

## Electrochemical Behavior of Carbon Electrodes as a Key to Supercapacitor Optimization

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The paper describes the electrochemical behavior of supercapacitor electrodes in both positive and negative ranges. This study has become possible due to development of a special reference electrode, which is stable in aprotic electrolytes like, e.g., 1.3 M Et<sub>3</sub>MeNBF<sub>4</sub> in acetonitrile. Three-electrode measurements have enabled us to find the boundary potentials for various nanoporous carbon materials to be then used in the supercapacitor technology. This article describes how the electrode size can be optimized to get the maximum charge value in the double electric layer at the electrode-electrolyte interface. Besides, we illustrate how the supercapacitor rated voltage can be increased up to 2.9 V as compared with the typical value of 2.7 V. This provides the 15 % increase in energy and power.

**Keywords:** Supercapacitor, Three-electrode cell, Boundary potentials, Rated voltage.

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### 1. INTRODUCTION

Development of new energy storage devices, which are more powerful and more reliable than batteries and which can be charged much faster than batteries, is of great interest, in particular, for hybrid automotive applications arising over the last decade. One of those new devices is the electrochemical double layer capacitor otherwise called as ultracapacitor or supercapacitor. Supercapacitor is an energy storage device resembling a conventional electrolytic capacitor, wherein the electrical energy is stored due to charge separation and formation of the electrical double layer at electrode-electrolyte interface when the capacitor plates are charged. This type of energy storage devices has some advantages and disadvantages. The main disadvantage is obviously the low energy density that can be stored in a supercapacitor. Though its electrodes are usually fabricated from activated carbon materials with a huge surface area (up to 2000 sq.m per gram) to increase the capacitance, the supercapacitor energy density is still much lower than that of batteries. On the other hand, the main advantages of supercapacitors against batteries are their high power density, high efficiency, long cycle life and safety [1, 2]. This is mostly due to the absence of any faradaic processes but electrolyte diffusion and double electric layer formation to be only involved in supercapacitor charge-discharge processes. As a result, these charge-discharge processes are very fast and supercapacitor specific power density is by orders of magnitude higher than that of batteries.

According to well-known equations [3] the power density is proportional to voltage squared and inversely proportional to resistance.

$$P = \frac{9(1-\eta)U^2}{16R} \quad (1)$$

where  $\eta$  is efficiently.

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Thus an increase in power density can be achieved in two ways:

- by reducing the supercapacitor resistance
- by increasing the supercapacitor rated voltage.

In this paper we analyze the effects of different material properties on the supercapacitor rated voltage and look for the ways to increase the voltage. Carbon materials used as supercapacitor electrodes have different surface area and pore size distribution. In addition, cations and anions in the electrolyte differ by their size and by their interaction with a conductive carbon matrix. That is why even if the same carbon is used in positive and negative electrodes, the electrochemical stability range is different. To optimize it we have developed a method for determining the boundary potentials for activated carbon materials, which are used in supercapacitor electrodes. Also we propose a methodology capable to predict what type of nanoporous carbon must be chosen for positive or negative electrode in supercapacitors with acetonitrile-based electrolytes.

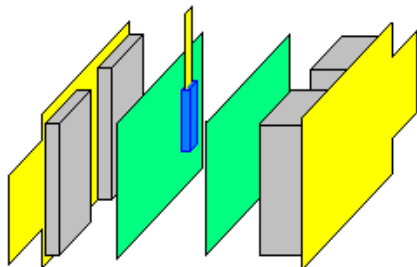
### 2. EXPERIMENTAL

After testing a number of commercially available activated carbons used in supercapacitor technology, two of them were selected as the most promising materials for detailed electrochemical studies. The specific surface area of activated carbons, according to DFT calculations, exceeds 1300 m<sup>2</sup>/g [4]. As an electrolyte 1.3 M triethylmethylammonium tetrafluoroborate (Et<sub>3</sub>MeN<sup>+</sup>BF<sub>4</sub><sup>-</sup>) dissolved in acetonitrile (CH<sub>3</sub>CN) as a solvent was used in our studies.

Electrodes were fabricated by rolling a mixture of carbon powder with a binder (Teflon suspension in water). Then the carbon electrode sheet was laminated on the surface of aluminum foil (current collector). The electrode dimensions were 3x5 cm and it had a notch for the reference electrode to be inserted. The electrodes

thus made were dried in vacuum at 220 °C followed by placing them in a glove box with dry argon atmosphere, where they were used for assembling supercapacitor prototypes with a reference electrode.

Schematic design of a three-electrode cell thus fabricated is illustrated in Fig. 1.



**Fig. 1** – Schematic design of a three-electrode supercapacitor cell

According to Fig. 1 the three-electrode cell has two carbon electrodes and one reference electrode. One of the carbon electrodes of 30 micron thick is the working electrode. Another carbon electrode of 300 micron thick is the auxiliary one. These carbon electrodes are separated by two separator sheets with the reference electrode in between. The reference electrode is positioned approximately in the center of the notch. This notch has been introduced in the cell design for two reasons:

a) it helps to position the reference electrode in the center of cell;

b) along the line “collector – separator – reference electrode – separator–collector” electrostatic field is low.

Measurements of current-voltage cell characteristics were performed with the use of Voltalab-80 (PGZ-402) potentiostat. In cyclic voltammetry (CV) measurements the scan rate was 10 mV/s. [5, 6]

Four three-electrode cells were assembled with the use of two different types of carbon. They were used as positive or negative working electrodes in the assembly design shown in Fig. 1. The auxiliary electrode behavior is not analyzed in this study.

### 3. RESULTS AND DISCUSSION

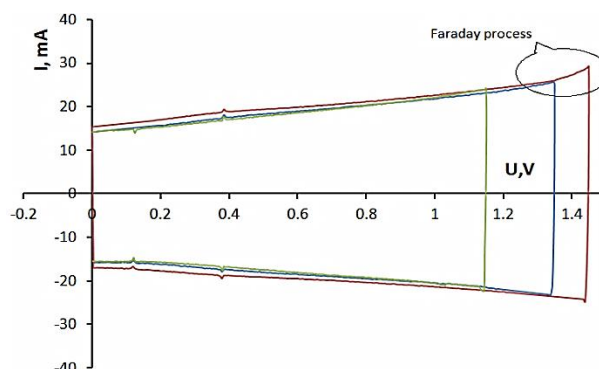
The reference electrode potential was of 3.4 V with respect to a pair of Li / Li<sup>+</sup>. The equilibrium potential of our electrode materials was of 3.2 V with respect to a pair of Li / Li<sup>+</sup>. We use this equilibrium potential as “zero point” in our scale of potentials.

Three-electrode CV measurements were used to study the behavior of selected carbon electrodes in either positive or negative potential range. As a result, we have found the boundary potentials for positive and negative ranges for both carbon electrodes. Depending on the voltage range wherein the carbon material is more stable, we select it as “Cathode Carbon” or “Anode Carbon”.

As an example, Fig. 2 illustrates the CV curves for one of the selected carbons as a working electrode in the positive direction.

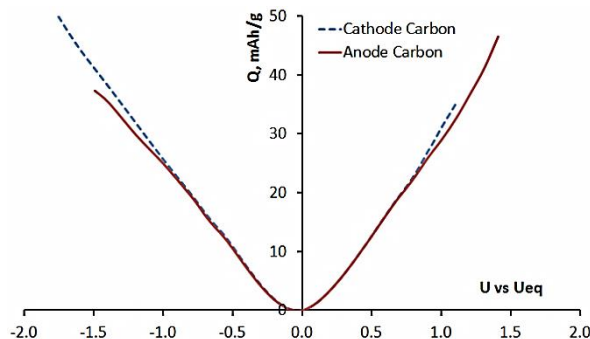
As can be seen from Fig. 2, when the potential value achieves 1.4 V vs. the equilibrium potential of electrode, a visible increase in current appears. This can be accounted for starting some faradaic processes at so

high potentials, the processes adding some extra current to that due to charging the double electric layer. So, if this carbon is used for preparing the positive supercapacitor electrode, the boundary potential of 1.3 V should not be exceeded.



**Fig. 2** – CV curves obtained by scanning the potential in the anode region with the sweep rate of 10 mV/s

The amount of charge, which can be accumulated due to charging the double electric layer by different carbons in different potential ranges, is also illustrated in Fig. 3 below. For Cathode Carbon (a blue dashed line) the maximum potential is 1.2 V in positive range, while the Anode Carbon (a red solid line) has the boundary potential at a higher value. On the other hand, in the cathode range the double layer is formed without faradaic processes up to -1.8 V for Cathode Carbon while the boundary potential for Anode Carbon is -1.5 V only.



**Fig. 3** – Amount of charge accumulated by two different carbons due to formation of double electric layer at different electrode potentials relative to the equilibrium potential

If we use the same carbon as both cathode and anode material and charge a supercapacitor to the rated voltage, two problems are possible:

a) one of the electrodes does not use its whole surface area for charge accumulation;

b) faradaic processes (e.g., electrolyte decomposition) occur on one of the electrodes.

For example, if the Cathode Carbon is used as both positive and negative electrode when assembling a supercapacitor, at the capacitor voltage of 2.6 V the positive electrode is charged to 1.2 V with respect to equilibrium potential, and the negative electrode is charged to -1.4 V. As a result, the cathode electrode does not reach its boundary potential by 400 mV. On the other hand, if the supercapacitor voltage is in-

creased to 2.7 V, the faradaic processes start occurring at the positive electrode, and this can shorten the supercapacitor life-time. This problem can partly be solved due to using the electrodes of different thickness. In this case the thickness of the cathode should be by 30 % less than the thickness of the anode, and this can proportionally reduce the energy stored in the device.

The behavior of optimized system is illustrated in

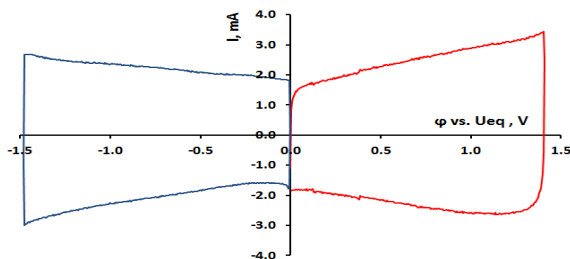


Fig. 4. In this case the Cathode Carbon has been chosen as that presented by blue dashed line in Fig. 3, and the Anode Carbon – as that presented by red solid line in Fig. 3. Also, we have calculated the thickness of electrodes to ensure the equal amount of charge in positive and negative electrodes during the charging process but not exceeding the boundary potentials. In this case the supercapacitor can work in a wide voltage range of 2.9 V and, correspondingly, can store more energy.

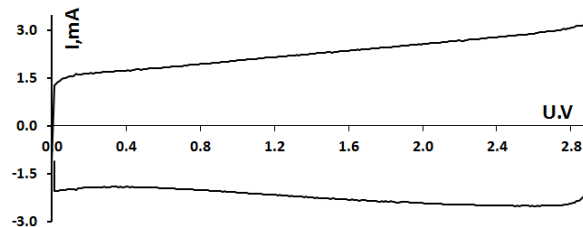


Fig. 4 – An example of optimized electrochemical system capable of providing the rated voltage of 2.9 V

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