Influence of carbon conductive additives on electrochemical double-layer supercapacitor parameters

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Abstract. Electrochemical double-layer capacitors (EDLC) offer energy storage technology, highly demanded for rapid transition processes in transport and stationary applications, concerned with fast power fluctuations. Rough structure of activated carbon, widely used as electrode material because of its high specific area, leads to poor electrode conductivity. Therefore there is the need for conductive additive to decrease internal resistance and to achieve high specific power and high specific energy. Usually carbon blacks are widely used as conductive additive. In this paper electrodes with different conductive additives—two types of carbon blacks and single-walled carbon nanotubes—were prepared and characterized in organic electrolyte-based EDLC cells. Electrodes are based on original wood derived activated carbon produced by potassium hydroxide high-temperature activation at Joint Institute for High Temperatures RAS. Electrodes were prepared from slurry by cold-rolling. For electrode characterization cyclic voltammetry, impedance spectra analysis, equivalent series resistance measurements and galvanostatic charge–discharge were used.

1. Introduction

Electrochemical double-layer capacitors (EDLC) are emerging energy storage technology, highly demanded for rapid transition processes in transport and stationary applications [1], concerned with fast power fluctuations, decreasing size of accumulator battery or saving organic fuel [2]. Electrode structure has significant impact on capacity and power output of EDLC.

So electrode materials and preparation procedure proper choice are very important to achieve high specific power and high specific energy. Rough structure of activated carbon, widely used as electrode material [3] because of high specific area, leads to poor electrode conductivity and needs conductive additive to decrease internal resistance. Usually carbon blacks, especially Vulcan XC 72 R (Cabot Corp.) [4] are widely used as conductive additive. Sometimes carbon nanotubes (multi- or single-walled) are also used for this purpose [5]. Carbon nanotubes are very attractive material for power sources application due to their high conductivity, chemical stability and excellent ability to form percolation clusters in electrode structure [6]. Attempts to apply carbon nanotubes to increase aqueous electrolyte-based EDLC are described in [5].
Potassium hydroxide-activated carbon nanotubes were used as electrode material in EDLC. Despite activation specific mass capacitance of such supercapacitors was not very high—about 40–50 F/g, mainly due to low specific area of carbon material. Activated carbon is more traditional and efficient electrode material which allows specific capacitance of about 100 F/g for organic electrolyte EDLC and 150–200 F/g for aqueous EDLC [7]. So high surface area can be considered as the main advantage of activated carbon as electrode material, but high surface area usually means rough surface, and, because of large structure defects amounts, low conductivity. It leads to losses of energy, stored in EDLC and low specific power, which is the most important EDLC parameter.

To increase specific power, carbon nanotubes or other conductive, chemically stable in electrolyte solution additive must be used in electrode structure. In [8] multi-walled carbon nanotubes were used as conductive additive to graphene-based electrodes of aqueous EDLC. Sophisticated electrode assembly technique resulted in specific capacity of 390 F/g and excellent conductivity. In this case carbon nanotubes served not only as conductive additive, but also as spacer between graphene layers preventing high-surface area graphene from agglomeration. [9] is devoted to organic electrolyte-based EDLC with onion-like graphitized conductive additive with high surface area in attempt to increase both specific capacity and electrode conductivity. The best results were shown by 10 wt% onion-like additive with specific area of 398 m$^2$/g (according to the Brunauer–Emmett–Teller measurement technique). Usage of additives with higher surface area (1389 m$^2$/g) led to larger capacity fade on high currents, with lower specific area (77 m$^2$/g) and high conductivity—to initial and high-current specific capacity decrease. This result shows importance of many electrode material parameters considering to optimize its performance.

2. Experimental
Strategy of our approach was to use high-quality carbon nanotubes (CNT), received from OCSiAl company [6] to improve conductivity of electrode and decrease weight percentage of carbon additive (due to high aspect ratio of these nanotubes) which does not participate in electric double layer formation. Some traditional additives (carbon blacks Vulcan XC72R and P267E from Institute of Hydrocarbon Processing, Siberian Branch, Russian Academy of Sciences) were used as reference materials to derive effect of carbon nanotubes and to compare them with traditional additives.

To characterize electrochemical behavior of different conductive additives, composite electrodes were prepared and tested in supercapacitor single cell. Slurry from activated carbon, conductive additive and polytetrafluorethylene (PTFE) emulsion were prepared, containing about 8 wt% (dry) PTFE, 10 wt% (dry) carbon additive (in case of carbon blacks) and 82 wt% (dry) of activated carbon.

In case of carbon nanotubes (Tuball™ deionized water dispersion of single-walled carbon nanotubes (0.1 wt% of CNT), received from OCSiAl company), dry weight of conductive additive was 0.005–0.012 wt% (because of addition 5–10 wt% of dispersion to slurry), and activated carbon share increased up to about 95–96 wt%.

Slurry was mixed mechanically using Ultra Turrax T10 during 10 minutes, after that solvent was partly evaporated to receive active mass which was fed to rolling press MSK-HRP-MR100DC (MTI Corp., USA) and rolled several times to obtain composite PTFE-bound carbon sheet with thickness of 100–140 m. More detailed routine for electrode preparation is given in [10]. These sheets were annealed at 250 °C in Binder™ vacuum chamber for 4 hours to finally remove residual water and solvent from electrode. After annealing, electrode specimen of 30 × 30 mm$^2$ area were prepared from sheets in Ar-filled glove box for testing in supercapacitor cells.

Specimens for scanning electron microscopy were also cut from these sheets. Aluminum carbon-covered foils from MTI-Corp (USA) were used as current collectors. Cells were assembled in dry atmosphere (dry glove box filled with Ar gas) and filled with 1 mol/L TEA-BF4
(tetraethylammoniumtetrafluoroborate) in electrochemical grade (water content is less than 50 ppm) dissolved in acetonitrile (AN) purchased from BASF, USA, using cellulose-based separator. Cell lamination to prevent moisture and impurities penetration from the environment was also conducted in dry box with Ar atmosphere. To analyze carbon nanotubes content influence, additional three groups of electrodes were prepared—with 0.005, 0.008 and 0.012 wt% of carbon nanotubes additive.

In all experiments activated carbon produced in Joint Institute for High Temperatures of RAS from pyrolyzed birch by alkaline activation technique described in [11] was used as active material of electrode. Structure research for obtained electrode material was carried out using Nova NanoSem 650 scanning electron microscope (SEM). Cyclic voltammetry (CVA) was carried out using an electrochemical analyzer VoltaLab PGZ 301, galvanostatic cycling (GC), with current density 10 mA/cm², and electrical impedance spectroscopy (EIS). All measurements were carried out in range from 1.25 to 2.5 V of cell voltage. Specific gravimetric capacitance and specific volume capacitance during discharging were calculated as follows:

\[ C_{spm} = \frac{4}{m} \int_{t_0}^{T} \frac{idt}{U}, \]  \hspace{1cm} (1)

\[ C_{spv} = \frac{1}{V} \int_{t_0}^{T} \frac{idt}{U}, \]  \hspace{1cm} (2)

where \( C_{spm} \)—specific gravimetric capacitance, \( C_{spv} \)—specific volume capacitance, \( t \)—time (\( t_0 \)—starting time of discharge (charge), \( T \)—end of discharging (charging) time), \( i \)—charging (discharging) current, \( U \)—cell voltage, \( m \)—total mass of the electrodes (i.e., considering carbon materials and the binder), \( V \)—total electrode volume (calculated by multiplication of area by thickness). For every type of electrode composition, three electrode pares were prepared and tested individually to calculate the mean value.

Electrical impedance spectra were recorded for 5 kHz 10 mHz with 10 points per decade and averaged over 5 measurements. Equivalent series resistance of the cells was calculated from voltage drop at the beginning of cell charge during GC. Energy efficiency of the cell was estimated as a ratio of cell discharge to cell charge:

\[ \eta_e = \frac{W_{dch}}{W_{ch}} \times 100\%. \]  \hspace{1cm} (3)

To compare long-term electrode stability for different additives, life cycle tests for electrodes with Vulcan XC72 (10 wt%) and Tuball carbon nanotubes (0.005 wt%) were made using chemical power source analyzer ASK2.5.10.8 (YAROSTANMASH Limited Liability Company, Russia) by GC at 10 mA/cm² between 1.25 and 2.5 V during 6000 cycles.

3. Results and discussion

SEM microphotographs for electrode specimen of different composition are shown in figure 1. In all cases electrode structure presents quite large activated carbon particles, bound with PTFE fibers. In case of Tuball as additive (figure 1) one can see different orientation of PTFE fibers though in other cases they are oriented along electrode rolling direction. This effect may be caused by high CNT aspect ratio and influence uniformity of binder distribution.

Results for primary GC and ESR measurements by voltage drop for different electrodes are given in table 1 (after 1000 cycles).

Table 1 data shows, that 0.005 wt% of single-walled carbon nanotubes is enough to reach capacity, efficiency and ESR, close to those for 10 wt% of carbon black. Slight increasing in capacity for Tuball CNT-containing electrode compared to carbon blacks can be explained by increasing of activated carbon weight share in electrode. This additional carbon, substituting carbon black, can introduce additional capacity. Further capacity growth (with CNT mass
Table 1. Results of primary GC for different electrode composition.

| Conductive additive                  | \( C_{spv} \) (F/cm) | \( C_{spm} \) (F/g) | ESR (Ohm) | \( \eta_e \) (%) |
|--------------------------------------|----------------------|---------------------|-----------|------------------|
| Tuball CNT 0.005 wt%                 | 20.42                | 123                 | 0.18      | 95.9             |
| Tuball CNT 0.008 wt%                 | 20.74                | 126                 | 0.15      | 96.7             |
| Tuball CNT 0.012 wt%                 | 23.80                | 152                 | 0.13      | 97.0             |
| P267E carbon black 10 wt%            | 18.80                | 122                 | 0.18      | 96.1             |
| Vulcan XC72R carbon black 10 wt%     | 19.10                | 114                 | 0.23      | 95.4             |

Figure 1. SEM microphotographs for EDLC electrodes with different conductive additives: (a) Vulcan XC72R carbon black; (b) P267E carbon black; (c) Tuball single-walled carbon nanotubes.

increase) may be caused by introduction of CNT between activated carbon particles thus preventing their agglomeration. Additional pore volume is available for electric double layer formation and electrode capacity increases.

Two types of carbon blacks, involved in experiments, demonstrate close to each other parameters with slightly higher ESR for Vulcan XC72R and slightly lower capacity for P267E, that can be explained by more rough surface structure in case of Vulcan XC72R.

Figure 2 depicts Nyquist plot for cells with electrodes with Tuball and Vulcan XC72R additives.
Figure 2. Nyquist plot (at 2.7 V) for electrodes with carbon additives: 1—0.005 wt% Tuball CNT; 2—10 wt% Vulcan XC72R.

Impedance hodograph for both specimens can be presented as two conditionally-straight lines. One of them at highest frequency (562 Hz for electrode with CNT additive and 1000 Hz for carbon black additive) cuts off value of ESR on Real axis and represents so-called “diffusion” area. This part of the curve for frequency range in 1–100 Hz can be interpreted as porous structure response, concerned with electrolyte diffusion in pores. Second part of the curve (“capacitive” area) with frequency decrease rushes to infinite value in Imaginary axis of Nyquist plot. So at low frequencies (1–4 Hz) impedance spectrum is close to vertical line with real impedance part. Figure 2 also shows some curve deviation from straight line which is caused by low adsorption processes on electrode. It is worth mentioning that transition from “diffusion” to “capacitive” spectrum parts for CNT-containing electrode occurs at higher frequency (around 1.2 Hz) than for carbon black containing electrode (insert in figure 2). Such difference in threshold frequency may be caused by additional electrolyte transfer channels alongside CNT.

Results of life cycle tests for electrodes with CNT and carbon black are presented in figure 3. Vertical line at 3000 cycles is caused by pause in cycling used to register impedance spectrum after 3000 cycles. Spectrum obtained was identical to one registered before the cycling beginning and presented in figure 2. One can also see very small capacity fade after 6000 cycles for both electrodes. Specific volumetric capacity for CNT-containing electrode is quieter than for carbon
Figure 3. Life cycle test results for EDLC electrodes with different conductive additive.

black-doped one during the whole period of cycling. Capacity stability during cycling means that CNT growth pro-catalysts (Fe-based) are reliably encapsulated in carbon on tips of nanotubes or removed from them. Surfactants, possibly used for CNT dispersion stabilization, are removed during electrode preparation routine or inert to electrolyte. This result allows to use Tuball CNT dispersion as prospective substitute for carbon black as conductive additive in EDLC electrodes.

4. Conclusion
EDLC electrodes with single-walled carbon nanotubes and two types of carbon black as conductive additives were prepared and tested in model EDLC cells with 1 mol/L TEA-BF4 solution in acetonitrile as electrolyte. CNT load of 0.005 wt% allowed to obtain cell equivalent series resistance and energy efficiency close to those for 10 wt% of carbon black. Substitution of carbon black with activated carbon allowed increasing specific capacity of electrodes. Increasing of CNT content up to 0.012 wt% led to 25% increasing of electrode specific volumetric capacity and further equivalent series resistance possibly due to percolation cluster formation from CNT and decreasing of activated carbon agglomeration degree. Additional life cycle tests (6000 cycles) did not show significant decreasing in electrode capacity, so introduction of CNT did not bring impurities (the main uncertainties were concerned with Fe-containing CNT growth pro-catalyst) into EDLC cell. So high-quality single-walled carbon nanotubes can be used as conductive additive to EDLC electrode instead of carbon blacks for increasing capacity and decreasing resistance.

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