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## Electrochemical studies of EDLC Cells fabricated using drum stick (DS) activated charcoal

Mukta Tripathi<sup>1</sup> and Anuj Kumar<sup>2\*</sup>

<sup>1</sup>Department of Physics, Jaypee University of Engineering and Technology, Guna-473226, Madhya Pradesh, India

<sup>2\*</sup>Department of Physics, C.C.S. University Meerut-200005, Uttar Pradesh, India

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### Abstract

In this article, biomass drum stick (DS) activated carbon has been synthesized and used as an electrode material for fabrication of electrical double layer capacitor (EDLC). Polymer gel electrolyte [PVdF-HFP (20 wt %) + EC-PC (1:1v/v)-TEABF<sub>4</sub> (1.0M)} (80 wt %)], optimized for highest conductivity, is used as an electrolyte for this EDLC cell. The performance of EDLC cell with drum stick (DS) activated carbon is tested using various techniques such as impedance spectroscopy, cyclic voltammetry and charge discharge techniques. The performance of drum stick (DS) activated carbon based EDLC cell is compared with EDLC cell fabricated using market purchased activated charcoal. DS activated carbon electrode based EDLC cell shows better results compared to the market purchased activated charcoal electrode based EDLC cell. The specific capacitance of DS electrode based EDLC cell is found to be  $\sim 178.7 \text{ mFcm}^{-2}$  and  $\sim 84.7 \text{ Fg}^{-1}$  in a single electrode system.

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*Keywords:* Polymer gel electrolyte, drum stick activated charcoal, Electrical double layer capacitor.

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\*Email address: [anujkumar.jiet@gmail.com](mailto:anujkumar.jiet@gmail.com)

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## 1 Introduction

The energy storage devices usage has increased excessively in daily life; therefore the research in the area of electrochemical devices has got wide attention in recent times. Improvement of the specific properties such as; specific energy, specific power, discharge time, charge time, charge-discharge efficiency, cycling stability, maximum voltage determinant, charge storage determinant, in the electrochemical devices is the biggest challenge for the research community. Different electrochemical devices have been developed such as; batteries, Supercapacitors, fuel cells etc., all showing their own specific properties. These electrochemical devices have found application in many portable electronics such as cellular phones, laptops, computers, and digital cameras etc., bio-medical devices to hybrid electric vehicles. Supercapacitors or electrochemical double layer capacitors (EDLCs) is one of the most applicable device which has made a global attention in research. Basically two types of EDLCs are reported by the researchers, first is pseudo capacitor or redox-capacitor and the second is electrochemical double layer capacitor or EDLCs. Electrochemical double layer capacitors (EDLCs) find wide applications due to higher power density, fast rate of charge/discharge, and long cyclic stability. EDLCs consist three parts namely electrode, separator and electrolyte [1,2]. Polymer based gel electrolyte and the carbon based electrode play major role in the application of EDLCs.

Usually the different composition of salt, polymer and plasticizer has been explored for electrolyte systems to improve the quality of electrochemical devices [3,4]. In recent years, polymer gel electrolytes have been investigated and attracted global attention due to their good electrochemical performance [4-9]. The formation of materials is based on the liquid electrolyte, for example solution of  $\text{LiClO}_4$  in EC,  $\text{MgClO}_4$  in EC - PC etc., prevents mobilization in the host polymer such as PVDF-HFP, PMMA, and PVA etc. [10-13]. Gel electrolytes are preferred as they reduce the leakage caused by liquid electrolyte systems and also give satisfactory results compared to the liquid electrolytes. They provide better electrode-electrolyte interfacial contact in electrochemical cell. In polymer gel electrolyte systems, electrical conductivity enhances and found  $\sim 10^{-3}$  S/cm due to the immobilization of salt ions in polymer matrix. Further the addition of plasticizers such as ethylene carbonate and propylene carbonate in polymer electrolyte increases mechanical stability as well as conductivity [14].

Biomass based activated carbon is very popular as electrode material in these devices and plays a major role in the high capacitance of EDLCs. Virtually all commercial Supercapacitors manufactured by Panasonic, Nesscap, Maxwell, Nippon Chemi-Con, Axion Power, and others use powdered activated carbon made from coconut shells [15]. Biomass based activated carbon has attracted wide attention in current research due to their low cost and easy availability in nature [16-19].

In this work, Biomass drumstick activated carbon is synthesized for electrode material and PVDF-HFP+EC-PC-TEABF<sub>4</sub> electrolyte system is used for the separator. Fabrication of EDLCs cells has been done using biomass drumstick activated carbon electrodes and market purchased activated charcoal electrode material and optimized polymer gel electrolyte. The performance of electrical double layer capacitor cell A: DS||PVDF-HFP+EC-PC-TEABF<sub>4</sub>||DS and cell B: AC||PVDF-HFP+EC-PC-TEABF<sub>4</sub>||AC have been analyzed and compared using various techniques such as impedance spectroscopy, cyclic Voltammetry and charge discharge techniques.

## 2 Materials and methods

### 2.1 Preparation of Electrolyte material:

The preparation of the [PVDF-HFP (20 wt %) + EC-PC-TEABF<sub>4</sub> (80wt %)] was reported by the Mukta *et al.*, and found the good ionic conductivity value equal to  $\sim 4.0 \times 10^{-3} \text{ Scm}^{-1}$  and mechanical stability which is required for use in the EDLCs [20].

### 2.2 Synthesis of biomass based activated carbon electrode material

For the synthesis of drumsticks (DS) based activated charcoal following mechanism is adopted [21]:

(1) Firstly biomass DS is washed properly to remove the dust particles and clean DS has been kept in the contact of sunlight for 7 days to dry completely. After drying material is burnt at 500 °C for 6 hours so that the charcoal is prepared. Crushed fine powder of charcoal was soaked in 5 molar concentration of  $\text{CaCl}_2$  in double

distilled (DD) water for 24 hours. After proper washing with (DD) water for removing the  $\text{CaCl}_2$  content, the sample is kept in the oven at  $110^\circ\text{C}$  for 12 hours to remove the water content. The sample is now ready for the next activation process.

(2) DS charcoal with KOH in (1:1) ratio is stirred at  $60^\circ\text{C}$  for 2 hours and then kept in the oven at  $110^\circ\text{C}$  and left for overnight.

(3) Now, the sample is placed in Tubular furnace at  $700^\circ\text{C}$  for 2 hours at nitrogen flow at the rate of 150 ml/min. The sample is now allowed to cool and taken away when the temperature is closed to room temperature. The sample is washed with 5 molar HCl and then washed with water several times till PH value become 7. Finally, the sample is kept in oven at  $110^\circ\text{C}$  to remove water content. Now activated carbon is ready to synthesize the electrodes.

### 2.3 Electrode preparation for EDLCs

For preparation of electrodes, we used Acetone as solvent, graphite sheet as a current collector, PVDF-HFP as binder and activated charcoal powder as electrode material. Taking (10 wt %) PVDF (HFP) and (90 wt. %) of activated charcoal and acetone. Homogeneous solution is prepared by dissolving PVdF (HFP) in acetone at  $60^\circ\text{C}$  and stirring for 2 hours. Addition of activated charcoal with continuous stirring prepares uniform slurry. This slurry is coated on graphite sheet and kept in the oven at  $70^\circ\text{C}$ . The electrode is ready for fabrication of cell. EDLC cell is fabricated by putting the PGE film between two AC charcoal electrodes.

## 3 Instrumentation

For electrical properties measurements, LCR Hi-TESTER (3522–50, Hioki, Japan) and CHI 608C, CH Instrument, USA was used.

## 4 Results and discussions

### 4.1 Electrochemical double layer capacitor performance analysis

The fabrication of EDLC cell has been done by sandwiching the optimized polymer gel electrolyte between the biomass DS activated charcoal and market purchased AC activated charcoal [20] based electrodes respectively. These EDLC cells, now onwards, will be referred as Cell A and Cell B respectively.

Cell A: DS || [PVDF-HFP (20 wt %) + EC-PC-TEABF<sub>4</sub> (80 wt %) || DS

Cell B: AC || [PVDF-HFP (20 wt %) + EC-PC-TEABF<sub>4</sub> (80 wt %) || AC

The performance of above EDLCs cells are analyzed by various techniques such as ac impedance spectroscopy, cyclic voltammetry and charge discharge technique and discussed.

#### 4.1.1 Impedance analysis

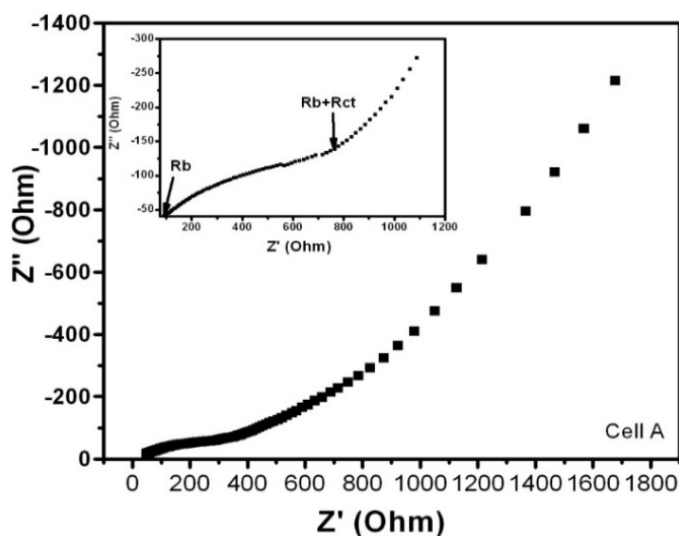
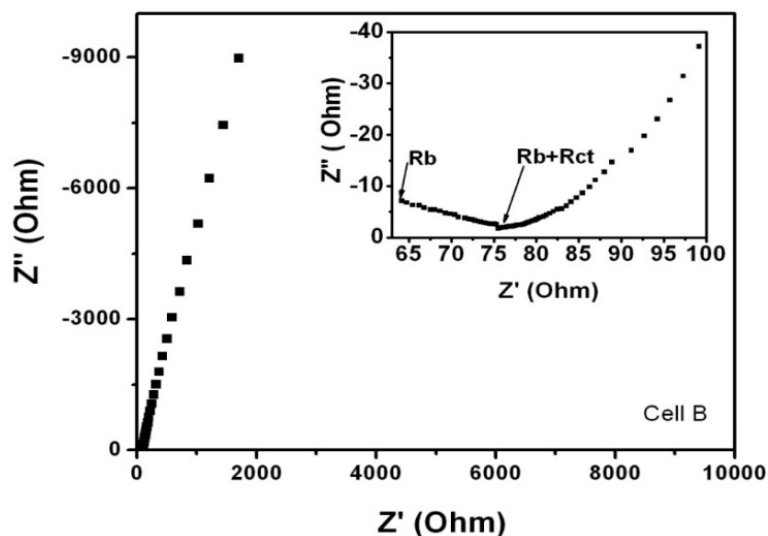
Impedance spectroscopy is one of the most important techniques which are used to evaluate the electrical parameters of Supercapacitors such as lower frequency capacitance, the bulky nature of the electrolyte, and charge transfer and ions aggregation at electrode electrolyte interfaces [22]. Overall specific capacitance of Supercapacitor was calculated by using the formula:

$$C = -1/\omega Z'' \quad (1)$$

Where,  $\omega$  is the angular frequency,  $Z''$  is the imaginary part of complex impedance. Table 1 shows calculated electrical parameters and Fig.1 and Fig.2 indicate the impedance plot of cell A and cell B. Two regions of the plot are visible in figures; one is higher frequency (semicircle) and the other is a lower frequency (straight line) region. From semicircle region, bulk resistance ( $R_b$ ) and charge transfer resistance ( $R_{ct}$ ) are obtained. Steep rise in lower frequency region confirms the capacitive nature of fabricated cells [23].

**Table 1. Electrical parameters of EDLC cell from impedance analysis.**

Cell	$R_b (\Omega \text{ cm}^2)$	$R_{ct} (\Omega \text{ cm}^2)$	10 mHz			1mHz		
			$R (\Omega \text{ cm}^2)$	$C (\text{mF cm}^{-2})^a$	$(\text{F g}^{-1})^b$	$R (\Omega \text{ cm}^2)$	$C (\text{mF cm}^{-2})^a$	$(\text{F g}^{-1})^b$
A	12.7	55.5	187.3	85.9	40.7	419.5	173.0	82.06
B	6.04	2.83	70.15	42.49	28.14	526.7	49.7	32.9

<sup>a</sup>Overall capacitance of the cell<sup>b</sup>Single electrodes specific capacitance of the cellFig.1. Typical impedance plot of Cell A: DS | [(1:4) PVdF-HFP +EC-PC (1:1v/v) +TEABF<sub>4</sub> (1.0 M) +] | DSFig. 2. Typical impedance plot of Cell B: AC | [(1:4) PVdF-HFP +EC-PC (1:1v/v) +TEABF<sub>4</sub> (1.0 M) +] | AC[20]

### 4.1.2 Cyclic Voltammetry studies

The cyclic Voltammetry responses of Cell A and Cell B obtained from CV analysis at different scan rates are shown in Fig. 3 and Fig 4 respectively. Rectangular shape of cyclic voltammograms at different scan rates for both cells indicates the involvement of the non faradic process only; this shows the formation of homogeneous and ideal polarized double layer at interfaces [23, 24]. The horizontal plateau region shows the ion diffusion at a constant scan rate with less effect of ohmic resistance.

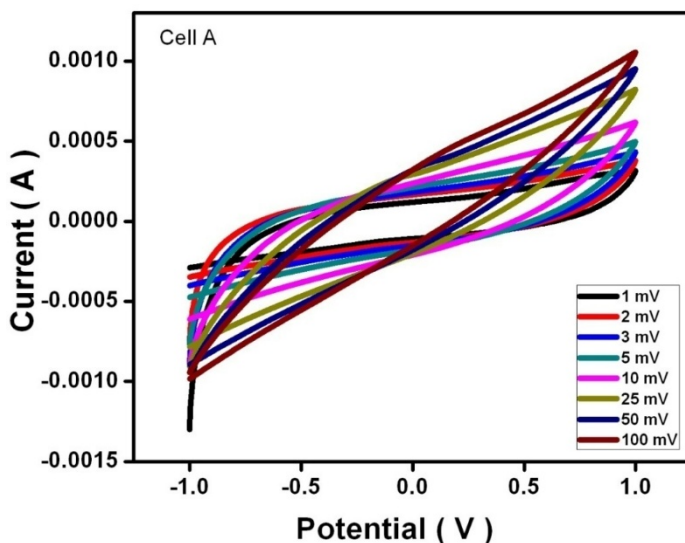


Fig. 3. Cyclic voltammogram of Cell A: DS | [(1:4) PVdF-HFP + EC-PC (1:1v/v) + TEABF<sub>4</sub> (1.0 M) + ] | DS at different scan rates

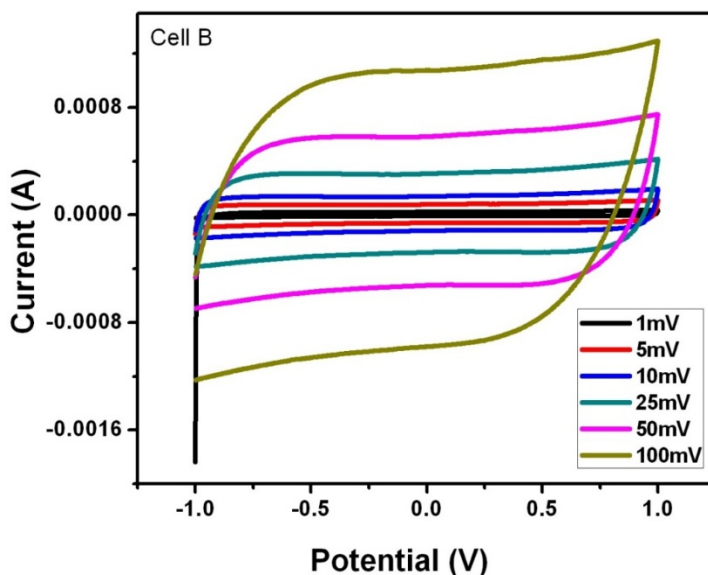


Fig. 4. Cyclic voltammogram of Cell B: AC | [(1:4) PVdF-HFP + EC-PC (1:1v/v) + TEABF<sub>4</sub> (1.0 M) + ] | AC at different scan rates [20]

The internal resistance and carbon porosity produces a current dependence of potential difference to the box like shape in CV [25, 26]. This is a basic characteristic of a good super capacitor cell and is due to fast ion switching at the electrode electrolyte interfaces. The specific capacitance is evaluated by following equation:

$$C = i/s \quad (2)$$

Where,  $i$  is the current and  $s$  is the scan rate.

The capacitance value found from CV, shows good agreement with the a.c. Impedance and charge, discharge techniques. The capacitance value of Cell A, at 1mV scan rate, calculated by Eq. 2, have been found equal to 178.7  $\text{mFcm}^{-1}$  which is equivalent to the single electrode specific capacitance of  $84.7 \text{ Fg}^{-1}$  for DS activated charcoal

powder based EDLCs. Cell B fabricated from market purchased untreated activated charcoal powder based electrodes, shows the capacitance value of  $60 \text{ mFcm}^{-1}$ , which is equivalent to single electrode specific capacitance  $39 \text{ Fg}^{-1}$ [22]. In case of DS activated charcoal powder based EDLC cell, the capacitance value is very high which proves synthesized activated charcoal to be a better quality electrode material.

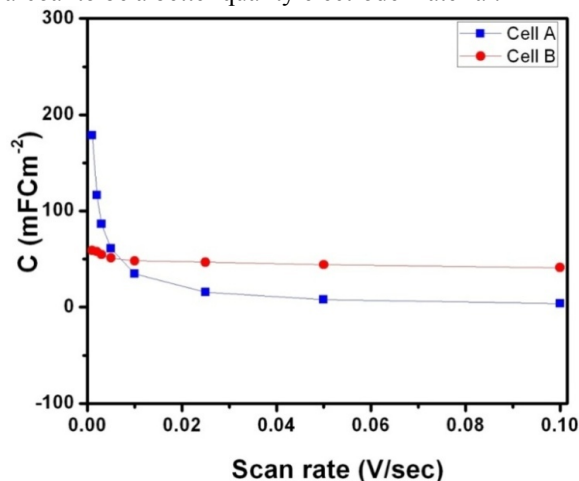


Fig.5. Variation of the capacitance of cell A and cell B as a function of scan rates.

Fig.5 shows the variation of capacitance as a function of scan rate and almost constant capacitance is obtained at higher scan rates except for few initial scan rates. Hence, these cells are also suitable for supercapacitor application at higher scan rates.

#### 4.1.3 Charge discharge

The charge, discharge profile for cells A and B is shown in Fig.6 and Fig.7. In charge, discharge characteristics, an ideal linear triangular shape profile has been observed which confirms the capacitive nature of cells and energy storage capacity.

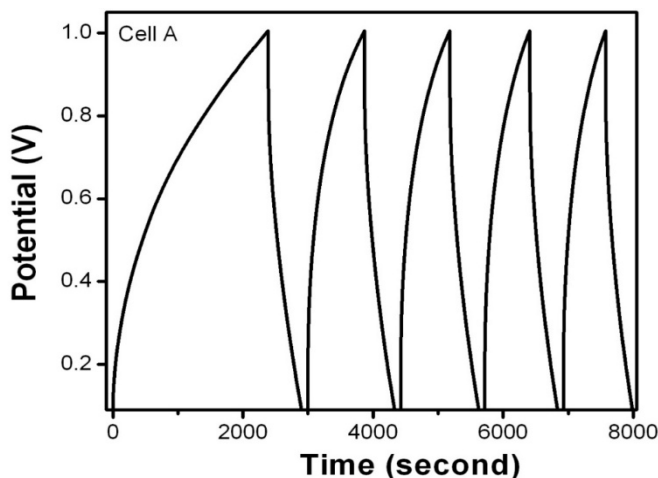


Fig.6. Charge discharge curve of Cell A: DS | [(1:4) PVdF-HFP + EC-PC (1:1v/v) + TEABF<sub>4</sub> (1.0 M) +] | DS at a current density of  $1.0 \text{ mA cm}^{-1}$

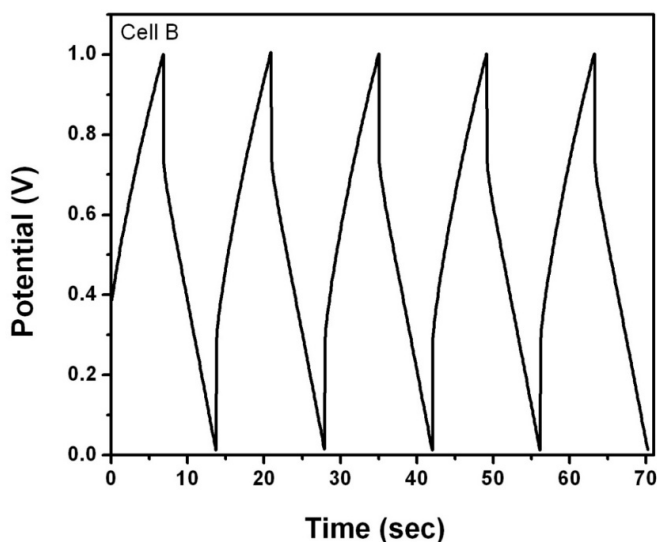


Fig.7. Charge discharge curve of cellB: AC| [(1:4) PVdF-HFP +EC-PC (1:1v/v) +TEABF<sub>4</sub> (1.0 M) +] |AC at a current density of 1.0 mA cm<sup>-1</sup>[20].

An initial voltage drop ascribed to internal resistance is observed during discharging of the cell [27]. The capacitance value from discharge curve is measured by mathematical relation:

$$C_d = i \Delta t / \Delta V \quad (3)$$

Where  $i$  is the constant current,  $\Delta t$  is the time interval and  $\Delta V$  change of voltage

Table 2. Typical charge-discharge characteristics of EDLC cell at current density of 1 mAcm<sup>-1</sup>

Discharge capacitance, C <sub>d</sub>							
Cell	Current Density	R <sub>i</sub> (Ω cm <sup>2</sup> )	(mF cm <sup>-2</sup> ) <sup>a</sup>	(F g <sup>-1</sup> ) <sup>b</sup>	Working Voltage	Energy Density (Wh kg <sup>-1</sup> )	Power Density (kWhkg <sup>-1</sup> )
A	1 mA	357.4	107.33	50.88	1	9.7	4.3
B	1 mA	16.9	38.7	22.4	1	3.1	1.6

<sup>a</sup>Overall capacitance of the cell

<sup>b</sup> Single electrodes specific capacitance of the cell

The capacitance values of cell A and cell B at constant current 1 mA are shown in table 2. Energy density (ED) and power density (PD) are also calculated from the capacitance using following relation.

$$\text{Energy density} = \frac{1}{2} CV^2 \quad (4)$$

$$\text{Power density} = \frac{1}{2} CV^2 / \Delta t \quad (5)$$

## 5 Conclusion

The EDLC cell was fabricated using Drum stick biomass based activated charcoal electrodes and PGE [PVDF-HFP (20 wt %) + EC-PC-TEABF<sub>4</sub> (80wt %)] as an electrolyte. The electrochemical performance of this device was analyzed using impedance spectroscopy, cyclic Voltammetry and charge discharge techniques. The performance of drum stick (DS) activated carbon based EDLC cell is compared with EDLC cell fabricated using market purchased activated charcoal.

Specific capacitance of the DS activated charcoal powder based EDLCs have been found equal to  $178.7 \text{ mFcm}^{-1}$  which is equivalent to the single electrode specific capacitance of  $84.7 \text{ Fg}^{-1}$  while EDLC Cell fabricated from market purchased untreated activated charcoal powder based electrodes, shows the capacitance value of  $60 \text{ mFcm}^{-1}$ , which is equivalent to single electrode specific capacitance  $39 \text{ Fg}^{-1}$ . These results confirm better performance of EDLC cell having DS activated charcoal electrodes then market purchased activated charcoal electrodes when same electrolyte is used.

### Acknowledgment

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### References

- [1]. C. Arbizzani, M. Mastragostino, F. Soavi J. Power Sources **100** (2001)164.
- [2]. JR Miller, P Simon Science **321** (2008)651.
- [3]. F.B. Dias, L. Plomp and J.B.J.Veldhuis J Power Sources**88**(2000)169
- [4]. W.A.V. Schalkwijk Scrosati B (ed) Advances in Lithium-Ion Batteries( 2002) (New York :Kluwer/Plenum Publisher)
- [5]. J.Y. Song, Y.Y. Wang and C.C. Wan J Power Sources**77** (1999)183.
- [6]. R.C. Agrawal and G.P. Pandey J Phys D Appl Phys **41** (2008)223001.
- [7]. F. Ciuffa, F. Croce, D. A. Epifanio, S. Panero and B. Scrosati JPower Sources**127** (2004)53.
- [8]. A.M. Stephan Euro Polym J **42** (2006)21.
- [9]. F.B. Dias, L. Plomp and J.B.J. Veldhuis J Power Sources **88** (2000)169.
- [10]. H.S. Kim, P. Periasamy, S.I. Moon J Power Sources **141** (2005)293.
- [11]. J. Vondrak, J. Reiter, J. Velicka, Klapste B, Sedlarikova M, Dvorak J et al. J Power Sources **146** (2005)436.
- [12]. H. Akashi, M. Shibuya, K. Orui, G. Shibamoto, K.Sekai J Power Sources**112** (2002)577.
- [13]. E.Quartarone ,C.Tomasi, P.Mustarelli, G.B. Appetecchi and F. Croce Electrochem Acta **43**(1998)1435.
- [14]. Pandey GP, Agrawal RC Hashmi SA J Solid State Electrochem **15** (2011)2253.
- [15]. Wikipedia.org, (accessed 15 september 2017),[https://en.wikipedia.org/wiki/Electric\\_double-layer\\_capacitor](https://en.wikipedia.org/wiki/Electric_double-layer_capacitor).
- [16]. W. Xing, S.Z. Qiao, R.G.,Ding F Li, GQ Lu, ZF Yan, HM Cheng, Carbon **44**(2006) 216–224,<https://doi.org/10.1016/j.carbon.2005.07.029>
- [17]. T.Z. Ren, L. Liu, Y.Y. Zhang, Z.Y. Yuan, J Solid State Electrochem **17**(2013)927–935 DOI.10.1007/s10008-012-1947-5.
- [18]. M. Mastragostino, C. Arbizzani, F. Soavi, J Power Sources **98**(2002) 812,[https://doi.org/10.1016/S0378-7753\(01\)00613-9](https://doi.org/10.1016/S0378-7753(01)00613-9).
- [19]. Y. Zhu, H. Hu, W.C.Li, X.Zhang,J Power Sources **162**(2006)738 <https://doi.org/10.1016/j.jpowsour.2006.06.049>
- [20]. M. Tripathi, A. Kumar (2017), Communicated.
- [21]. A. Jain and S. K. Tripathi, J Solid state electrochemistry **17**(2013)2545 DOI10.1007/s10008-013-2140-1.
- [22]. B.E. Conway Electrochemical supercapacitors:. Kluwer Academic/Plenum, (1999) New York.
- [23]. B. Ganesh, D. Kalpana, N.G.Renganathan, Ionics **14**(2008)339,DOI 10.1007/s11581-008-0230-3
- [24]. C.P.Tien, W.J.Liang, P.L.Kuo, H.S.Teng, Electrochim Acta **53**(2008) 4505 <https://doi.org/10.1016/j.electacta.2008.01.021>
- [25]. Niu JJ, Pell WG, Brian E J Power Sources **156**(2006) 725, <https://doi.org/10.1016/j.jpowsour.2005.06.002>.
- [26]. E. Frackowiak, Béguin F, Carbon(2001)39:937,[https://doi.org/10.1016/S0008-6223\(00\)00183-4](https://doi.org/10.1016/S0008-6223(00)00183-4).
- [27]. C.RMariappan.,G.Govindaraj,S.VinothRathan,V. G Prakash, Mater Sci Eng.,**63**(2005)123B(1) <https://doi.org/10.1016/j.mseb.2005.06.022>