HIGH POWER AND ENERGY DENSITY ULTRACAPACITORS

IN SPACE ENVIRONMENT

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INTRODUCTION

The electric double layer capacitors (EDLC) also known as ultra- or supercapacitors are widely used as energy storage devices (ESD) in applications that require additional power during short time. Ultracapacitors' high power density and long lifetime accompanied with a very low temperature dependency allows using them in various critical applications, among them space- and military industry.

Since first space flight, satellites and other space vehicles have carried rechargeable batteries to store electrical energy. While this is still true, the space industry has undergone tremendous changes and now demands significant performance improvements from battery systems that sometimes cannot be delivered by the existing battery technology. Today, spacecraft range in scope from small, cost-effective microsatellites that orbit Earth in a relatively low orbit to massive geostationary communications satellite systems, depending on segments of the space industry. Since the primary role of batteries in these craft is to provide power when the Earth's shadow blocks the satellite's exposure to the Sun, the performance demands vary significantly depending on the orbit and power needs of the satellite. According to Maxwell Technologies, Inc. (a global leader in ultracapacitor development and production), ultracapacitors have already been recognized as a standard energy storage and power delivery element for commercial applications, such as transportation systems, grid storage or renewable energy. It would be a reasonable expectation that with the development and space-proofing of ultracapacitors, these energy storage devices could be applied successfully in the space industry.

Due to late advancements in ultracapacitor cost and technology, ultracapacitors are being considered as viable alternatives to batteries in existing or future applications, where batteries fail to deliver the required performance. For instance, spacecraft developers and system integrators face increasing pressure to increase the technological and functional capability of the spacecraft while decreasing spacecraft volume and mass. Ultracapacitors with high specific energy and power could become practical alternative energy storage device to batteries due to their long cycle life and ability to supply high power at low mass and volume. To summarize, in space, smaller is usually better as it is much less expensive to manufacture and launch a small object than a big one. This trend is especially true with the advancing privatization of the space industry.

According to Shimizu and Underwood , ultracapacitor-based power subsystem is best suited for missions where the payloads, or the other subsystems on board, require high power for short operating times (milliseconds to a few minutes). This enables the operation of a high power consumption mission (e.g. radar imaging) on micro-satellite platforms and this may lead to a breakthrough in terms of platform choice for payloads [1]. To summarize, the ultracapacitor-based Secondary Power Source (SPS) offers the following benefits over rechargeable batteries (e.g. Li-ion batteries):

- longer cycle life under multiple charge/discharge cycles, hence longer satellite life time;
- ability to operate high power demanding payloads within lower mass and volume;
- high charge/discharge efficiency;
- easily measurable State of Charge (SoC), improving power distribution management;
- less sensitive to temperature, therefore simpler thermal system and lower mass;
- high power that is possible to obtain with the ultracaps for low temperatures (i.e. below zero).

The development of space-suitable ultracapacitors is a challenge as the requirements differ significantly from commercial applications. The technical objectives of Skeleton Technologies are aimed at developing more efficient, reliable and cost-competitive power delivery system. First application area, which Skeleton Technologies is targeting, is commercial satellite power systems to cover short term peak and back-up power needs.

Depending on the specific requirements reaching the technical objectives influences the industry in two ways:

1. space and weight constraints are crucial in upstream space components, by raising the energy and power density less volume and weight shall be used for the same component performance;
2. higher power density provides superior performance per mass and volume as potential alternative technologies.

Reaching the objectives provides a potential to open up new applications and provide enhanced functionalities in upstream power delivery systems. In perspective, successful R&D work will create novel market niches for Skeleton´s ultracapacitors.

The key element of the ultracapacitor is the electrochemical system and more precisely - the electrode material, i.e. porous carbon, which basically determines the energy density of ESD and also, has a major influence into the internal resistance and power capability of the ESD. In recent years, a lot of research has been carried out on the energy storage capability of high-surface carbons of different origin and different microstructure. One of them is the nanoporous carbide-derived carbon (CDC), which is a unique material with highly amorphous curved graphene-like structure [2].

CDC is produced from metal or metalloid carbide by extracting all non-carbon atoms from the crystal lattice of carbide that leaves behind the carbon skeleton [3]. Usually the extraction is performed by treating the carbide in chlorine flow at high temperature. The nanostructure, porosity and physical properties, e.g. density and electrical conductivity, of CDC are mainly determined by the structure and elemental composition of precursor carbide, but also by the method and conditions used to remove the non-carbon atoms. Most common carbides used for CDC are titanium and silicium carbides. By varying the above-mentioned parameters, it is possible to synthesise either completely amorphous porous carbon or carbon nanoparticles (e.g. nanobarrels, or nanotubes), or nano-diamond or perfect graphite. Most attractive so far have been the highly nanoporous CDC, which has an applicability in energy storage, purification of gases, or as a material for membranes and electromechanical actuators. The advantage of nanoporous CDC in comparison with the other activated high-surface carbon materials is the homogeneity and chemical purity, which is due to the highly ordered crystalline precursor – the metal carbide. Nanoporous CDC may also possess very narrow pore size distribution with more than 90% pores having diameters between 5 and 15 angstroms. Concerning the energy storage, the high content of nanopores gives opportunity for effective usage of carbon surface for the adsorption of electrolyte ions and, consequently, to reach the excellent energy densities [4-5].

This paper summarizes the research and development achievements of Skeleton Technologies in advanced ultracapacitor prototypes, so-called SpaceCaps. During the ESA PECS project Skeleton Technologies carried out application-oriented work in the field of CDC-based nanoporous electrode materials. Several CDC materials were synthesized and characterized by means of adsorption and electrochemical analysis. Selected carbon materials were used to manufacture ~100F SkelCap prototypes, which were systematically tested in wide range of currents and voltages and in wide range of temperatures.

EXPERIMENTAL

Manufacturing of Carbide-Derived Carbon Electrodes for the EDLC

Titanium carbide powder (APS <5µm) placed in the quartz-boat was reacted with a flow of chlorine gas (99.99%) for 1h in a horizontal quartz tube reactor at a chosen fixed or stepwise changed temperature within the interval of 400-1200°C. The by-product, titanium chloride, was removed by the stream of excess chlorine. During heating and cooling, the reactor was flushed with a slow stream of argon. After chlorination, all CDC products were annealed in hydrogen, whereby **TiC-3**, **TiC-4** and **TiC-6** were additionally post-treated (PT) by H_2O.

Carbon materials were characterized by means of low-temperature nitrogen adsorption (at 77K). From the adsorption isotherms were calculated specific surface areas (S_{BET}), total pore volumes (V_{total}) and micropore volumes (V_{micro}), which are presented in Table 1.

The CDC electrodes were made by cold rolling method from 92 %wt of CDC powder and 8 %wt of PTFE (as a 60% suspension in water) as described elsewhere [6]. Thereupon the ethanol was evaporated; the dry cake was then impregnated with heptane and shaped to a raw sheet. After removal of heptane at ~75ºC, the cake was rolled stepwise to the desired thickness, dried in vacuum at 170ºC and coated from one side with an aluminium layer with a thickness of ~2 µm by using a physical vapour deposition (PVD) method [7].

Table 1. Porosity parameters of CDC materials synthesized within the project

CDC	Origin carbide/$T_{synthesis}$	S_{BET}, m^2g^{-1}	V_{total}, cm^3g^{-1}	V_{micro}, cm^3g^{-1}
TiC-1	TiC/600	1200±50	0.56±0.02	0.52±0.02
TiC-2	TiC/800	1400±50	0.66±0.02	0.60±0.02
TiC-3	TiC/1000-800+PT	1500±50	0.70±0.02	0.62±0.02
TiC-4	TiC/1000+PT	1800±50	1.00±0.02	0.61±0.02
TiC-5	TiC/700	1300±50	0.62±0.02	0.57±0.02
TiC-6	TiC/800+PT	1450±50	0.68±0.02	0.62±0.02

Electrochemical Testing Procedures

Galvanostatic cycling at RT was performed in a voltage range of 1.425V to 2.85V with the current values from 50mA to 30A. At lower temperatures, the limiting factor was the discharge time t ≥ 0.5s and therefore the highest current values were not always used. Galvanostatic cycling tests were made at temperatures +60°C; +25°C; -15°C; -25°C and -40°C. In Fig. 1a, the constant current charge/discharge profile in time is shown. The linear voltage behaviour is typical for the pure EDL capacitors [8].

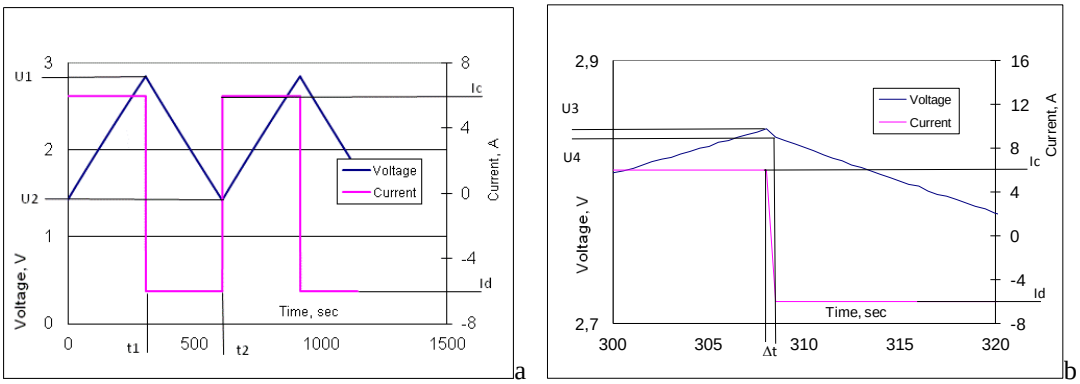


Fig. 1. Typical current-voltage profiles of the constant current charge/discharge tests of the ultracapacitor

Cycling voltammograms were recorded in voltage range of 0V to 2.85V with the applied voltage scan rates of 2 mV/s, 5 mV/s, 10 mV/s and 50mV/s at RT.

Electrochemical impedance spectroscopy (EIS) measurements were recorded at fixed ultracapacitor voltages in frequency range of 100kHz to 10mHz with AC signal of 5mV.

Self-discharge testing was performed at RT, whereby the capacitor was charged up and kept at fixed voltage of 2.85V during 30min. Thereafter the current was turned off and voltage decrease during 18h was recorded.

Numerical values of the capacitance, internal resistance, energy and power of ultracapacitors were calculated as described in details elsewhere [9]. The R value was calculated by IR drop, in accordance with Fig. 1b, whereas time interval Δt = 10msec was used. The delivered energy (E) and power (P) were calculated by using equations:

$$E = \int_{U1}^{U2} I\,dt \tag{1}$$

$$P = \frac{E}{t2-t1} \tag{2}$$

The energy and power characteristics at different application times were calculated by using linear Ragon plot as for example is presented in Fig. 2.

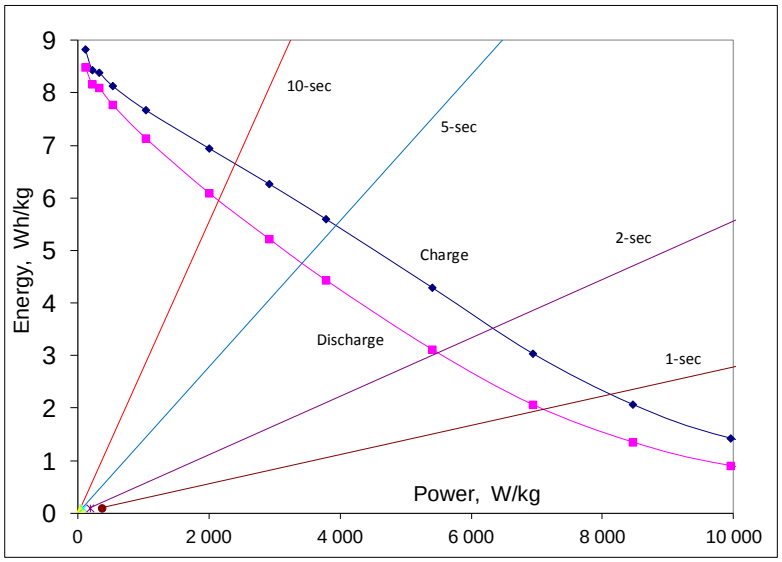


Fig. 2. Typical profile of energy-power dependency of the ultracapacitor as calculated from the constant current charge/discharge profiles. 10-, 5-, 2- and 1-second timelines are shown for the application time calculations

MODELING AND TESTING THE ELECTROCHEMICAL SYSTEMS FOR SPACECAP PROTOTYPE

Basic Principles for SpaceCap Development

One of the ideas, while designing the CDC-based electrochemical system for SpaceCap, was to be flexible and not to stay limited by certain application. It is known that the double-layer capacitance and inner resistance of carbon EDLC devices follow opposite trends. The smaller are pores, the higher capacitance (i.e. energy density). On the other hand, small pores increase the steric restrictions inside pores, which slows down the response of electrolyte ions to the changes of external potential field, which therefore increases inner resistance and worsens the power characteristics of EDLC. Therefore, to meet requirements of wide range of applications, selection of the electrode materials and balancing of the electrodes was reasonable to do in parallel for 3 different electrochemical systems:

1) the high-energy ultracapacitor (i.e. HE), fine-tuned to maximum energy density;
2) the high-power ultracapacitor (i.e. HP), fine-tuned to the lowest inner resistance;
3) the ultracapacitor with optimized energy and power characteristics (i.e. ME) to combine both, the good energy density and high specific power (Pmax).

The other principles applied, were that the high-energy capacitors require nanoporous (ultra-microporous) carbon, the high-power capacitors require micro-mesoporous carbon and the ultracapacitors with optimized energetic performance use basically microporous carbon electrodes with slightly modified pore size distribution for the better access of micropores.

Set-Up of EDLC Test-Cells

The EDLC test-cells (see Fig. 3) of 40x40x9 mm were specially designed to evaluate the different configurations of CDC electrode pairs and for modeling the performance of larger ultracapacitors at variable application conditions. They were also suitable for testing stacks of multiple electrode pairs. The energy and power performance as well as cycle characteristics of variable CDC electrode configurations were tested by these cells in wide temperature range of -40ºC to +60ºC.

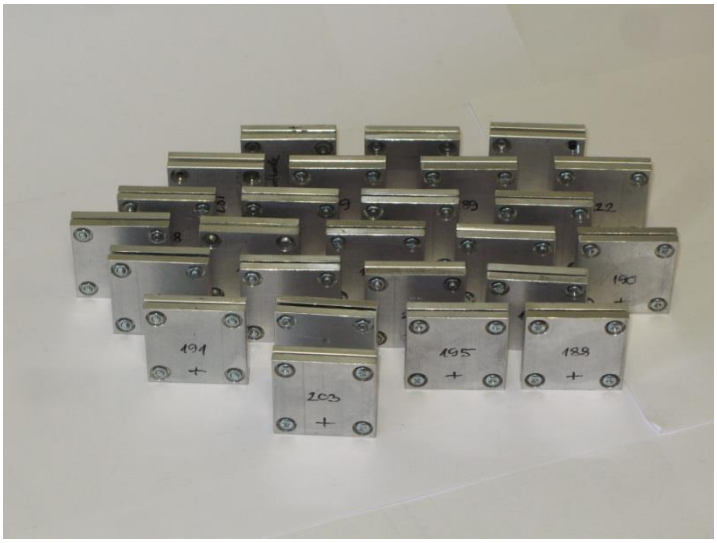


Fig. 3. EDLC test-cells used to research the performance of components and different electrochemical systems for SpaceCap prototype

Different configurations of the EDLC test-cells, comprising different electrode materials, different separators, different thickness of electrodes and current collectors, were assembled as presented in Table 2.

Table 2. General parameters of EDLC test-cells

EDLC #	Anode	Cathode	Separator / Current collector- µm	Electrode thickness [µm]	No. of electrode layers
203	**TiC-1**	**TiC-1**	TF4030 / Al-11	60	8+8
221	**TiC-1**	**TiC-1**	TF4030 / Al-11	62	8+8
186	**TiC-1**	**TiC-1**	TF4030 / Al-11	70	7+7
187	**TiC-1**	**TiC-1**	TF4030 / Al-11	90	6+6
188	**TiC-1**	**TiC-1**	TF4030 / Al-11	110	5+5
189	**TiC-1**	**TiC-1**	TF4030 / Al-11	130	4+4
225	**TiC-1**	**TiC-2**	TF4030 / Al-11	140	4+4
191	**TiC-3**	**TiC-4**	TF4030 / Al-14	60	8+8
192	**TiC-3**	**TiC-4**	Celgard 2500 / Al-11	60	8+8
211	**TiC-3**	**TiC-4**	TF4530 / Al-11	60	8+8
193	**TiC-3**	**TiC-3**	TF4030 / Al-11	60	8+8
195	**TiC-5**	**TiC-6**	TF4030 / Al-11	90	6+6
197	**TiC-6**	**TiC-6**	TF4030 / Al-11	90	6+6
167	**TiC-3**	**TiC-3**	TF4030 / Al-11	90	6+6

The electrodes, cut in a size of 18mm x 20mm, were collected in 4 to 8 electrode pairs, stacked and connected in parallel. Each electrode pair therein comprised the positively and negatively charged electrodes interleaved with the porous separator material, which was varied. The variety of separators tested included cellulose-based separator materials TF4030, TF4530 and polypropylene based Celgard 2500. Still, in most cases the cellulose-based separator was chosen, because of its good temperature endurance until at least +180°C. In comparison, the PP separator is stable only up to 140°C. For collecting the current in the capacitor, the aluminum foils with different thicknesses were tested. Based on electrical conductivity of aluminum it was estimated that sectional area of 11 µm thick foil should be sufficient for efficient current collection. According to calculations, the 11 µm thick foils contribute ca 5-10% to the overall internal resistance of the cell. Therefore, most of the experiments were done by using 11 µm foil. For

comparison, 14 µm thick Al-foil was tested (SkelCap #191), which, was expected to result in the lowest internal resistance and consequently the best power characteristics of respective test-cell. The active volume of all test-cells was kept in the range of 0.65 ± 0.05cm^3. Active volume includes electrodes, Al-current collectors and separators. After assembling the test cells were degassed in vacuum chamber at +105°C for 48h to remove trapped gasses and moisture. After that the cells were cooled down to RT, weighted to obtain the mass loss and finally filled with the electrolyte solution.

Electrochemical Characterisation

To achieve the best performance of EDLC in terms of energy and power density in wide temperature range many cell components were varied. The variables included different electrode materials (e.g. CDC with different pore-size distribution) and separator materials with different thickness. Also the thicknesses of electrodes and current collector was varied.

Influence of Carbon

Six different CDC carbons were synthesised and evaluated as EDLC electrode materials. The specific capacitance values of CDC materials evaluated in 2-electrode test-cells by using symmetric configuration of electrode pair are given in Table 2.

Table 2. EDL capacitance of CDC materials* expressed per one carbon electrode

CDC	Origin carbide/$T_{synthesis}$	Cv [F/cm^3]	Cg [F/g]
TiC-1	TiC/600	105	120
TiC-2	TiC/800	95	128
TiC-3	TiC/1000-800LPT	90	124
TiC-4	TiC/1000LPT	82	120
TiC-5	TiC/700	95	125
TiC-6	TiC/800LPT	95	132

*thickness of electrode ~100µm

All carbons had gravimetric capacitance (Cg) over 120F/g and volumetric capacitance (Cv) over 90F/cm^3, except the **TiC-4**, which had somewhat lower Cv (i.e. 82 F/cm^3) due to larger average pore size and, therefore, the lower bulk density of carbon. The highest volumetric capacitance had **TiC-1**, which also had the highest relative nanopore content and smallest nanopores (the lower the chlorination temperature, the smaller nanopores CDC has). The highest gravimetric capacitance was observed for **TiC-6**. **TiC-2**, which is made by using similar synthesis conditions as for **TiC-6**, but lacks the post-activation with water vapor, has slightly higher bulk density and, therefore, the lower Cg value. Additionally, different combinations of anode / cathode materials were investigated, which results are presented in next chapters.

Influence of The Electrode Thickness

The electrode thickness was varied in the range of 60µm to ~140µm. The purpose of the study was to establish the influence of CDC electrode thickness on different electrode characteristics (e.g. capacitance and resistance) and also on capacitor properties like energy- and power density. For these tests the highly nanoporous **TiC-1** carbon was chosen. Results reveal that this type carbon has very high volumetric capacitance ~100F/cm^3 and also outstanding gravimetric capacitance ~120F/g (calculated per weight of dry electrode) over all thickness range (cf. Fig. 4). The slightly bigger effect (C vs. thickness) was seen at thicknesses below 90 µm, which may be due to better packaging density and better electrical contacts between carbon particles in the electrode body. Nevertheless, the general observation was that specific capacitance has only little dependence on the electrode thickness.

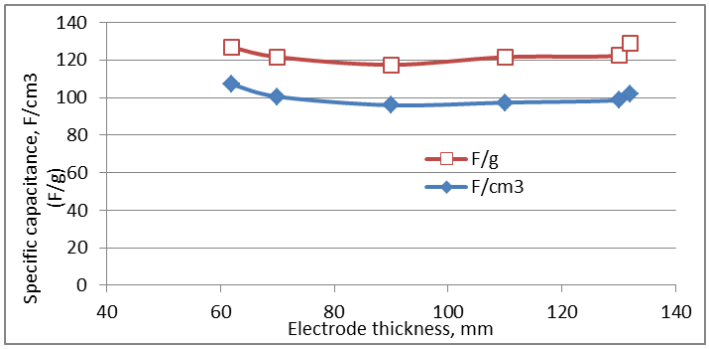


Fig. 4. Influence of electrode thickness on the gravimetric and volumetric capacitance of **TiC-1** electrodes tested at RT

Modeling the EDLC parameters also requires to know capacitance values per active volume and specific resistance per visible surface area of one electrode. The „active volume" as above-defined, means the volume of active components, i.e. the volume of unpackaged ultracapacitor (without external casing). In the figure below (Fig. 5) it is seen that ~100F/cm^3 per electrode volume results in approximately 14 - 16 F/cm^3 per active volume of capacitor. In the same time the specific resistance changes from 0.69 to 1.1 Ω*cm^2, i.e. the difference is about 1.6 fold. According to these observations the highest electrode thickness was selected for the high-energy capacitors.

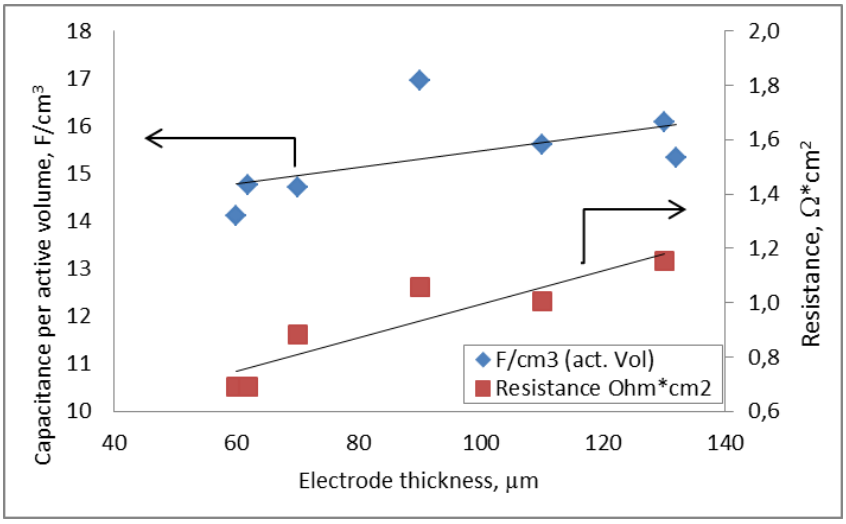


Fig. 5. Volumetric capacitance (per active volume) and specific resistance of EDL test-cells with different electrode thicknesses, obtained from the HE test-cell data at RT

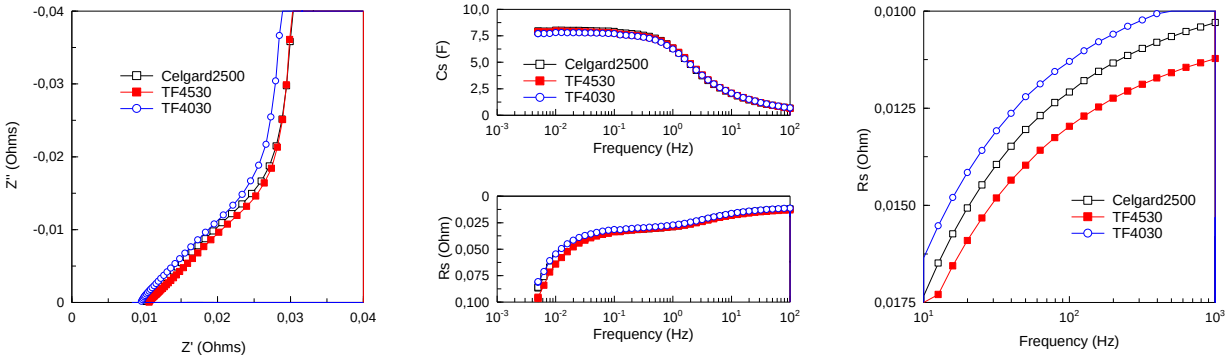
Influence of The Separator

There are a wide range of separators that qualify for the ultracapacitors. Our selection was made among the commercially available materials, whereby looking for the thicknesses of 30 µm and less. Based on the previous study, the thinner separator yields better power performance of the ultracapacitor [10]. Two classic materials - cellulosic paper from Nippon Kodoshi and polypropylene film from Celgard, - were tested in this project. For testing the separators, the thin CDC electrodes were used, which have the lowest internal resistance due to good packaging factor of carbon particles.

Table 3. Properties of different separators

Separator	Material	Thickness [µm]	Density [g/cm^3]	Porosity [%]
TF4030	Cellulosic Paper	30	0.40	55
TF4530	Cellulosic Paper	30	0.45	40
Celgard 2500	Polypropylene	25	0.51	55

The separator tests were performed by using **TiC-4** and **TiC-3** for negatively and positively charged electrodes, respectively. The thickness of electrodes in these tests was ~60-65 µm. The thinnest available electrodes were selected with the purpose to minimize the ohmic resistance across the electrodes and to evaluate the maximum performance of separators. According to the EIS results (Fig. 6a-c) the resistance, Rs, increases in the order: TF4030; Celgard 2500; TF4530, whereas Rs values at 100Hz are commonly used.



a b c

Fig. 6. Nyquist plot (a), capacitance *Cs* and resistance *Rs* vs. frequency (b) for test cells with different separator materials, calculated from EIS measurements at 2.7V DC; in (c) the high-frequency part of Rs vs. frequency is magnified

Additionally, with different separators the self-discharge tests during 2 days were performed. As it can be seen in Fig. 7, the paper and PP-film type separators behave rather similarly. During the first hours the decrease of voltage for paper type separator was little bit faster, which could be due to funcional groups on the cellulose material. However, after 40-50 hours the voltage of capacitors was almost the same.

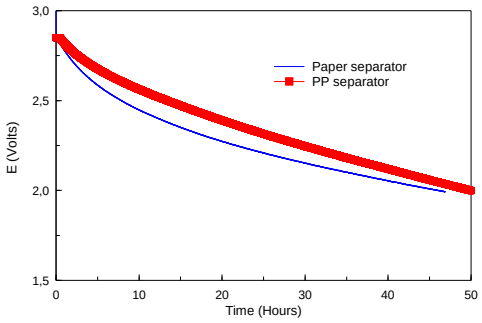


Fig. 7. Self-discharge test for two different type of separator materials

Generally, it may be concluded that there is practically no difference in the ultracapacitor electrochemical properties between selected separator materials. Nevertheless, for building the SpaceCap prototype the TF4030 paper type separator was selected, because it has higher thermal stability, which enables to use higher temperature during degassing of the supercapacitor and guarantees the better drying of the nanoporous electrodes in vacuum prior to filling with electrolyte.

Summary of the test-cells evaluation

Electrochemical testing of the test cells and capacitor prototypes by using DC- currents at different temperatures where shown in tables 5 and 6. The most important characteristics of test-cells including the temperature dependencies of capacitance and inner resistance (Table 5) and the temperature dependency of power characteristics at 1-second and 10-seconds applications (Table 6).

Table 5. Capacitance (C) and inner resistance (R) of the 10F cells evaluated with constant current charge discharge regimes at different temperatures

Test-cell	+60°C		+25°C		-15°C		-25°C		-40°C	
#	C [F]	R [mΩ]	C [F]	R [mΩ]	C [F]	R [mΩ]	C [F]	R [mΩ]	C [F]	R [mΩ]
High Energy Type (HE)										
203	9.4	22	9.6	24	8.8	39	7.6	54	3.8	102
221	9.4	25	9.7	24	8.7	41	7.4	61	4.8	101
186	10.0	26	10.0	35	8.8	60	7.3	84	2.5	126
187	10.6	33	10.9	49	9.4	57	N/A	N/A	N/A	N/A
188	10.7	46	10.8	56	9.2	119	8.5	141	3.6	235
189	10.2	98	10.4	80	9.0	143	8.3	157	3.6	307
225	10.0	73	10.3	69	9.9	85	9.4	134	7.0	226
High Power Type (HP)										
192	7.7	26	7.9	29	7.7	33	7.7	32	6.5	55
211	7.7	16	7.9	19	7.7	27	7.7	30	7.7	53
191	7.6	15	7.6	30	7.5	25	7.6	50	N/A	N/A
Optimised Energy and Power (ME)										
193	8.9	29	9.1	31	8.7	37	7.7	44	4.8	116
195	10.4	27	10.5	29	10.1	47	9.7	59	5.6	123
197	10.2	24	10.6	27	9.9	51	9.8	58	5.1	N/A
167	8.9	23	8.9	26	8.5	35	8.3	42	N/A	N/A

„N/A“ not measured

Table 6. 10-sec and 1-second power values (W/g per active weight) calculated for dischargetimes 10-s and 1-s at different temperatures

Test-cell	+60°C		+25°C		-15°C		-25°C		-40°C	
#	10-s	1-s	10-s	1-s	10-s	1-s	10-s	1-s	10-s	1-s
High Energy Type (HE)										
203	2.4	13.8	2.3	12.7	1.7	8.1	1.3	5.9	0.6	2.7
221	2.3	13.5	2.3	13.3	1.6	7.6	1.2	5.1	0.7	2.6
186	1.9	10.2	1.9	8.4	1.2	4.8	0.9	3.4	0.4	1.8
187	2.4	10.9	2.2	8.3	1.5	5.7	N/A	N/A	N/A	N/A
188	2.0	8.1	1.9	6.8	1.1	3.5	1.0	3.0	0.4	1.5
189	2.0	6.1	2.0	6.1	1.3	3.6	1.1	3.0	0.4	1.3
225	2.0	6.6	2.1	6.3	1.7	4.9	1.4	3.7	0.9	2.2
High Power Type (HP)										
192	2.0	12.6	2.0	11.9	1.9	10.2	1.9	9.8	1.6	6.5
211	2.2	16.0	2.3	15.0	2.1	12.0	2.1	10.8	1.8	7.4
191	3.1	21.9	3.0	17.5	2.9	16.7	2.7	12.7	N/A	N/A
Optimised Energy and Power (ME)										
193	3.0	16.9	3.0	16.1	2.7	12.7	2.2	10.6	1.0	4.7
195	2.6	13.5	2.6	12.6	2.1	8.3	1.8	6.8	0.9	3.1
197	2.7	14.6	2.7	13.6	2.2	8.3	1.9	7.3	0.5	1.2
167	2.2	12.9	1.9	10.2	1.4	5.7	1.8	8.0	N/A	N/A

„N/A“ not available

From the galvanostatic cycling (GC) with DC-current and impedance measurements (EIS), carried out at the room temperature, the average specific capacitance values per dry electrode were calculated (see Fig. 7). In most cases the EIS values are slightly smaller than respective GC values, which is due to the different testing conditions. Intrestingly, the capacitance values by both methods are almost overlapping for the carbon electrodes having cathode material with larger average pore size (**TiC-4**) in HP-type cells.

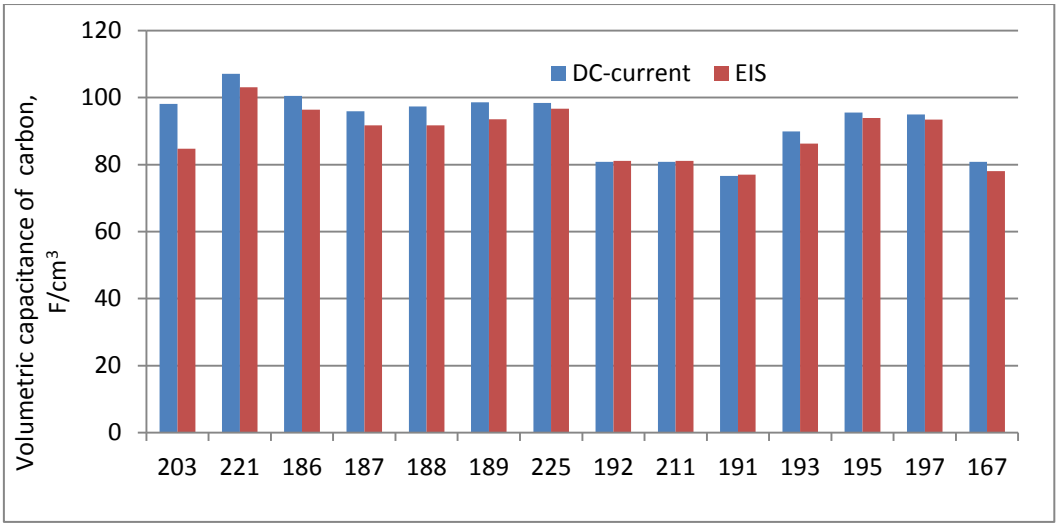


Fig. 7. The average volumetric capacitance of dry carbon electrode in the test cells

On the graphs below, the temperature-dependencies of volumetric capacitance per active volume (Fig. 8) and internal resistance, calculated per visible surface area of the one electrode, (Fig. 9) are shown for all test-cells of this project.

The results were divided in two different groups according to classification electrochemical systems explained before: HE-type cells on one plot (a) and the rest of cells including HP- and ME-cells – on the other plot (b). High-energy cells (i.e. HE) characterised in Fig. 8a and Fig. 9a are composed of highly nanoporous CDC electrodes (**TiC-1**), in which the pore resistance obviously is highest due to small pore dimensions and defficiency of transport pores. Therefore, this type cells showed more noticeable temperature dependence, particularly below -20°C. Significantly less temperature dependency has a cell **#225**, where the cathode **TiC-1** was replaced by **TiC-2**, whereas the volumetric capacitance of 15F/cm^3 (per active volume) at RT remains almost the same as of the cell **#189** with **TiC-1** electrodes having the similar electrode thickness (see Fig. 8a). This lower temperature dependency is best explained by slightly larger nanopores of **TiC-2** that seems to have very sensitive influency for TEMABF4/AN electrolyte especially at low (below -10°C) temperetures. This interesting phenomenon was used for further designing of SpaceCap prototypes.

The HP-type cells (Fig. 8b) have large variation in volumetric capacitance (10-14F/cm^3) values, but their temperature dependency is very low. These cells use the CDC electrodes with high pore volume and noticeably larger micropores, which probably are better accessible by the electrolyte ions also at lower temperatures. The ME-type cells (Fig. 8b) behave very similarly and have capacitance in the range of 14-15F/cm^3. The temperature dependency of ME-type cells is somewhat similar to HP cells at temperatures above -20°C. However, rapid decrease of capacitance is observed below -20°C, whereas HP-type cells maintain rather stable capacitance over the all temperature range tested, i.e. -40°C to +60°C.

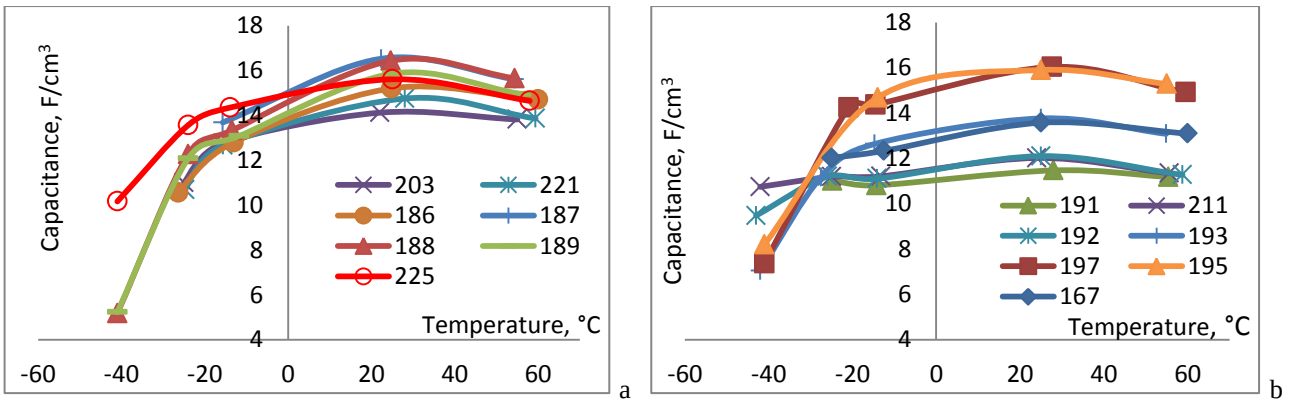


Fig. 8. Volumetric capacitance per active volume of the HE- (a), HP- and ME-type (b) test-cells at different temperatures

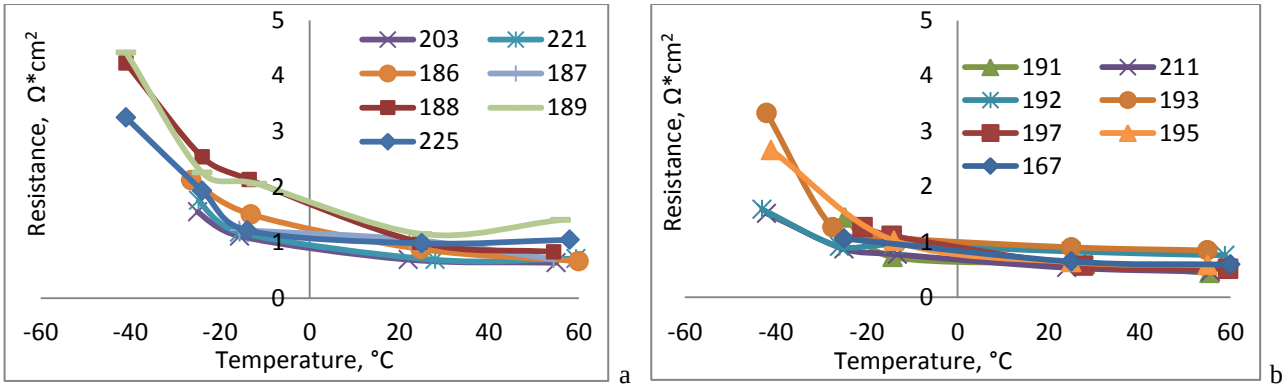


Fig. 9. Specific resistance (per visible surface area) of the HE (a), HP and ME (b) type test-cells at different temperatures

The cycling voltammograms (CV) for a cell #186, expressed as a capacitance vs. voltage, are shown in Fig. 10. It can be seen that the capacitance in most cases does not depend on the applied voltage. However, a little distortion effect is observed at higher scan rates (>10mV/s), which is due to steric hindrance of electrolyte ions in the nanopores of carbon electrodes.

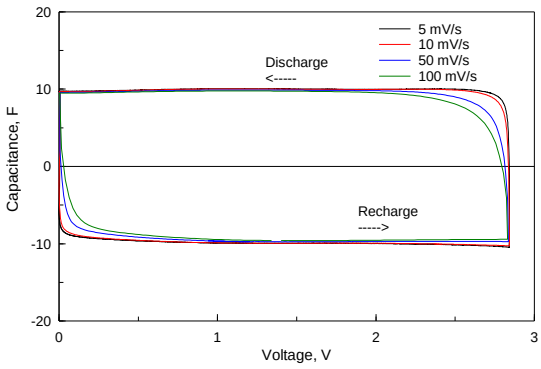


Fig. 10. Capacitance dependency for the HE-type ultracapacitor **#186** at different voltage scan rate calculated from the CV measurements

SPACECAP PROTOTYPE

Design and Structure of SpaceCap Prototypes

The SpaceCap prototypes were designed with prismatic shape (see Figs. 11-12). The casing was made from stainless steel (SS304) with dimensions of 27×32×16 mm (H×L×W) and wall-thickness of 0.3mm, which assures the mechanical strength of the capacitor and possibly gives better radiation resistance compared to aluminium casings, which is a common standard in supercapacitor industry. The ultracapacitor current terminals were made from the aluminium rod (6082-T6) and threaded with the M3. The terminals were hermetically sealed by EPDM resins, which were placed outside of casing, and electrically isolated by PTFE washer inside of the casing.

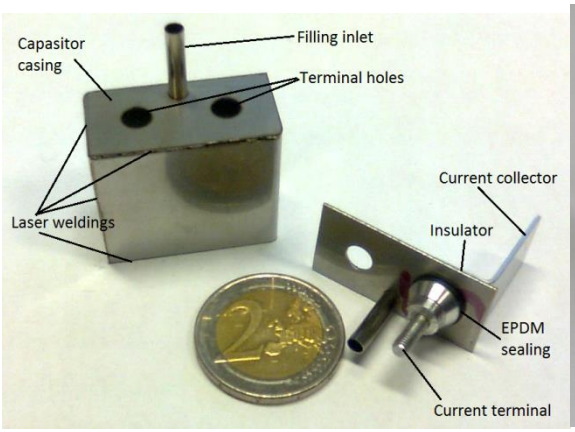


Fig. 11. Picture of the casing components of a SpaceCap prototype

Fig. 12. Completed SpaceCap prototypes

According to the test-cell results it was confirmed that highly nanoporous carbon material such as **TiC-1** is a suitable electrode material for high-energy **HE ultracapacitors**. Furthermore, it was found out that using thinner electrodes together with the highly nano-porous carbon the power performance can be significantly increased. Additionally, by using of thinner electrodes, the stored energy of capacitor slightly decreases; because of less carbon material is used in the same volume of capacitor. Finally, it was established that for the high-energy ultracapacitor the thicker electrodes must be used. That guarantees the highest energy capacity for the ultracapacitor. It was observed that if carbon **TiC-1** is used for anode and cathode electrodes, the respective capacitor has significant temperature dependency, which does not depend on the electrode thickness. Therefore, instead of **TiC-1** it was reasonable to use for the cathode of HE ultracapacitor the **TiC-2** carbon with slightly increased average pore size.

For the optimized energy/power **ME ultracapacitor**s the **TiC-3**, **TiC-5** and **TiC-6** carbons were suitable, because these materials have slightly larger nano-pores and less pore resistance compared to **TiC-1**. The electrode thickness for ME capacitors was chosen 90-100µm, because it guarantees higher energy and power density compared to thicker electrodes.

For the high power **HP ultracapacitor**s the **TiC-4** carbon with the highest pore volume was selected. Evaluation of test-cells revealed that the lower electrode thickness, the less the internal resistance and higher power density of the ultracapacitor. The negative aspect is that the lower electrode thickness also needs more composition materials (e.g. separator, aluminum foil) and, therefore, the "ballast" weight in capacitor increases and overall capacitance of the ultracapacitor decreases.

The electrochemical system of SpaceCap prototypes is given in the Table 7 below. Total volume of each prototype is 14.3 cm^3. In all capacitors the 1.8M $TEMABF_4$ / acetonitrile electrolyte and TF4030 separator were used. Different types of prototypes use different electrode materials and electrode thicknesses that results in different capacitance and internal resistance of the SpaceCap prototypes.

Table 7. List of the SpaceCap prototypes.

Type	SpaceCap #	Anode/Cathode	Electrode thickness [µm]	Al foil thickness [µm]	Total weight [g]
HE-1	220	TiC-1/TiC-2	130/144	11	25.0
HE-2	230	TiC-1/TiC-2	130/144	11	25.6
ME-2	227	TiC-6/TiC-3	90/100	11	25.5
ME-3	228	TiC-6/TiC-3	90/100	11	25.3
ME-4	229	TiC-3/TiC-3	90/100	11	25.3
HP-1	223	TiC-3/TiC-4	60/66	14	25.4
HP-2	226	TiC-3/TiC-4	60/66	14	25.2

Electrochemical Performance of SpaceCap Prototypes

Procedures used to measure the electrochemical characteristics of SpaceCap prototypes were described above. Fig. 13 shows that stable capacitance is observed for all SpaceCaps in voltage range of 0-2.85V. General energetic characteristics of prototypes are presented in Tables 8-9.

Table 8. Electrochemical testing results of the HE, ME and HP ultracapacitor prototypes with comparison to commercially available analogues

SpaceCap	At DC current		EIS (2.85V)		Energy density		Power density	
#	C [F]	R [mΩ]	C [F]	R [mΩ]	[Wh/L]	[Wh/kg]	[kW/kg]	[kW/L]
230	132.5	4.5	132.5	3.6	10.5	5.8	17.7	32
220	136.1	4.4	132.9	3.6	10.5	6.0	18.3	32
227	124.6	3.3	121.2	2.9	9.8	5.5	24.1	43
228	124.5	2.4	124.7	1.8	9.8	5.5	33.1	59
229	121.6	2.5	121.2	1.8	9.6	5.4	32.1	57
223	97.5	1.9	100.7	1.2	7.9	4.5	42.7	75
226	101.1	1.8	103.3	1.2	8.1	4.6	44.9	79
BCAP0100					5.9	4.4	5.3	7.1
BCAP0150					6.1	4.7	3.7	4.8
RSC2R7107SR					5.9	5.1	24.6	28.8

The SpaceCap prototypes were tested at room temperature by using of DC current in the interval of 0.5A to 30A and EIS measurement techniques at 1.5V DC and 2.85V DC. The capacitance and resistance values at different temperatures are presented in Table 9.

Table 9.Temperature dependence of the HE, HP and ME ultracapacitor prototypes

SpaceCap	-25°C		+25°C		+60°C	
#	C [F]	R [mΩ]	C [F]	R [mΩ]	C [F]	R [mΩ]
230 HE	123.2	7.9	132.5	4.5	-	-
227 ME	121.3	7.2	124.6	3.3	124.2	2.2
223 HP	97.0	3.8	97.5	1.9	96.6	1.6

- not measured

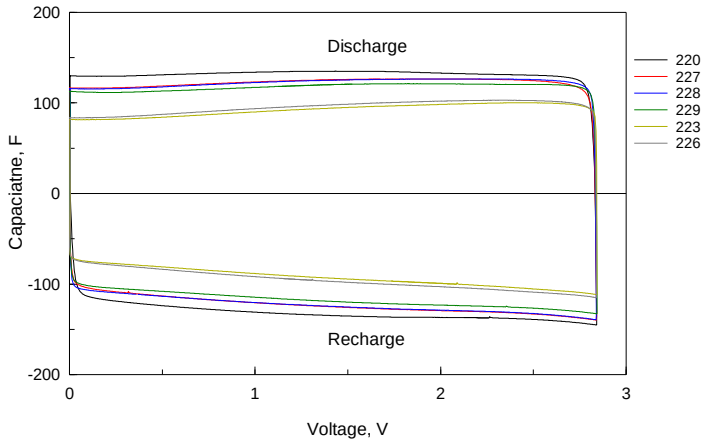


Fig. 13. Capacitance of different ultracapacitor samples (noted on figure) at voltage scan rate 10mV/s calculated from the CV measurements

CONCLUSION

Skeleton Technologies has achieved a significant breakthrough in ultracapacitors, which can create novel applications and enhance the technological capabilities by providing efficient and reliable energy storage and pulsed power for a variety of applications. The HE prototypes developed possess the energy density of 10.8 Wh/L, which exceeds by ~50% of commercially available devices with similar energy capacity. The HP prototypes developed possess the power density of ~79kW/L, which exceeds by 4 times the commercially available devices with similar energy capacity.

Further R&D has to be carried out in order to move from a single cell prototype level towards a reliable product level and assemble working modules from the prototype. Also in parallel with the latter further research has to be done in order to achieve beyond state-of-the-art electrochemical characteristics. This is expected to be achieved by modifying carbon pore size and structure. Also it is of critical importance to move forward to the electrochemical systems of the highest purity that would enable to raise the working voltage of ultracapacitor cells.

REFERENCES

[1] T. Shimizu, C. Underwood, "Super-capacitor energy storage for micro-satellites: Development and potential mission applications," in proceedings of 62nd International Astronautical Congress; Cape Town, Republic of South Africa; October 3-7, 2011. University of Surrey, published by IAF, pp. 1-9, 2011.

[2] M. Arulepp, J. Leis, M. Käärik, A. Perkson, „Carbide-derived carbons as capacitor materials," in proceedings of The 6th International Symposium on Large EC Capacitors: Technology and Applications. Advanced Automotive Battery and EC Capacitor Conference; Omni Orlando Resort, Orlando, Florida, USA; May 17-21, 2010. Orlando, Florida, USA: Advanced Automotive Batteries, pp. 55-64, 2010.

[3] G. Yushin, A. Nikitin, Y. Gogotsi, "Carbide-derived carbon," in *Nanomaterials Handbook*. Y. Gogotsi, Ed. CRC Taylor&Francis, pp. 269-273, 2006.

[4] J. Chmiola, G. Yushin, Y. Gogotsi, C. Portet, P. Simon, P.L. Taberna, „Anomalous increase in carbon capacitance at pore sizes less than 1 nanometer," *Science*, vol. 313, pp. 1760-1763, 2006.

[5] R. Dash, J. Chmiola, G. Yushin, Y. Gogotsi, G. Laudisio, J. Singer, J. Fischer, S. Kucheyev, „Titanium carbide derived nanoporous carbon for energy-related applications," *Carbon*, vol. 44, pp. 2489-2497, 2006.

[6] J. Leis, M. Arulepp, A. Kuura, M. Lätt, E. Lust, „Electrical double-layer characteristics of novel carbide-derived carbon materials," *Carbon*, vol. 44, pp. 2122-2129, 2006.

[7] K. Rumma, A. Kuura, A. Perkson, J. Leis, M. Arulepp, „The role of PVD aluminium coating to the performance of EDL capacitors," in proceedings of The Baltic Electrochemistry Conference; Tartu, Estonia, April 30, 2008.

[8] BE. Conway, *Electrochemical Supercapacitors*. *Scientific Fundamentals and Technological Applications*. New York: Kluwer Academic Publishers/Plenum, 1999.

[9] A. Arulepp, L. Permann, J. Leis, A. Perkson, K. Rumma, A. Jänes, E. Lust, „Influence of the solvent properties on the characteristics of a double layer capacitor," *J. Power Sources*, vol. 133, pp. 320-328, 2004.

[10] A. Jänes, K. Tõnurist, T. Thomberg, E. Lust, „Comparison of Electrospun and Commercially Available Separator Materials for Supercapacitors," in ECS Transactions: 215th ECS Meeting; San Francisco, CA, USA; May 24 - May 29, 2009. J. Weidner, Ed. *ECS Trans.*, vol. 30, pp. 23-32, 2009.