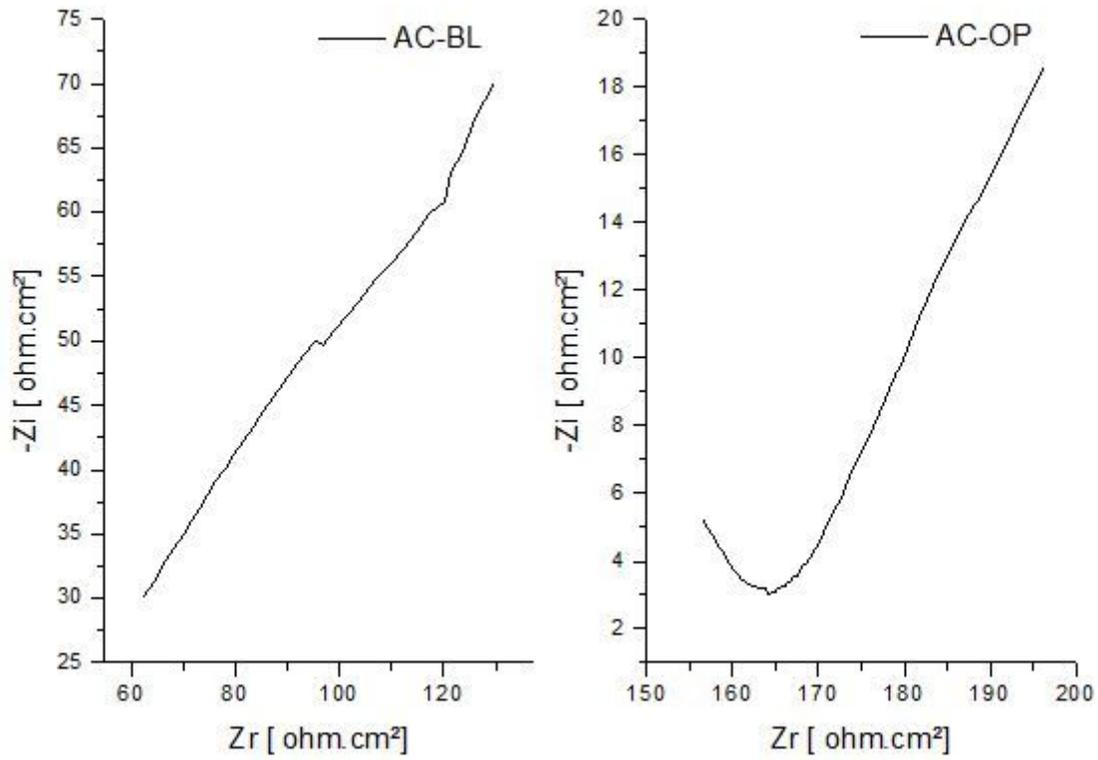


Figure 9

Nyquist plots of as prepared samples AC-OP and AC-BL