

April 2014

EFFECT OF BALL MILLING ON PEAK CURRENT AND EQUIVALENT SERIES RESISTANCE OF METAL OXIDE BASED ELECTROCHEMICAL DOUBLE LAYER CAPACITOR

ATUL KUMAR SINGH

Electronics and Telecommunication Army Institute of Technology, Pune, India, uncleshi@gmail.com


ANKIT DHIMAN

Electronics and Telecommunication Army Institute of Technology, Pune, India, ankwilco@gmail.com

ANAM KAMAL

Electronics and Telecommunication Army Institute of Technology, Pune, India, anam_shiner@yahoo.com

Follow this and additional works at: <https://www.interscience.in/ijeee>

 Part of the [Power and Energy Commons](#)

Recommended Citation

SINGH, ATUL KUMAR; DHIMAN, ANKIT; and KAMAL, ANAM (2014) "EFFECT OF BALL MILLING ON PEAK CURRENT AND EQUIVALENT SERIES RESISTANCE OF METAL OXIDE BASED ELECTROCHEMICAL DOUBLE LAYER CAPACITOR," *International Journal of Electronics and Electrical Engineering*: Vol. 2 : Iss. 4 , Article 10.

Available at: <https://www.interscience.in/ijeee/vol2/iss4/10>

This Article is brought to you for free and open access by Interscience Research Network. It has been accepted for inclusion in International Journal of Electronics and Electrical Engineering by an authorized editor of Interscience Research Network. For more information, please contact sritampatnaik@gmail.com.

EFFECT OF BALL MILLING ON PEAK CURRENT AND EQUIVALENT SERIES RESISTANCE OF METAL OXIDE BASED ELECTROCHEMICAL DOUBLE LAYER CAPACITOR

ATUL KUMAR SINGH¹, ANKIT DHIMAN² & ANAM KAMAL³

^{1,2&3}Electronics and Telecommunication Army Institute of Technology, Pune, India
Email:email-uncleashi@gmail.com, ankwilco@gmail.com, anam_shiner@yahoo.com

Abstract: Recently, advances have been made in improving both energy and power density of energy storing devices. Electrochemical Double Layer capacitor (EDLC) is one of the technologies that we are looking forward to fulfill the low power- low energy applications such as memory back up. EDLC is mainly a pulse power device even though it is seen as a replacement to battery in low power applications. At present EDLC technology is under development stage. Power density, energy density, specific capacitance, internal resistances are required to be improved. Electrochemistry plays a crucial role in the storage as well as in the generation of energy. Hence, the particles size and distribution are need to be optimized. Ball milling is the tool for optimizing the size of the components used to make the EDLCs. Ball milling has significant effect on the various parameters of the EDLC. It was found that as we increase the time of ball milling the Equivalent Series Resistance (ESR) decreases and the peak current increases. But the changes are significant for higher time of ball milling.

Keywords - EDLC, Peak current, optimization, Capacitance, ESR

I. INTRODUCTION

Objective of research work was to study the effect of ball milling on pulse current capability and ESR of the EDLC.

The scope of the work includes development of EDLC through ball milling. Time for crushing was changed to study its effects on pulse current capability and ESR.

At present EDLC technology is under development stage. Power density, energy density, specific capacitance, internal resistances are required to be improved. Use of low cost material is also essential for its commercialization. Manufacturing aspects are unattended as very few companies are manufacturing this device around the globe. Constructional issues, modeling and its power electronic based interface are at research stage. Many areas of this device have not come in academic research. Industry research is also lagging in this regard. Researchers generally concentrate on capacitance and internal resistance of the EDLC. However main function of the EDLC is to give pulse current. Issues related to the effect of the electrode material loading on current collector on pulse current capability of the EDLC is addressed in this work.

As double layer capacitor is interdisciplinary in nature, researchers from various branches have worked in this area. Some scientists like Andrew Burke, B E Convey, Nelms and Spykens have done significant contribution in this area. Variety of aspect of this device has been considered so far (J.M Miller, 2011) and (R.L.Spyker and R.M. Nelms, 2011). Various parameters of the double layer capacitor like specific surface area of activated carbon sample, type of electrolyte (which include organic and aqueous electrolyte, molarity etc.), electrode material, porosity

etc. has been taken as input (Y Zhang et al., 2009). Various parameters like capacitance, internal resistance, pulse current etc. have been taken as an output in various models. Research work is broadly carried out by groups such as: Electrochemistry Groups- worked to increase power density, energy density, specific capacitance, volumetric capacitance, voltage etc; Metallurgy Groups- worked to increase surface area, porosity, pore size distribution measurement, new materials development, study of activated carbons, use of nano-materials and composite materials. Electrical Groups- worked for application of double layer capacitor with direct/semi-active, fully active power electronic interfacing, modeling for the double layer capacitor applications etc. (work not suitable for device development) (P B Karandikar et al.,2012). Mechanical Groups- very few have worked in this area. Statistical modeling is used for engineering problems (T. Brousse et al., 2007). Concept of material composition modeling, constructional issues and selection of other parameters has been rarely addressed by any one so far (P B Karandikar et al., 2011).

II. EDLC MAKING PROCESS

Electrode making is a complicated process. It requires proper selection of material and then, the deposition of the electrode material on current collector is an issue. Binders such as PTFE or Nafion, which can sustain electrolytic environment, are generally used to hold the electrode material on current collector. In stacked type of double layer capacitor structure, it is found that life of the double layer capacitor device gets affected due to poor quality of electrode material binding on current collector. Innovative binder free electrode construction is proposed which consist of

current collector and electrode material, sandwiched between two separator pieces. One of our patent in this regards have been published on Indian patent office website. Trials on this type of double layer capacitor were carried out. Fig 1 shows the detail of this construction. Advantages of this new type of structure is: 1) low cost and low internal resistance 2) suitable for rectangular and rolled structures 3) easy to prepare and the main drawback is that, the cavity effect reduces life and performance of the device.

Specific capacitance achieved by using this structure is $0.22\text{F}/\text{cm}^2$. Energy density of $0.7\text{wh}/\text{kg}$ and power density of $1620\text{w}/\text{kg}$ is achieved with these constructions. These values have been achieved by systematic selection of electrode/ electrolyte material and by adopting modeling approach. It can be further improved by reducing cavity effect. Modeling approaches used are presented in the following section in brief. Manganese oxide and activated carbon is used in the weight ratio of 1:1 as an electrode material. Dilute sulphuric acid is used as an electrolyte.

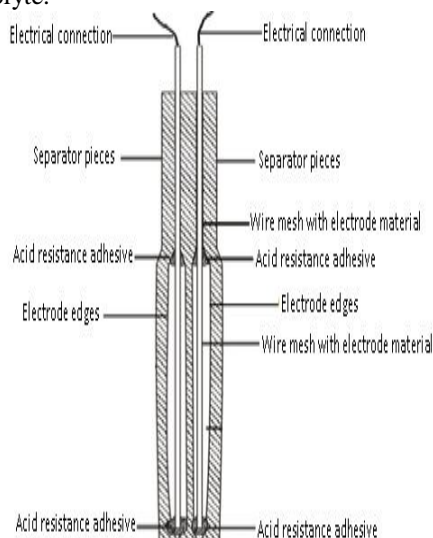


Fig.1. Sectional front view of assembly of EDLC construction

III. BALL MILLING

A ball mill, a type of grinder, is a cylindrical device used in grinding material like ores, chemical, ceramic raw material and paint. Ball mills rotate around a horizontal axis, partially filled with the material to be ground or grinding the medium. Different materials are used as media, including ceramic balls, flint pebbles and stainless steel balls. An internal cascading fed at one end and discharged at the other end. Large to medium-sized balls mills are mechanically rotated on their axis, but small ones normally consist of a cylindrical capped container that sits on two drive shafts (pulley sand belts are used to transmit rotator motion). High-quality ball mills are potentially expensive and can grid mixture particles to as small as 5 nm, enormously increasing surface area and reaction rates. The grinding works on principle of critical speed. From the SEM done on

the previous electrodes samples it was found that the clusters of activated carbon and MnO_2 formed are not as per the requirement. This was due to the significant difference between the size of activated carbon and MnO_2 . Hence, ball mill is used for crushing and mixing of the activated carbon and MnO_2 . From this the desired particle size are obtained. For the present experiment the ball mill used is 100 rpm. Activated carbon and MnO_2 are fed into it in 1:1 ratio. The samples are taken out after every hour up to 5 hour.

Double layer capacitor is a multi-input multi-output system which can have output factors such as specific capacitance, power density, energy density, operating voltage, equivalent series resistance, self-discharge, life, shape, size and reliability etc. It can have input factors such as input voltage, current, electrode material related parameters, electrolyte related parameters and separate parameters etc. Important evaluation parameters from user point of view were selected for modeling, which includes capacitance, internal resistance and pulse current.

TABLE 1- Probable input factors affecting output parameters

1.	Electrode making process	1) Separator material used 2) Mixing method 3) Crushing Period 4) Mixing Period 5) Adhesive used 6) Pressure on electrode 7) Crushing method
2.	Electrode	1) Impurities in electrode material 2) Type of metal oxide 3) Cavity effect 4) Loading of electrode material 5) Activated carbon with different SSA
3.	Electrolyte	1) Strength of acid 2) Impurities in electrolyte
4.	Collector Current	1) Number of holes per unit area of wire mesh 2) Thickness of wire mesh

IV. INPUT FACTORS

For aqueous metal oxide based double layer capacitor with stacked type of electrode structure, following parameters, as listed in Table 1 were found to be the probable factors affecting the value of capacitance, pulse current and internal current. These parameters were obtained from literature available on double layer capacitor.

The specific area of activated carbon used is $1500\text{m}^2/\text{gram}$. Loading of electrode material on current collector is $30\text{mg}/\text{cm}^2$ of electrode area. And 6 molar sulfuric acid is used as electrolyte. The electrode used is of dimension $4.5\text{cm} \times 1\text{cm}$.

V. EFFECT OF BALL MILLING ON THE SIGNIFICANT FACTORS

In figure 2, the discharging rate of 1 hour, 2 hour and 3 hour sample is almost constant throughout the entire time of testing. But there is significant change from 4 hour sample to 5 hour sample. The discharging rate is very high for 5 hour sample as compared to other sample. With increase in time for crushing the particle size of activated carbon particles and MnO_2 becomes comparable. Due to which the MnO_2 particles enters in the cracks of activated carbon particles which result in the increase in conductivity of the capacitor.

In figure 3, the as the crushing time increases the peak current capability of capacitor also increases. There is significant increase from 4 hour sample to 5 hour sample. As the size of the particles become comparable the distribution of the MnO_2 particles become uniform around the activated carbon clusters. This also increases the uneven surface density on the electrode which increases the gaps for charge accumulation which results in increase in the conductivity of the capacitor. Hence the capacitor pulse current capability increases with increase in time of crushing.

In figure 4, with increase in time of crushing the ESR of the capacitor goes on decreasing. This is associated with the increase in pulse current capability for higher time of crushing.

5.0 CONCLUSIONS

It was observed that with increase in crushing time the peak current capability of the capacitor goes on increasing and the ESR goes on decreasing. There is significant change for 5 hour sample. This can be explained as with the increase in the time for crushing the particle size of the activated carbon and MnO_2 become comparable. And MnO_2 is expected to enter in the cracks/pores of activated carbon particles. This is happening with more balls milling which increase the conductivity of the capacitor. This also results in the decrease in the ESR value of the capacitor. This can be associated with the faster discharging rate for high time of crushing of the particles. Hence, higher peak current and low ESR is obtained for 5 hour sample.

VI. ACKNOWLEDGMENT

We acknowledge the support from management of Army institute of Technology, Pune for providing research facilities. We also thank Dr (Mrs.) M.Y. Khaladkar (HOD Applied Science) and Dr D. B. Talange of College of Engineering, Pune for providing ball milling facility. We also acknowledge the contribution of Kaushal Sharma and Priyank Saklani of second year Electronics and

Telecommunication Engineering, Army Institute of Technology, Pune.

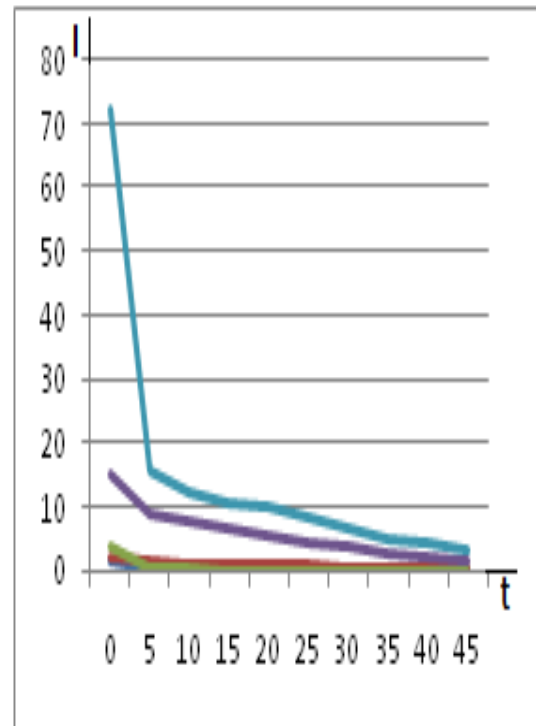


Fig 2-Discharging Curve

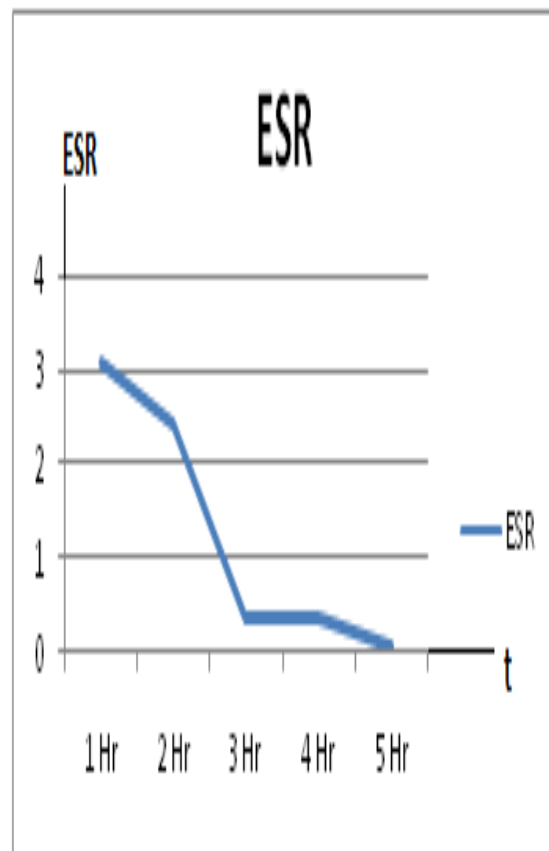


Fig 3- Peak Current Curve

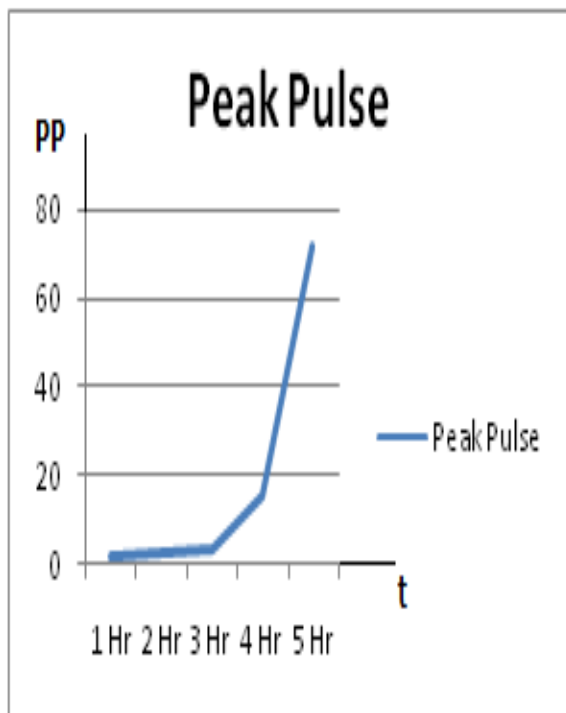


Fig 4- Equivalent Series Resistance curve

REFERENCES

- [1] Electrochemical Double Layer Capacitor- Available on http://www.nesscap.com/product/edlc_small.jsp, Site of NESSCAP ultracapacitor.
- [2] WIMA EDLCs- Available on http://www.wima.com/EN/products_pcm7_5_metall.htm, Site of WIMA capacitors.
- [3] R.L.Spyker, R.M. Nelms, "Analysis of Double layer capacitors supplying constant power loads", IEEE transactions on Aerospace and electronic systems, Vol-36, No-4, October 2000, Pg 1439-1443.
- [4] T. Brousse, P. Taberna, O. Crosnier, R. Dugas, P. Guillemet, Y. Scudeller, Y. Zhou, "Long-term cycling behavior of asymmetrical activated carbon/ MnO₂ aqueous electrochemical EDLC," Journal of Power Sources (2007)173, pp 633-641.
- [5] Y Zhang, H Feng, X Wu, L Wang, A Zhang, T Xia, H Dong, X Li, L Zhang, "Progress of electrochemical capacitor electrode materials: A Review", International Journal of Hydrogen Energy. 2009, pp 4889-4899.
- [6] P B Karandikar, Akshay Dekate, Atul Kumar Singh etc. Al., Indian patents , 2858/MUM/2010, Filed on 2010-10-14, Publication date 2011-01-07, 843/MUM/2011, Filed on 2011-03-23,
- [7] Chemistry World: New carbon material boosts EDLCs. Rsc.org. 13 May 2011. Retrieved on 13 September 2011.
- [8] P B Karandikar, D B Talange, Uday Mhaskar, Ramesh Bansal, "Development, characterization and modeling of aqueous metal oxide based EDLC", Energy, Elsevier, vol 40, April 2012, pg 131-138.
- [9] P B Karandikar, D B Talange, " Future trends in Electrochemical Capacitors", vol 52 No 7, July 2012, pg 100-103.
- [10] <http://www.waterstones.com/waterstonesweb/products/j-m-miller/ultracapacitor+applications/7092877/>: Book by Dr. J.M Miller on Ultracapacitor Application(Published on 7/7/2011).

