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# THE EFFECT OF NANOPOROUS ELECTRODE COMPOSITION ON SUPERCAPACITOR PERFORMANCE

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Electrochemical double-layer capacitors (EDLC), otherwise known as supercapacitors or ultracapacitors, have become an integral part of various energy storage technologies, wherein EDLC low internal resistance is one of the key advantages, which predetermines the effectiveness of EDLC application in combined power supply units.

In this study the influence of different types of conductive additives in composite electrodes on supercapacitors performance has been investigated. Nano-porous activated carbon YP-80F (Kuraray, Japan) was selected as the active electrode material with appropriate pore size distribution between 1 and 5 nm. Two types of conductive additives were used: low surface area carbon black (less than 100 $m^2$/g, Super P-Li, Timcal, Switzerland) and high surface area carbon black (SC2, Cabot, USA) with a specific surface area of about 1500 $m^2$/g. The electrodes were typically prepared by mixing the nanoporous activated carbon powder with conductive additive and PTFE suspension in water (Sigma-Aldrich). Galvanostatic charge-discharge cycling in the voltage range from 2.7V to 1.35V and current from 0.5A to 3A was used to measure the electrical parameters of EDLC prototypes. As a result, the use of 2% of Super P-Li leads to 7% decrease of internal resistance. Compared to Super P-Li, the SC2 conductive additive in amount of 20 mass% allows more than 20% increase in gravimetric capacitance at the same level of the internal resistance.

Electrical double-layer capacitors (EDLCs, also known as supercapacitors or ultracapacitors) are energy storage and power delivery devices with high power capability, high efficiency and long lifetime durability [1]. EDLCs are currently widely used in various energy storage technologies, wherein their low internal resistance and long cycle life are at an advantage (electric vehicles, energy recuperation modules, systems for uninterrupted power supply, fast recharging energy modules for high-power applications, wind energy, etc.) [2]. EDLC devices, which

do not involve any mass or charge transfer through the electrode-electrolyte interface, demonstrate much faster charge/discharge operations and longer cycle life as compared with conventional batteries. Therefore, EDLC devices can ensure a number of efficient power solutions that are mainly related to various backup systems to compensate short-term voltage surges or drops or with load leveling the batteries in various combined power sources.

The electrochemical performance of EDLCs depends on the pore structure, and high energy and power values can be achieved for high surface area materials, such as nano-porous carbon, which is an excellent active electrode material for EDLC due to its tremendous specific surface area, usually exceeding 1500 $m^2$/g [3]. However, nano-porous carbon materials (typically powders) are not converted into final EDLC electrodes easily, and various types of binders are used to fabricate an electrode. Besides, low internal resistance can be one of key advantages of EDLC over all other types of energy storage devices since the efficiency and power capability are inversely proportional to internal resistance [4]. To increase the intrinsically low electrical conductivity of some nano-porous carbons, various types of conductive additives can also be added [5]. A high-performance composite electrode thus formed must demonstrate [6]:

- low ohmic resistance;
- good electrolyte accessibility and wettability;
- low contact resistance, stable interface with the current collector;
- high volumetric capacitance (F/$cm^3$);
- chemical stability;
- low level of electrochemically active impurities;
- mechanical stability;
- the required "form factor", i. e. thickness, flexibility.

So, the particles of both activated carbon and conductive additive must be held together in a compact manner to ensure a high-density electrode with low ohmic resistance. This necessitates the use of a polymeric binder, which can maintain particle-to-particle contact, give the electrode mechanical integrity and provide stable, low-resistance bonding to a current collector. The binder must be inert toward the electrolyte, be stable at both negative and positive electrochemical potentials of the electrodes, be effective at low concentrations, and must not block more than a small fraction of the nano-porous carbon surface. A list of binders that meet these requirements and demonstrate good chemical and electrochemical stability include polytetrafluoroethylene (PTFE), polyvinylidenedifluoride (PVdF), polyvinyl alcohol (PVA), sodium carboxymethyl cellulose (CMC) and styrene-butadiene rubber (SBR) [7].

Compared to other listed binders, PTFE forms a network of fibrils instead of a polymer film. This results in a structure with good particle-to-particle contact and low internal resistance. Besides, the surface of carbon remains accessible for electrolyte ions, and the electrode does not become liophobic.

### Experimental

Commercially available coconut shell derived activated carbon YP-80F (Kuraray, Japan) was used as an electrode active material. Different types of conductive additives were used: low surface area (less than 100 $m^2$/g) carbon black (Super P-Li, Timcal, Switzerland) and high surface area carbon black (SC2, Cabot, USA) with a specific surface area of about 1500 $m^2$/g. The Super P-Li conductive additive was added to the active material in an amount of 2 mass% and 4 mass%. In the case of SC2 carbon black, the mass fractions were as follows: 5%, 10% and 20% ('100%' with respect to the total carbon mass with binder).

The electrodes were typically prepared by mixing the nano-porous activated carbon powder with conductive additive and PTFE suspension in water (Sigma-Aldrich) until a homogeneous mixture was obtained. The mixture was rolled to form sheets of 100 micron thick followed by cutting off the separate carbon electrodes. The active carbon electrodes thus obtained had their geometric surface area of 15 $cm^2$ each and contained 7% of PTFE binder, (93-x)% of activated nano-porous carbon and x% of conductive additive, where x=0;2;4;5;10;20 in compliance with conductive additive type. They were then applied onto electric-spark treated aluminum foil [8] used as a current collector of 20 micron thick and dried at 220 °C under vacuum for 8 hours. A couple of electrodes were then interleaved with a porous insulating sheet (separator) and placed into laminated aluminum shell. The prototypes thus fabricated were filled with 1.3 M $Et_3MeNBF_4$ (TEMA) in acetonitrile and sealed. All the assembly operations were carried out in a dry box filled with argon.

Galvanostatic charge-discharge cycling in the voltage range from 2.7V to 1.35V and current from 0.5A to 3A with the help of Arbin SCT 5-25 testing unit was used to measure the electrochemical parameters of EDLC prototypes.

### Results and Discussion

The porous structure of selected activated carbon YP-80F has been studied from nitrogen adsorption/desorption isotherms at 77 K using a Nova 2200e Surface Area & Pore Size Analyser (Quantachrome Instruments), and the results are illustrated in Figure 1.
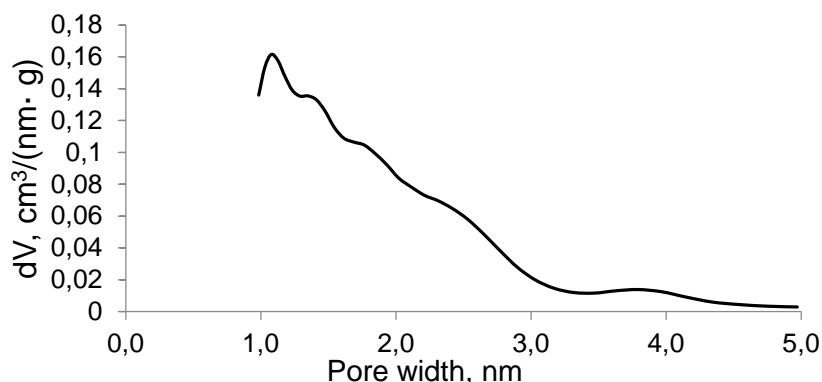
**Figure 1.** *Pore size distribution obtained from nitrogen adsorption/desorption isotherms with the use of DFT calculations*

This nano-porous carbon has its pore size in the range between 1 and 5 nm with a large portion concentrated between 1 and 3 nm.

Testing results of EDLC prototypes with their electrodes fabricated either with the use of Super P-Li conductive additive or, for comparison purposes, with „pure" activated carbon electrodes (without any conductive additive), are listed in Table 1 below.

*Table 1. Electrochemical parameters of EDLC with different content of Super P-Li conductive additive*

| Super P-Li, mass% | Electrode's density, g/cm$^3$ | Specific capacitance, F/g | Volumetric capacitance, F/cm$^3$ | Specific resistance, Ohm·cm$^2$ | RC-constant, s$^{-1}$ |
|---|---|---|---|---|---|
| 0 | 0,47 | 32,4 | 14,2 | 0,85 | 0,24 |
| 2 | 0,5 | 30,5 | 14 | 0,79 | 0,22 |
| 4 | 0,51 | 30,5 | 13,9 | 0,8 | 0,22 |

As can be seen from this Table, addition of Super P-Li conductive additive in amount of 2 mass% allows to achieve 7% reduction of internal resistance. Further increase in the Super P-Li content does not reduce the resistance significantly. At the same time, an increase in Super P-Li content results in some decrease in volumetric capacitance due to lower specific surface area of the conductive additive.

Testing results of EDLC prototypes, whose electrodes were fabricated with SC2 conductive additive in comparison with „pure" activated carbon electrodes (without any conductive additive), are listed in Table 2 below.

*Table 2. Electrochemical parameters of EDLC with different content of conductive additive SC2*

| SC2, mass % | Electrode's density, g/cm³ | Specific capacitance, F/g | Volumetric capacitance, F/cm³ | Specific resistance, Ohm·cm² | RC-constant, s⁻¹ |
|---|---|---|---|---|---|
| 0 | 0,47 | 32,4 | 14,2 | 0,85 | 0,24 |
| 5 | 0,49 | 32,4 | 14,0 | 0,82 | 0,23 |
| 10 | 0,51 | 33,8 | 14,3 | 0,78 | 0,22 |
| 20 | 0,52 | 39,7 | 15,1 | 0,78 | 0,23 |

Gradual increase in SC2 content allows reaching the minimum of internal resistance at 10 mass% of SC2. Further increase in the content of SC2 does not provide lower resistance, but significantly affects the gravimetric capacitance, which can be seen in Figure 2.
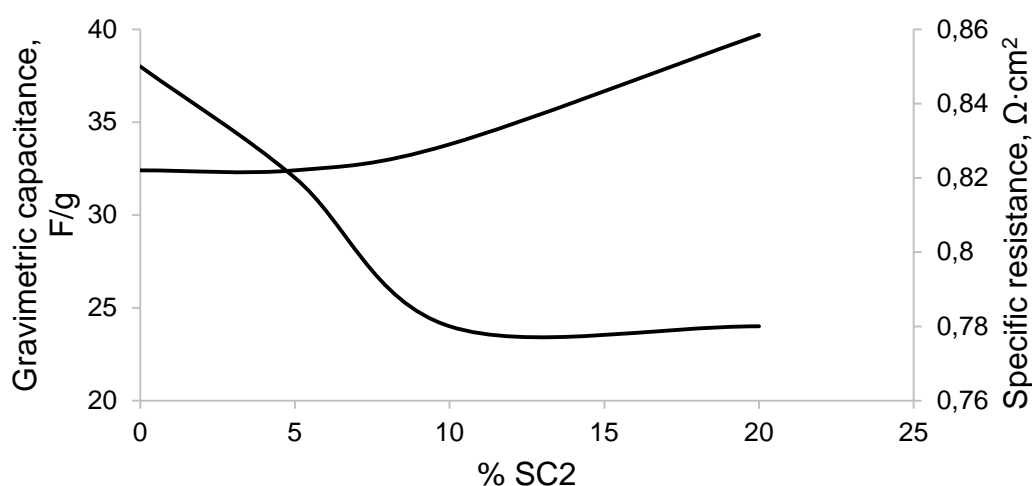


*Figure 2. Dependence of EDLC specific parameters on SC2 content*

In accordance with testing results, the use of SC2 conductive additive in amount of 20 mass% allows more than 20% increase in gravimetric capacitance of such composite electrodes.

**CONCLUSIONS**

The optimized ratio of various ingredients (nano-porous carbon, polymer binder and conductive additive) in composite EDLC electrodes enables one to improve the electrode's mechanical strength and EDLC performance significantly.

The use of conductive additive SC2 in amount of 20 mass% besides reducing the internal resistance also increases gravimetric capacitance by 20%.

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