Development of low-cost technology to obtain carbon based supercapacitors

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Abstract. Recent advances in supercapacitor technology reveals new opportunities for energy storage devices for application in electro-transportation and renewable energy sectors. In this paper results on device fabrication are reported. A low-cost screen-printing technology to obtain electrodes of supercapacitor has been applied. The device structure is based on Cu plate/hydrocarbon ink electrodes and gel electrolyte. Carbon ink is prepared from naturally occurring not full carbonized particles in the chimney’s soot. The cyclic charge/discharge measurements confirm supercap behaviour and specific capacitance around 5 F/g at discharge current of 0.62 A/g. The flat configuration of the supercaps allows easy connection in series and adjustment to DC loads. A pack of four supercaps driving conventional LED has been thoroughly tested for more than 100 cycles.

1. Introduction

Nowadays supercapacitors are used frequently in autonomous power supply systems. Large capacitance allows generating a small value current for a long period time or alternatively to provide high value current for a short period.

The electrode material is a key component that determines the electrical capacity of the device [1]. Supercapacitors based on activated carbon electrodes have a wide pore size distribution [2], consisting of micropores (< 2 nm), mesopores (2 – 50 nm), and macropores (> 50 nm). Mesopores contribute the most to the capacitance in an electrical double layer capacitor (EDLC) [3]. In principle, pores greater than 0.5 nm are electrochemically accessible for aqueous electrolytes [4].

A typical supercapacitor cell is comprised of two microporous electrodes that are isolated from electrical contact by a separator. Metallic current collectors are used to conduct electrical current from each electrode to outside circuitry. The separator and the electrodes are impregnated with an electrolyte, which allows ionic current to flow reversibly between the electrodes [5]. Active electrode material could be produced from many sources [6 - 9] but in this investigation the emphasis is placed on low-cost resource - domestic soot.
Soot is a particulate carbonaceous matter with a characteristic lattice structure. It is formed during high temperature pyrolysis or combustion of hydrocarbons. It consists mainly of carbon and small amounts of other elements, such as hydrogen and oxygen [10]. Assuming that soot is formed as is described in [11] they consist of internal graphite core and nascent poly-aromatic hydrocarbons (PAHs) with different functional groups [12] which increase absorption capability of the material [13].

This paper presents results of identical supercapacitors connected in series. Each element is operating at (1.0-1.1 V) and utilizes stable inorganic electrolyte.

2. Experiment

2.1. Ink preparing

In this experiment we test ink produced from particles derived from soot. The recipe is as next: The soot was collected from a chimney of domestic fire system, after pine tree burning. The collected soot is flooded in ethanol 96% and treated in ultrasonic wane for 10 minutes. After that the mixture is sieved through primary 150µm mesh and washed with additional amount of ethanol. All contents which pass through the mesh are collected and sieved again with a secondary 47 µm mesh and washed with additional amount of ethanol. The mixture is left for 48 hours to allow the particles to precipitate, after that the liquid is removed and the grouts are dried in air at 150°C.

To prepare the ink dried grouts are added to PVA / DI water solution. PVA acts as a binder. By screen-printing technology or brush the as prepared ink is deposited on the Cu foil. The electrode with approx size 4 x 5 cm is ready after careful drying to avoid cracking and defoliation. The deposited ink mass is measured at 0.06g using microbalance.

![Figure 1](image)

Figure 1. An electrode surface with as prepared ink, 3D surface roughness a); optical image b)

2.2. Device assembling

Symmetric capacitor is prepared in sandwich structure by pressing together two electrodes and separator film in between. The separator and electrolyte are added together. Filter paper (2-3 µm pore size) soaked with the electrolyte (3ml, 5M KOH) solution is used as separator. The composite is dried in the air at 90°C for about 15 min. The volume and concentration defines the exact amount of KOH (~0.86g). The as prepared capacitor is encapsulated in PE plastic foil pack using hot lamination technique. Electrical measurements are then carried out.

2.3. Electrical measurements

Measurement procedures include electrochemical measurements and device parameters such as electrode mass and thickness. Cell capacitance is best determined from galvanostatic or constant current (CC) discharge curves. In our case self-made CC charge/discharge testing tool has been developed. The charging current is controlled by a simple C++ code, current source and an open-source programmable microcontroller. In order to increase the activation of micro pores charge/discharge cycle in a ratio of 10:1 is applayed. At the initial stage, the voltage is starting from 0V, the supercapacitor testing structure is charged at 20 mA for 8 s up to 1.0V, held at open circuit for 2 s, and subsequently discharged for 10 s at 2 mA. As can be seen at Figure 2, the sequences are repeated.
with slow drift up to the limit of 1.2V to prevent splitting of the water content of the electrolyte. The slow increase of trapped charge is an indication of supercapacitor behaviour.

The voltage versus time profile during the constant current discharging process can be approximated with a straight line after a correction of the initial voltage drop (IR drop), and the slope of the line can be used to calculate the cell capacitance from the relation \( C = I / (dV/dt) \).

![Figure 2. Charging/Discharging profiles of test structures a) narrow gap - 5min, b) nearly 4 hour charge/discharge.](image)

Portable electronics needs operating voltages in the range of 1.5V - 3 V which determines the voltage window of energy storage devices. To testify the real potential application of the devices, we connected four capacitors in a pack. The useful voltage window of the device is extended to 4.2V. The charge-discharge duration of the developed device is nearly the same as for individual element suggesting consistent capacitance performance of each supercapacitor.

Finally, we tried to charge the serial pack of capacitors and succeed to light up a blue light-emitting diode (LED) which has operating potential at about 3.0V (illustrated in figure 3). The LED can light up over 300 seconds thus it proves the potential of LED driving application.
3. Conclusions

A supercapacitor based on waste material without expensive intentionally created carbonaceous materials has been fabricated, tested and demonstrated in an application. The analysis of the results revealed a potential for soot implementation in supercapacitor devices with a suitable treatment for increasing the parameters of the capacitors. Connection in series is possible and blue LED may be operated for 300s with a prototype. The specific capacitance (F/g) of whole capacitor in our case simply could increase with increasing quantity of KOH, by using thinner separator and by charging at a maximal voltage.

References

[1] Vasile V N, Obreja 2014 AIP Conference Proceedings 98 1597
[2] Wu F, Tseng R L, Hu C C, Wang C C, 2004 Journal of Power Sources 138 351–59
[3] Gryglewicz G, Machnikowski J, Lorenc-Grabowska E, Lota G, Frackowiak E, 2005 Electrochimica Acta, 5 1197-1206
[4] Frackowiak E, Beguin F 2001 Carbon 39 937–50
[5] Sakka M A, Gualous H, Omar N, Mierlo J Van 2012, Batteries and Supercapacitords for Electric Vechicles 5 http://dx.doi.org/10.5772/53490
[6] Pérez-Madrigal M M, Edo M G, Alemán C, 2016 Green Chem. 18 5930
[7] Adinaveen T, Vijaya J J, Sivakumar R, Kennedy L J 2016 Materials Science Poland 34(2) 302-14
[8] Farma R, Deraman M, Awitdrus, Talib I A, Omar R, Manjunatha J G, Ishak M M, Basri N H, Dolah BN M 2013 Int. J. Electrochem. Sci. 8 257 – 73
[9] Rufford T E, Hulicova-Jurcakova D, Fiset E, Zhu Z, Lu G Q 2009 Electrochemistry Communications 11 974 - 77
[10] Xi J, Zhong B J 2006 Chem Eng Technol 29 65–73
[11] Kholgby M R, Veshkini A, Thomson M J 2016 Carbon 100 508-36
[12] Raj A, Robert da Silva G, Chung S H 2012 Combustion and Flame 159 3423–36
[13] Ternero-Hidalgo J J, Rosas J M, Palomo J, Valero-Romero M J, Rodriguez-Mirasol J, Cordero T 2016 Carbon 101 409-19