Carbon additive structure influence on electrochemical double-layer capacitor electrode behavior

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Abstract. Electrochemical double-layer capacitors (EDLC) are widely used as power sources for peak load or peak generation leveling in transport and stationary applications sometimes in combination with accumulator battery. For such applications EDLC need low sensitivity (from lifetime and capacity point of view) to high current mode operation, which is usually crucial for traditional accumulators’ types. Capacity loss in high current mode operation due to both transport and resistive limitations is observed both for accumulators and supercapacitors but much less for latter due to initial low internal resistance and electrochemical reactions absence. Carbon nanotubes (CNT) and nanofibers (CNF) as alternative to carbon blacks as conductive additive for electrodes are good possibility to improve high current operation both for accumulators and EDLC. This paper is devoted to investigation of carbon nanotubes and nanofibers comparison with traditional carbon black additive. CNF structure usually contains more defects and has lower aspect ratio than single-walled nanotubes but this kind of materials is less expensive than CNT, that is also important for final customer. Electrode samples with Vulcan XC72R carbon black were prepared for reference measurements. All electrode samples were tested in galvanostatic charge-discharge mode at different current levels in laboratory-scale EDLC cell, characterized by impedance spectroscopy. Obtained results showed improved high-current operation for CNT-containing electrodes. Economic estimation for different kinds of additives has also been carried out.

1. Introduction

Supercapacitors are special sort of energy storage devices, operating on electrochemical double electric layer charge and discharge. Double electric layer occurs on the interface of porous carbon electrode and liquid electrolyte, penetrating into porous structure and forming large interface surface area leading to high electric capacity of such devices [1]. Faradic processes on electrodes are absent, contrary to electrochemical accumulators [2]. So high lifetime and depth of discharge, close to 100% are available for supercapacitors, but specific energy is very low. So usual applications of electrochemical double-layer supercapacitors (EDLC) are concerned with high electric power generation or consumption in short time periods due to low energy value stored. Usually transportation [3], large or micro-grid parameters regulation [4] and different ways of energy recuperation are reviewed as application niches for supercapacitors. Different ways to increase stored energy (without significant losses in power rate) are under investigation – organic electrolytes with
high voltage limit [5], new carbonaceous materials [6] with high surface area. It’s worth mentioning that high surface area of carbonaceous materials usually leads to their poor electron conductivity [7], so different conductive additives are used in supercapacitor electrode to conserve power rate of the whole device in these conditions. Carbon blacks are usual product for this purpose, especially wide use in electrochemical devices has Vulcan XC72R from Cabot Corp., USA [8]. Carbon nanotubes and nanofibers, graphene-based materials are under investigation too, due to their high stability and electron conductivity [9].

Purpose of this research is to compare two kinds of industrial produced carbon nanostructures – Tuball™ single-walled carbon nanotubes (SWCNT) from OCSiAl LLC (Novosibirsk, Russia), carbon nanofibers (CNF) Taunit™ (NanoTechCenter, Tambov, Russia) with larger diameter than Tuball, but less expensive, then high-quality Tuball, with traditional additive Vulcan XC72R. Comparison includes technical and economic issues – optimal additive mustn’t decrease capacity, lifetime or power rate and increase cost of electrode.

2. Experimental details

To evaluate electrochemical parameters of electrodes with different carbon additives, laboratory-scale test pouch cells were assembled. First slurry from activated carbon, conductive additive and polytetrafluorethylene (PTFE) emulsion was prepared, containing PTFE, carbon conductive additive and activated carbon. Slurry was mixed mechanically using Ultra Turrax T10 during 10 minutes, after that dried at 250 °C in Binder™ vacuum chamber for 4 h, then frictioned through mesh with 2 mm cell diameter to obtain non-agglomerated carbon material, relatively uniform covered with PTFE. As-received mass was fed to rolling press MSK-HRP-MR100DC (MTI Corp., USA) and rolled several times to obtain composite PTFE-bound carbon sheet with thickness 100-140 μm. 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. In all experiments activated carbon produced in Joint Institute for High Temperatures from pyrolyzed birch by alkaline activation technique based on described in [11] was used as active material of electrode.

| Table 1. Electrode specimens’ composition (dry weight). |
|---------------------------------------------------|
| Conductive additive type | Activated carbon, mass, % | Conductive additive, mass, % | PTFE, mass, % |
| Tuball Batt | 91.09 | 0.01 | 8 |
| Vulcan XC72R | 82 | 10 | 8 |
| Taunit | 82 | 10 | 8 |

As-prepared electrode series with composition, given in Table 1, were tested in lab-scale laminated pouch cell with 30*30 mm active area. 1 M tetraethylammonium tetrafluoroborate (TEA-BF₄) in electrochemical grade (water content <50 ppm) dissolved in acetonitrile (AN) purchased from BASF, USA, using cellulose-based separator. Cells lamination to prevent moisture and impurities penetration from the environment was also conducted in dry box with Ar atmosphere. Galvanostatic cycling was the main approach for cell characterization. All measurements were carried out in range from 1.25 up to 2.5 V of cell voltage. Specific gravimetric capacitance during discharging was calculated via (1):

\[ C_{sp} = \frac{4}{m} \int_{t_0}^{T} \frac{i dt}{U} \]  

(1)

with specific gravimetric capacitance \( C_{sp} \), time \( t \) (\( t_0 \) 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). For every type of electrode composition, three electrode pairs were prepared and tested individually to calculate a mean value. Testing routine included long-term charge-discharge cycling at current density 25 mA/cm², short periods (about 100 cycles) at 2 mA/cm², then about 900 cycles at 167 mA/cm². After that test cells were cycled at 25 mA/cm² again to observe capacity loss after cycling mode change (first of all, after fast cycling at 167 mA/cm²). Results were registered for last cycles. ASK2.5.10.8 (YAROSTANMASH LLC, Russia, [12]) chemical current source analyser was used to perform cycling at given current densities. Results for long-term cycling are given in Fig. 1, for different current densities – in Fig. 2, calculated specific capacity loss for all cells at different cycling modes – in Table 2. Specific capacity loss was calculated as

$$L_c = \frac{C_0 - C_{\text{fin}}}{C_0} \times 100,$$

(2)

$C_0$ is initial specific capacity (before series of tests) and $C_{\text{fin}}$ is specific capacity after series of tests. In this paper two series of tests are considered – 40000 cycles at 25 mA/cm² and 100 cycles at 167 mA/cm², followed by 100 cycles at 25 mA/cm². In the first mode $C_0$ is $C_{\text{sp}}$ after 100-th cycle and $C_{\text{fin}}$ is $C_{\text{sp}}$ after 40100-th cycle (100 first cycles are needed for cell polarization and training, after which parameters are more stable). In the second mode is $C_{\text{sp}}$ after 40100-th cycle at 25 mA/cm² and $C_{\text{fin}}$ is $C_{\text{sp}}$ after 100 cycles at 167 mA/cm² and 10 cycles at 25 mA/cm². Additional

![Figure 1. Long-term stability tests. Electrode parameters according to Table 1.](image1)

![Figure 2. Cells specific capacity for different cycling current density and different conductive additives. Electrode parameters according to Table 1.](image2)
Impedance spectra were also registered for specimens with different conductive additives to evaluate electrode transport properties. Electrochemical analyser VoltaLabPGZ 301 was used for impedance measurements. Nyquist plots for all specimens are shown in Fig. 3.

**Table 2.** Specific capacity loss at different modes. Electrode parameters according to Table 1.

| Conductive additive type | After 40000 cycles at 25mA/cm² | After 100 cycles at 167 mA/cm² |
|--------------------------|---------------------------------|-------------------------------|
| Tuball Batt              | 7                               | 1                             |
| Vulcan XC72R             | 3                               | 3                             |
| Taunit                   | 8                               | 1                             |

Impedance spectra were also registered for specimens with different conductive additives to evaluate electrode transport properties. Electrochemical analyser VoltaLabPGZ 301 was used for impedance measurements. Nyquist plots for all specimens are shown in Fig. 3.

**Figure 3.** Nyquist plot for electrode specimens with Vulcan, Tuball and Taunit conductive additives. Electrode parameters according to Table 1.

3. **Economic estimations**

It is necessary to estimate different conductive additives influence on supercapacitor costs, because cost is one of the most important parameter from consumer’s point of view. For this purpose, current prices for all components were reviewed. According to authors purchase experience, carbon black Vulcan XC72 R price can be estimated as 4.3 USD/kg [13], Taunit – 2000 USD/kg [14], and 8000 USD/kg for Tuball Batt (for dry weight, because price for deionized water suspension with 0.2 mass.% of CNT is about 16 USD/kg, according to consultations with OeSiAl specialists). Activated carbon, synthesised in RAS JIHT, can have specific cost as high as 15 USD/kg in case of industrial scale production. According to table 1, costs for electrode materials can be estimated as (for 1 kg of electrode active mass):

\[
E_{el} = (E_c \ast (1 - \phi) + E_{add} \ast \phi) \ast m,
\]

(3)

where \(\phi\) is mass share of conductive additive in electrode, \(E_c\) – specific cost for activated carbon (USD/kg), \(m\) – electrode active mass (1 kg) and \(E_{add}\) - specific cost for conductive additive (USD/kg). Taking into account different electrode specific capacity values for different additives, we consider test results for specimens after 40000 cycles at 25 mA/cm²: 96 F/g for Tuball-doped electrode, 85 F/g for Vulcan-doped electrode. For Taunit 10% are not optimal, so, considering 5 mA/cm² results for 3 mass.%, specific capacity for Taunit-doped electrode can be estimated as 94 F/g at 25 mA/cm².
Further specific capacity cost (USD/F) for 1 kg of active mass with different additives is calculated as:

\[ E_{cap} = \frac{C_{sp} \cdot m}{E_{el}}, \]

where \( C_{sp} \) – specific capacity of electrodes after 40000 cycles at 25 mA/cm\(^2\), obtained in experiment. Calculation results are summarized in Table 3.

Table 3. Specific capacity cost estimation for electrodes with different conductive additives.

| Conductive additive type | Tuball, 0.012 mass.% | Vulcan XC 72 R, 10 mass.% | Taunit, 3 mass.% |
|--------------------------|----------------------|--------------------------|------------------|
| E_{cap}, USD/F           | 0.17*10^{-3}         | 0.16*10^{-3}             | 0.79*10^{-3}     |

Additional research has been carried out to evaluate optimum load for Taunit CNFs. Cells based on the same technology and the same activated carbon as described above with different Taunit load were prepared and tested. Testing protocol included charge-discharge cycles at 3 mA/cm\(^2\). Specimens with 1, 3 and 10 wt% of CNF were prepared and tested. The results are shown at Fig. 4.

Figure 4. Load optimization for Taunit conductive additive. Current density 5 mA/cm\(^2\)

4. Analysis and discussion
Carried out experiments shows that structures with high aspect ratio (nanotubes and nanofibers) show much less amount of conductive additive to obtain the same electrochemical parameters than carbon black. Moreover, SWCNT with small diameter demonstrate the smallest load of additive to provide good electrochemical performance due to their ability to form percolation conducting cluster in electrode in less concentrations, that is needed for carbon blacks, forming long micelles at large concentrations. It is possible that percolation cluster in case of long nanostructures is formed not only for electron conductivity, but also for electrolyte transfer channels along the additive – Fig. 3 shows smaller diffusion (close to horizontal) part of the impedance curve for nanotubes and nanofibers, than for carbon black. According to Fig. 2, SWCNT-based electrode lost only 10% of its capacity during transition from 25 mA/cm\(^2\) to 167 mA/cm\(^2\) cycling current density, compared to 12% for Vulcan and 18% for Taunit. So SWCNT in electrode structure makes electrodes less sensitive to power rate increase, than in case of carbon blacks.

As a whole, specific capacity of nanotubes and nanofibers (Figs 2,4) increased in case of their optimal concentration because of the fact, that less mass of conductive additive (with low surface
area) allowed to increase portion of activated carbon having larger surface area and providing additional capacity.

The results obtained during long-term stability tests shows that capacity losses are smaller for carbon black than for nanotubes and nanofibers. But during short-term high current tests situation is reverse (Table 2). The possible cause is that accumulating of gas phase during electrolyte or active carbon degradation during cycling can occur in larger volumes for nanostructure-based electrodes due to higher amount of activated carbon – possible catalyst for electrolyte electrolysis. Additional problem for Taunit can be residual transition-metall based carbon fiber synthesis procatalyst. which also accelerates electrolyte degradation. Supplier data shows that CNFs contains about 95 mass.% of carbon and SWCNT – about 99 mass.%, though capacitive (upside) part of impedance curve on Fig 3 doesn’t demonstrate larger tilt angle for CNF, than for SWCNT or carbon black.

Economic estimation shows that despite lower cost, CNFs are less competitive with carbon black than SWCNT – much higher load of CNFs demanded. In addition, Tuball is supplied as uniform slurry of SWCNT on deionized water and CNFs – as powder-like material that can influence uniformity of conductive additive distribution in electrode structure during its formation. High-quality SWCNT can be competitive with traditional carbon blacks, especially in high-power applications.

5. Conclusions
High-quality SWCNTs are competitive with carbon blacks as conductive additives to supercapacitors electrodes due to larger amount of activated carbon which substitutes carbon black, increasing electrode active area. SWCNTs also can provide additional ion transport channels along themselves, which is necessary for better operation at high power rates. CNFs provide worse performance than SWCNT due to their lower aspect ratio. Higher optimal load of CNF worsens economic competitiveness of such electrodes compared both with SWCNT and carbon black. Larger share of activated carbon in SWCNT and CNF – based electrodes can increase degradation rate in long-term stability due to larger amount degradation centers on carbon surface.

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