Parametric Analysis of Fabricated Supercapacitors from Raw Clay

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Abstract
Energy-storage devices have been the subject of many research studies in both experimental and theoretical schemes. Recent interests have been developed in the fabrication and technological application of supercapacitors.Throughout a designed procedure and methodology. A number of supercapacitor has been fabricated by using simple methods, with high capability. therefore , the made the supercapacitor from available material in natural and easy obtain of that, and this material is raw clay with separation between the electrodes LDPE is used in shopping as the carries bag of treatment it. Of fabricated supercapasitor have capacity 3.5F of discharge time 1500s at voltage 50 mV of specific power 24w/Kg of energy 145J.

1 Introduction

Supercapacitors are electrical storage devices which have relatively high energy storage density and high power density. In a supercapacitor, the electrical energy is achieved, due to existence the reaction process reduction-oxidation (redox) in electro-active materials. Supercapacitors are also characterized as devices with high capacitance and a low internal resistance with long life operation [1]

For known the electrochemical capacitor EC must divided to classifications, the electrochemical capacitor EC classify to two types, are symmetric and asymmetric. The symmetric is divided to two kinds, are without hybrid behavior and hybrid devices. The symmetric without hybrid is consist from two, the first electrical double-layer capacitors EDLC, which depend on large area of active carbon A.C., and consider non faradic reaction [2,3], and potential of this capacitor depend on electrostatically surface charges density, and has been accumulated in the near region of interface of separator, together with counter balancing of charges accumulated on another side of electrolytic in solution side at electrode interfaces [3,4]. The second pseudocapacitors, which depend on faradic reaction, i.e. redox reaction, and the electrode contain from metal oxide and conductive polymer as polyanilin, polythiophene, polypyrolle, polyacethylene and others, which has been consist on two bond, and this process called electrochemical doping polymers [2,3,5], and the motion of charges is involving the passage across the double layer as the battery at charge and discharge, but at capacitance depend on reasons thermodynamic between the accept of charge with change the potential [4]. The symmetric hibrid, is supercapacitor, which consider faradic reaction, has been hybrid type, the symmetric electrode is containing from active carbon and metal oxide [3,6], while the asymmetric electrode is containing from, the positive electrode from metal oxide, and the negative electrode from active carbon, e.g. NiOOH/KOH/AC or PbO2/H2SO4/AC [5,3], which have good characteristic, as high energy density, large power density and long lifetime [7].

Shudi Min construct composite to made electrode [RGO/Ni (OH)/NF] by reduced graphen oxide (RGO) on nickel hydroxide (Ni $(OH)_2$) film and reduced by nickel foam (NF). The results the composite electrodes exhibited supercapacitive performance with capability 2500 mF.Cm^{-2} at current density of (5 mA.Cm^{-2}) [8].

Yanqun Shao prepare electrode from poorly crystalline ($Ru_{0.4}Sn_{0.6}O_2$) solid solution with size 2nm coated on Ti substrate. The electrode has stable electrochemical capacitor with the maximum specific capacitance of 648 F/g within a scan potential window (-0.1_1.0) V in 0.5 M (H_2SO_4) electrolyte solution [9].

Yong worked mesoporous (Mn-Co) oxide for supercapacitors from mixed oxalate ($Mn_{0.8}Co_{0.2}C_2O_4.nH_2O$) and decomposed in air at 250^{o}c. Resulting tetragonal spinel (Mn-Co) oxide with particle size less than 100 nm. And area reach of 120 $m^2.g^{-1}$, then(Mn-Co) oxide electrode investigated by cyclic voltammetry and galvanostatic charge/discharge in 6 mol.L^{-1} (KOH) electrolyte. And, delivered specific capacitances of 383 F.g^{-1} and 225 F.g^{-1} respectively [10].

ZhiqiangNiu prepares assembling compact-designed supercapacitors using flexible single-walled carbon nanotube (SWCNT) films as both anode and cathode by the floating chemical vapor deposition method. And then ethanol was evaporated therefore the SWCNT films can adhere firmly to the separator and these two pieces of separator were stacked together and rolled up. The specific capacitance of this kind is about 35 F.g^{-1} and has power densities (197.3 KW.Kg^{-1}) [11].

Venkata compared between (SnO_2) ,(RuO_2) and (Sn_Ru)O_2 electrode after prepared nono-sized of all metals , therefore make supercapacitors , the result has been specific capacitance were (1.84, 6.08, 10.19) F.g^{-1}

of SnO_2, $(Sn\_Ru)O_2$ and RuO_2 electrode respectively.[12]

M.Selvakumar has been fabricated supercapacitor via use nanostructured zinc oxide activated carbon composite electrodes and used binder poly vinylidiene of fluoride (PVDF). And he found the capacitance of the electrodes decreased with increase in (ZnO) content. Also, that the specific capacitance is reach to 160 $F.g^{-1}$ for (1:1) composition by measur cyclic voltammetry in (0.1) M (Na_2SO_4) electrolyte [13].

2 Experimental procedures

2.1 Materials and preparation:

The scope of this section focuses on the various materials which were used to construct the capacitors under study. These materials are presented as follows. The present work deals with supercapacitors which are composed of the following main two parts:

A. Electrodes

These electrodes were fabricate with the following aim

A-1 Carbon fiber texture:

This material was selected as substrate of composite material as well as electrodes. The main characteristic feature of electrodes is that they are flexible, reinforced and porous for efficient ion adsorption.

A-2Composite material

This was normally spreaded on the carbon fiber after being made homogeneous. For constituents including active carbon (AC), ZnO, clay and electrolyte 2M from the solution Na_2SO_4, were mixed to obtain this composite which ought to have the following characteristics:

1. Highly porous
2. Large area
3. Effective homogeneity of AC with other oxides
4. To upgrade diffusion between the Na_2SO_4 and enhance adsorption–absorbtion.

A-2-1 Composite performance

1) Active Carbon:

Activated carbon is another amorphous, noncrystalline form of carbon possessing a large number of micropores and a high surface area [14]. AC depends on pore volume and pore size distribution, and that depend on treatment method the carbon for obtain on active carbon [15].

2) Zinc Oxide:

It has been known as transition metal oxide with high current density which allowed its use in a with range of research studies.

3) Clay:

It is the major molding content of the supercapacitor which is used to bring up required form. The clay is characterized by high porosity, diffusion, metal oxides as well as it is a binding material.

4) Electrolyte Solution:

In the present work, aqueous Na_2SO_4 solution has been used over the whole experiment an electrolyte solution with concentration (2M) for high volume requirement to match the macro size in the AC and composite.

A-2-2 Configuration of Blending:

The first mixing ZnO in certain percentage (calculated from previous with remain materials) with aqueous Na_2SO_4 solution of time two minute and then mixture with AC of time 3.5minute and jumble with clay of same time.

B. Separator

The separator from LDPE and has thickness reach to (1µm).

Sample Preparation:

This section is description the use of the above mentored materials to fabricate a sample of supercapacitor. These materials are active carbon, ZnO, Clay, Na_2SO_4 solution.

Prepared of the composite stands with the formation of the composite which is perform as follows, and addition to12ml from electrolytic Na_2SO_4 in concentration 2M. At this stage the composite is ready to be spread on the carbon fiber texture. The taken was (5cm×5cm)in dimension and 3.5g mass from composite for each electrode.The sample is the packed with slight pressure on the surface of the composite for each electrode.The assembly was the then connected to copper wire via the fiber whisker.

3. Results and Discussion

The raw clay is considering from important material because characteristic in good dielectric constant, oxides metal, clays mineral, the structure of clay forming from layers from SiO_2 or Al_2O_3 that lead to difference potential inner the raw clay structure and have hydrous silica which has ability of forming bond Si—OH at available water which support formation backbone from different structure [16][17].

3-1 XRD analysis

The XRD analysis sure, the clay contains on clays mineral and non-clays mineral, and the figure appear that.

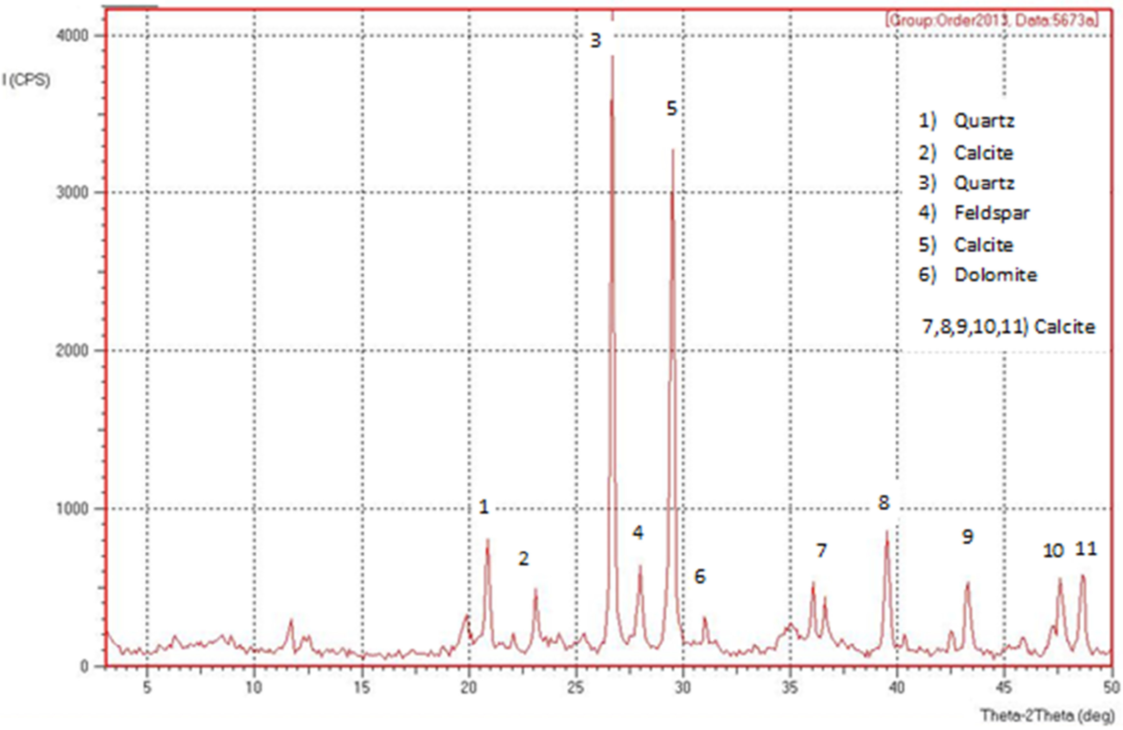

Figure (1) appears XRD of clay.

The raw clay is divided to two types, the first clay mineral, and the most common of properties clay minerals have ability formation process in case present water for become plasticity, as Kaolinite $[Al_2(Si_2O_5)(OH)_4]$, Montmorillonite $[Na_{0.33}(Al_{1.67}Mg_{0.33})(Si_2O_5)_2(OH)_2]$, Polygorskite$[(Mg,Al)_2Si_4O_{10}(OH)_4(H_2O)]$ and Illite $(K_{1-1.5}Al_4[Si_{7-6.5}Al_{1-1.5}O_{20}](OH)_4)$, but there second type, they are non-clay mineral, which has been nonplastic as Quartz SiO_2, Calcite CaCO3, Feldspar $[Na_2O, K_2O]\cdot Al_2O_{3\cdot 6}SiO_2$, Gypsum $[CaSO_4\cdot {}_2H_2O]$, Dolomite $[CaCO_3.MgCO_3]$ and the plagioclase $[NaAl_2Si_2O_8]$. The show of all the clay has ability of formation process and also has high oxides is supporting polarization process, and increase transition metal oxide.

3.2 SEM

The figures are representing these images of old active carbon, new active carbon, composite finally supercapacitor. The figure (2) is displaying the active carbon old.

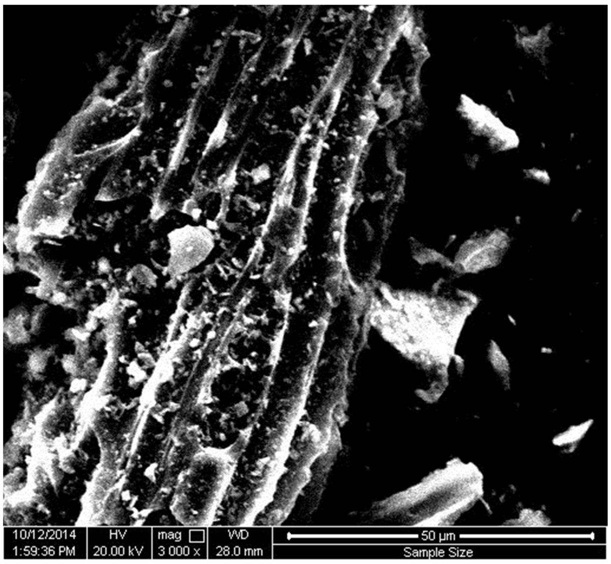

Figure (2) is appearing the active carbon particle.

This image display view of active carbon particle. That is taking rod shape is containing on lines porosities, and addition, to smallest particles, from through that saw ability the active carbon of have large area which increase the proceeding to redox processes. The size used in test of average particle is 54µm. For the comparing between the particles shapes before and after prepare, that see from the figure (3) and (4) the composite particles of C_{2-4}, which consist from ratio clay 30%, A.C. 65% and ZnO5%, of zooming reach to (10,50)µm.

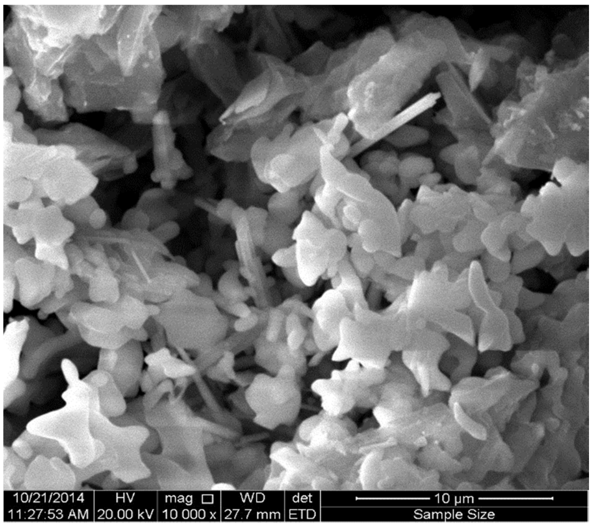

Figure (3) is appearing the composite powder of C_{2-4} to zoom reach 5µm.

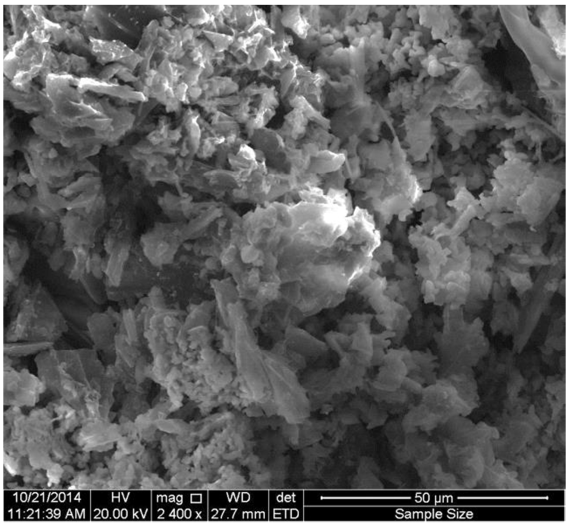

Figure (4) is appearing the composite powder of C_{2-4} to zoom reach 50µm.

That find in figure (3) is containing on the image of composite is appearing clearly, the coating of ZnO on to activated carbon with clay. And have size is reaching between (3.5-5) µm, and the particle is taking star and rod shapes, under zoom (5-50) µm, also is having very more space. The difference between two cases is generating small size particles as the figure (3) and that due to fracturing and occurring the dividing in big particle of clay of reason the mixing. And that small particle of clay is mixing with small particle active carbon which previously saw in figure (2). The composite of clay and active carbon is coating by ZnO of reason small quantity that using, which consider lowest density from two materials the clay and active carbon, due to very small weight used of ZnO which solve in Na_2SO_4 of prepare the composite. Also saw in figure (4) irregular feature and rough of composite which, that surface morphology consider ideal of fabricate high area and that agree of researcher M.Selvakumar[13] get same morphology surface nearly.

And that is assured the researcher M Jayalakshmi[18], of obtaining on good electrode in using small amount of transition metal oxides, also from through the previous results of open circuit and potentio stat test which are assuring the obtaining on good electrode. Each particle in the composite will be small electrode, for making large area of active electrode, have high capability.

3.3 The open circuit

The relation between average voltages with ratios ZnO, of all groups clay (50%, 30% and 10%) as the following.

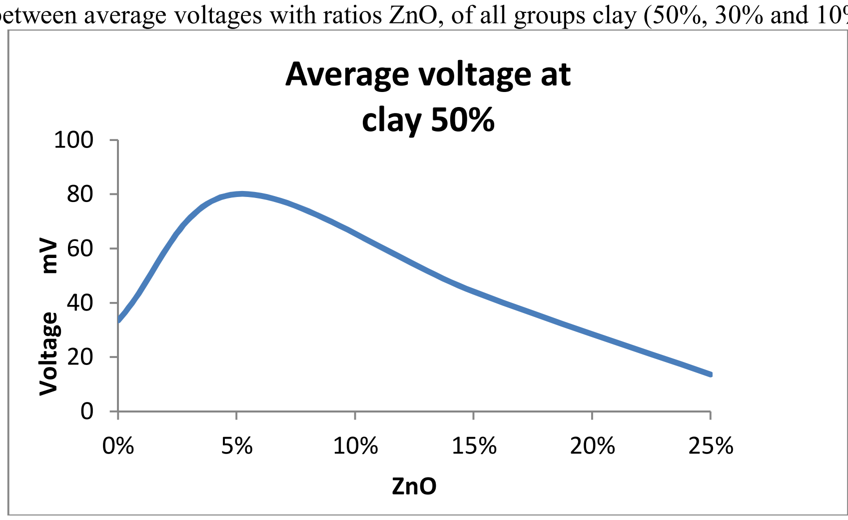

Figure (5) explain the behaving of voltage capacitors with change percentage ZnO and A.C at constant percentage of clay at 50%.

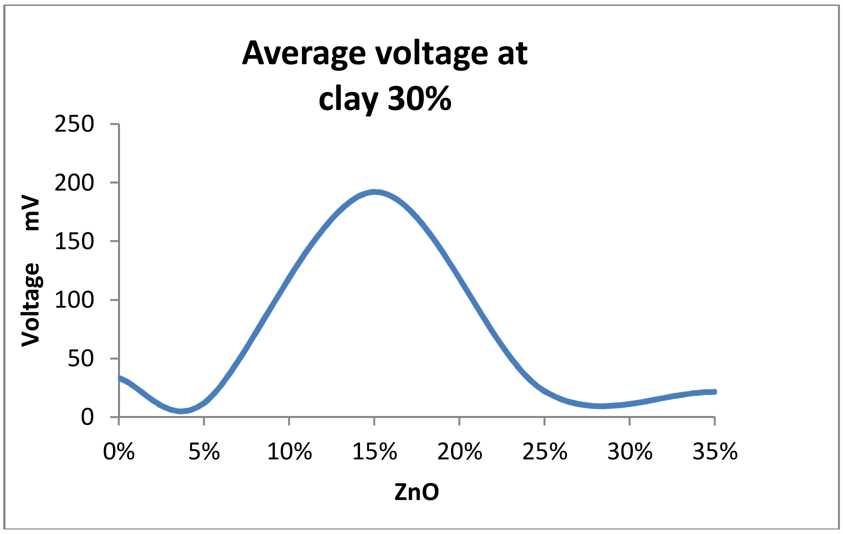

Figure (6) explain the behaving of voltage capacitors with change percentage ZnO and A.C at constant percentage of clay at 30%.

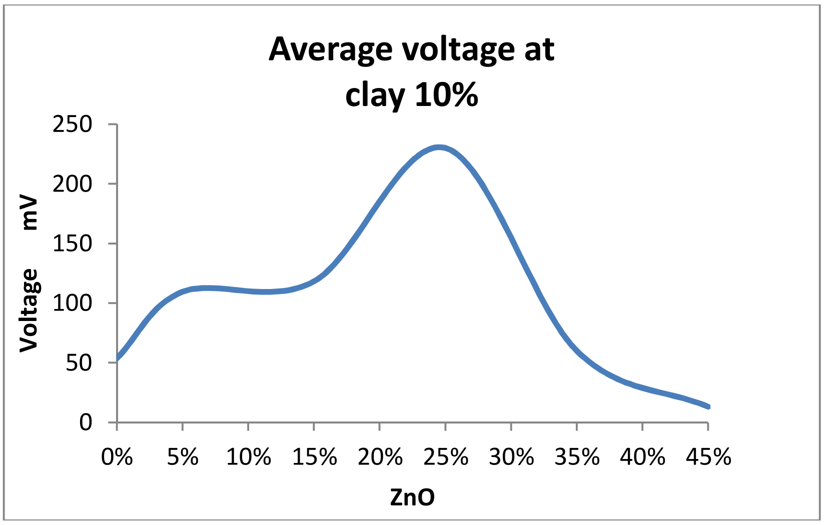

Figure (7) explain the behaving of voltage capacitors with change percentage ZnO and A.C at constant percentage of clay at 10%.

From this charts display the following:

A) The voltage change with add percentage ZnO, and the figures (5, 6 and 7) of average voltage in up exhibit that, from through calculated average voltage of composites. The charts are assuring to obtained change of voltage with change ZnO, at ratios ZnO determinant at ratio ZnO 5% of figure (5), ratio ZnO 15% of figure (6) and ratio ZnO 25% of figure (7), the looked highest voltage is recording, but, decreased in the average voltage with others percentages of ZnO.

B) 1) There shift in highest voltage value with ratio ZnO, at each group of ratio clay,

At group of ratio clay 50%, the high voltage has been at ratio ZnO 5%.
At group of ratio clay 30%, the high voltage has been at ratio ZnO 15%
At group of ratio clay 10%, the high voltage has been at ratio ZnO 25%

These shifts in highest voltage value with ratio ZnO via reason change ratio of all A.C., and clay.

2) Also, there important notice, the highest peak of voltage value of each curve is increasing successional, with increase ratios of ZnO on decrease account ratio of clay.

The increase in average voltage which indicates to at these ratios has been too accompanied of decrease of percentage clay. That led to increase average voltage values with decrease percentage clay of reach to highest average voltage value to 230mV at lowest ratio of clay at 10% while the average voltage at group clay 30% is 192.04mV of decrease the average voltage at group 50% of reaching to 80.06mV. Which mean the clay is playing important role with ZnO and A.C. in increase average voltage value. That real is obtaining potential wall which lead to increase resistance due to increase concentration charge on side the electrode at these percentages, therefore show at potentio stat test of examine the behavior current of capacitor at these ratios became very low, and at before or after these ratios that occurring increase in the average current due to obtaining break down of potential wall as the figure (8, 9 and 10).

As we know, the clay is containing much material from ferroelectric; therefore, the ferroelectric materials are generating electric field invers to electric field supply, also the ZnO matter consider the meter ability of polarization, accordingly, the are generating invers potential due the polar, and then, we get in specific percentage of ZnO, that mean is became high resistance. Due to little ratio from clay is became as doped process of ZnO, which is bringing or available the more electron due to obtain deformation in crystal constructor, that lead to generating clogs current about the doping ZnO inverse the original direction current, due to increase resistance of cause obtaining doped process.

After that, the ZnO is became conduction mater of reason obtaining fill up of vacant orbitals, and that lead to breakdown of potential wall, of lead to increase the current output of capacitor at the ratios which before or after this percentage.

The carbon is semiconductor, because amorphous phase, therefore, we can convert to good conductor, if we immersed with electrolytic solution or contain on good ratio from crystalline phase. In this case consider as electrode.

That Analysis is agreeing of M Jayalakshmi analysis on use the transition metal oxides for pseudocapacitor applications, for purpose the obtaining on high specific capacitance and rate capability and could be obtained, when a small amount of metal oxide is uniformly dispersed on the conductive and porous carbonaceous materials, also with a very high surface area, due to the increased electrochemical utilization of the metal oxide and low concentration polarization of the electrolyte [18].

3.4 Potential stat

In this test, the voltage has been constant is reaching to (2000mV), but consider changeable current. Therefore, we would study the first, relation between the current and time, for known current value to all capacitor, at constant voltage.The charts following express the relation between, current values with time.

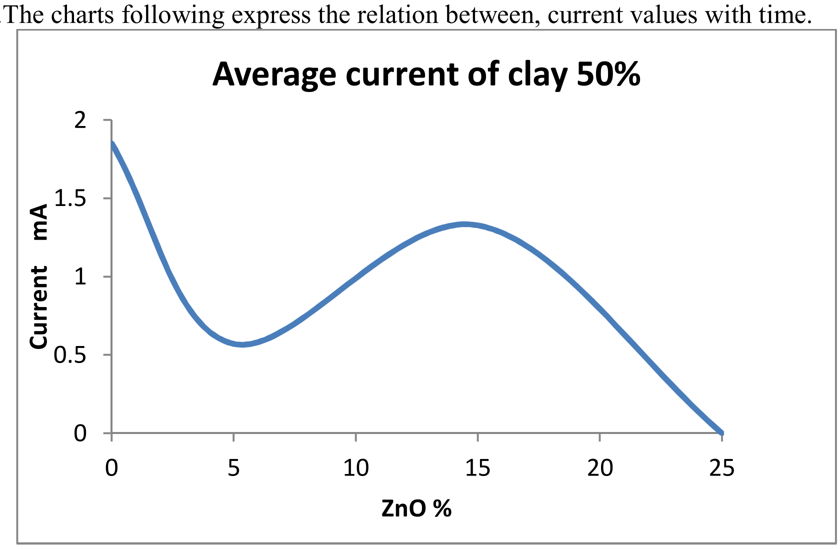

Figure (8) explain the relation between current and ZnO of group clay 50%.

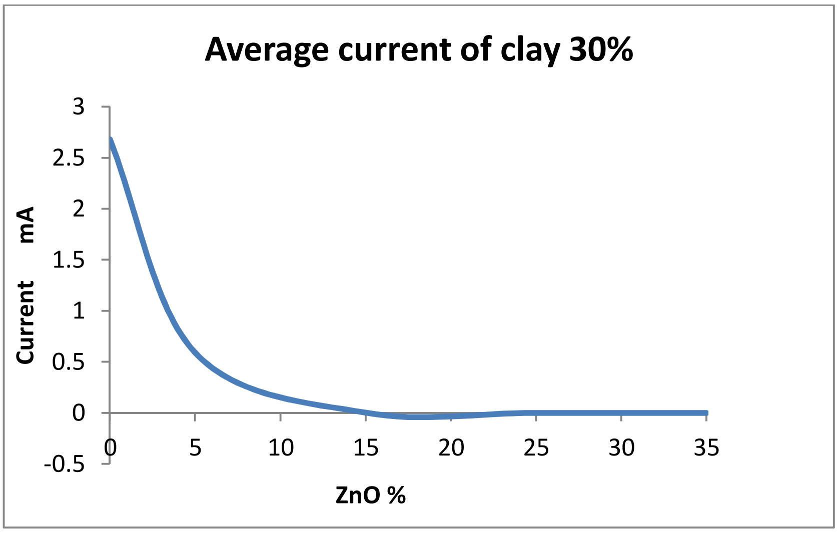

Figure (9) explain the relation between current and ZnO of group clay 30%.

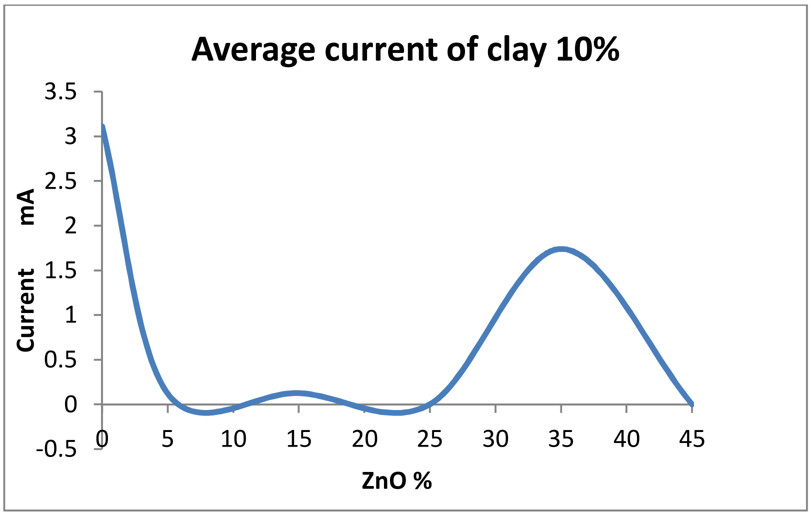

Figure (10) explain the relation between current and ZnO of group clay 10%.

That can extract from charts as the following

The ZnO is considering from semiconductor matter, transition material oxide. Therefore, when availability electron or ion at presence of ion solution; it will be conductor matter. From this reason increase at average current.

While at average voltage charts, is existing when ZnO is semiconductor, the composite has resistance due to generator eddies current around ZnO, clogs current direction, and inverse original current direction lead to increase the resistance which lead to increase the voltage. But, when ZnO became conductor matter which leads to decrease the resistance, and then lightly voltage.

Also, there relation between ZnO and clay, is generator potential differential at was ZnO semiconductor, and this potential differential proportional with amount ferroelectric matters is existing in clay. Because, ferroelectric matters is generating electric field inverse to electric field supply. Therefore, get shift in average voltage at decrease percentage of clay, therefore would need to large ratio of ZnO, until increase voltage, therefore we see there shift in top the curve of charts average voltage.

Now, for selected best capacitor, we found the capacitor of group ratio clay 30% with ZnO 5% and A.C. 65% for following reasons. This capacitor has highest current value and low average voltage. As we know, the voltage inverse proportional with capacitor value.

Charge-discharge circuit

The figures (11 and 12) express the relation between voltage drop and time, capacity with voltage drop.

1) The charge circuit

The circuit series between the supply voltages D.C., resistance 7Ω, the capacitor resought calculate and breaker circuit.

2) The discharge circuit. The circuit series contain on the charged capacitor with resistance 100Ω, and breaker circuit.

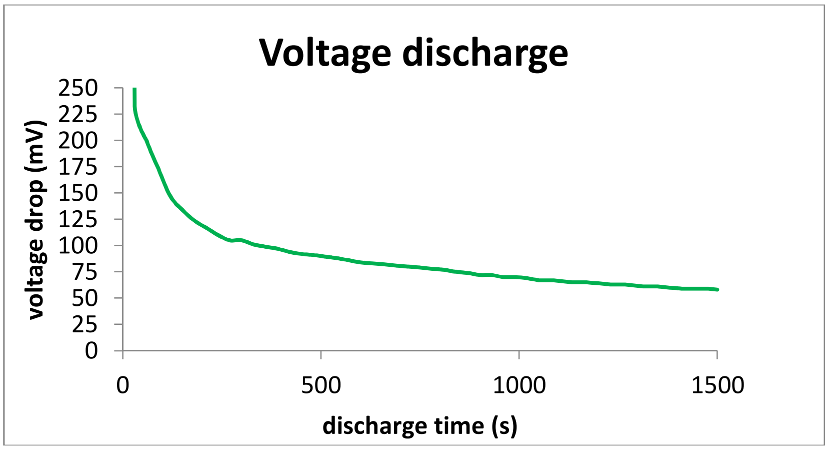

Figure (11) appear the relation between the voltage drop and discharge time.

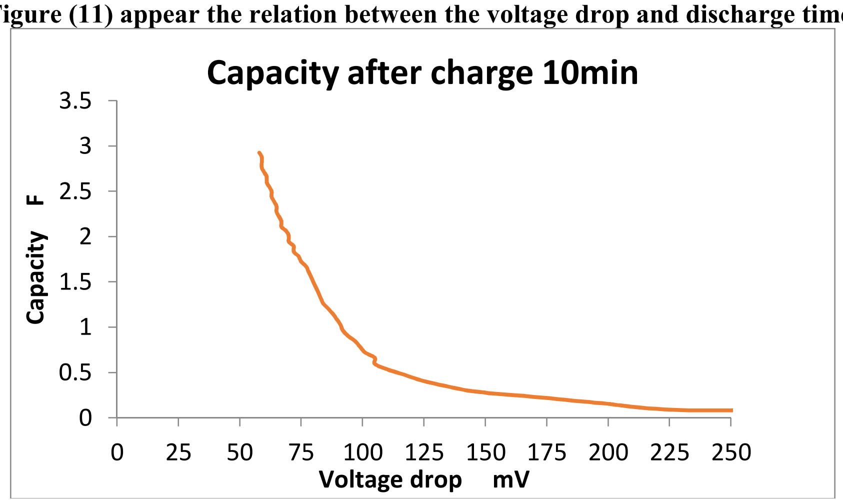

Figure (12) appear the relation between the capacitance and voltage discharge.

The clay material is having high diffusion character, i.e. ability of penetration the electrolytic solution between the particles clay and that is supporting the polarization of ions the clay and electrolytic solution which increase conduction of ZnO of work in high capability.

The capacity is reaching to 3.5F of discharge time 1500s at voltage 50 mV of specific power 24w/Kg of energy 145J.

Therefore, the used the clay in supercapacitor fabricated consider the beginning in obtaining on inexpensive cost and as well as that more friend to environment, also easy the dealing with clay without dangerous.

Conclusion

The clay material play role very important in formation and fixing process of the content the composite as well as having high diffusion character, which increase conduction of composite. Also, had role in doping process which create deformation crystalline constructor, which lead to available the more electron to increase potential wall before breakdown, for obtaining high current.

Reference

[1]Adrian Schneuwly and Roland Gallay," Properties and applications of supercapacitors from the state-of-the-art to future trends", PCIM, montena components SA, 1728 Rossens, Switzerland, (2000).
[2]M. Selvakumar, D. Krishna Bhat, A. Manish Aggarwal, S. PrahladhIyer and G. Sravani," NanoZnO-activated carbon composite electrodes for supercapacitors", Physica B, V.(405), PP.(2286), 2010.
[3]Silvia Roldan, Daniel Barreda, Marcos Granda, Rosa Menendez, Ricardo Santamarıa and Clara Blanco," An approach to classification and capacitance expressions in electrochemical capacitors", Phys. Chem. Chem. Phys, V. 17, PP. (1084-1092), 2015.

[4]B.E.Conway," Electrochemical Supercapacitors Scientific Fundamentals and Technological Application", printed in the unit U.S.A., New York, pp.(7), 1999.
[5]Yu.M. Volfkovich, A.A. Mikhailin, D.A. Bograchev, V.E. Sosenkin and V.S. Bagotsky," Studies of Supercapacitor Carbon Electrodes with High Pseudocapacitance", Recent Trend in Electrochemical Science and Technology, Edited by Ujjal Kumar Sur, InTech, PP.(160), 2012.
[6]Qian Cheng, Jie Tang, Jun Ma, Han Zhang, Norio Shinya and Lu-Chang Qin,"Graphene and nanostructured MnO2 composite electrodes for supercapacitors", CARBON, V.49, PP (2917-2925), 2011.
[7]Charl J. Jafta, FunekaNkosi, Lukas le Roux, Mkhulu K. Mathe, MesfinKebede, KatlegoMakgopa, Yang Song, Dennis Tong, MunetakaOyama, NcholuManyala, Shaowei Chen and Kenneth I. Ozoemena,"Manganese oxide/graphene oxide composites for high-energy aqueous asymmetric electrochemical capacitors", ElectrochimicaActa, V.(110), PP.(228), 2013.
[8]Shudi Min, Chongjun Zhao, Guorong Chen and Xiuzhen Qian," One-Pot Hydrothermal Synthesis of Reduced Graphen Oxide/Ni(OH)2 Films on Nickel for High Performance Supercapacitors", ElectrochimicaActa, V.115, PP(155-164), 2014.
[9]Yanqun Shao, Zhanghua Yi, Fenghua Lu, Fenyong Deng and Beibei Li," Poorly Crystalline Ru0.4Sn0.6O2 Nano Composites Coated on Ti Substrate with High Pseudocapacitance for Electrochemical Supercapacitors", Advances in Chemical Engineering and Science, V.2, PP (118-122), 2012.
[10]Yong Yan, Binycai Wu,Cuihoy Zheng and Daolai Fang," Capacitive Properties of MesoporousMn-Co Oxide Derived from a Mixed Oxalate", Materials Sciences and Applications, V.3, PP (377-383), 2012.
[11]ZhiqiangNiu,WeiyaZhou,JunChen,GuoxingFeng,HongLi,WenjunMa,JinzhuLi,HaiboDong,YanRen,Duan Zhao and SishenXie," Compact-design supercapacitors using free-standing single-walled carbon nanotube films", Energy &Environmental Science, V.4, PP(1440-1446), 2011.
[12]VenkataSubba Reddy Channu, Rudolf Holze, Scott Ambrose Wicker Sr., Edwin H. Wlker Jr., Quinton L. Williams and Rajamohan R. Kalluru," Synthesis and Characterization of (Ru-Sn)O2 Nanoparticles for Supercapacitors", Materials Sciences and Applications, V.2, PP (1175-1179)2011.
[13]M.Selvakumar, D.KrishnaBhat, A.ManishAggrwal, S.PrahladhLyer and G.Sravani," NanoZno-Activated Carbon Composite Electrodes for Supercapacitors", Physica B, V.405,pp.(2286-2289), 2010.
[14]Edward Furimsky,"Carbons and Carbon-Supported Catalysts in Hydroprocessing", IMAF Group, Published by The Royal Society of Chemistry, Canada, pp(6), 2008.
[15]Deborah D. L. Chung," Carbon Fiber Composites", Butterworth-Heinemann, Oxford, PP (3-6), 1994.
[16]C. Barry Carter and M.Grant Norton," Ceramic Materials Science and Engineering", springer, PP.(3-4,15),2007.
[17]M. N. Rahaman," Science of Colloidal Processing", Ceramic Processing and Sintering, Second Edition, Marcel Dekker. Inc., New York, PP.(191-195), 2003.
[18]M Jayalakshmi and K Balasubramanian,"Simple Capacitors to Supercapacitors - An Overview", Int.J.Electrochem.Sci., V.3, PP (1196-1217), 2008.

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