

LAPPEENRANTA UNIVERSITY OF TECHNOLOGY

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CARBON NANOTUBES AS MATERIAL FOR SUPERCAPACITOR ELECTRODES

Examiners: Professor Jari Backman

Professor Juha Pyrhönen

Lappeenranta, 2013

ABSTRACT

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Master's Thesis

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Electrochemical double-layer supercapacitors have an intermediate position between rechargeable batteries, which can store high amounts of energy, and dielectric capacitors, which have high output power. Supercapacitors are widely suggested to be used in automobiles (recuperation during braking, facilitate engine starting, electric stabilization of the system), industry (forklifts, elevators), hybrid off-road machinery and also in consumer electronics.

Supercapacitor electrodes require highly porous material. Typically, activated carbon is used. Specific surface area of activated carbon is approximately 1000 m² per gram. Carbon nanotubes represent one of prospective materials. According to numerous studies this material allows to improve the properties of supercapacitors. The task of this Master's Thesis was to test multiwalled carbon nanotubes and become confident with the testing methods.

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Andrey Chekannikov

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LIST OF ABBREVIATIONS

EDLC	Electrochemical double-layer capacitor
RES	Renewable energy sources
CNT	Carbon nanotubes
EV	Electric vehicle
DVR	Dynamic voltage restorer
MWCNT	Multiwalled carbon nanotubes
SWCNT	Singlewalled carbon nanotubes
PV	Photovoltaic panel
PP	Polypropene
LED	Light-emitting diodes

LIST OF SYMBOLS

C	Capacitance (F)
ε	Dielectric constant
S'	Specific surface area (m^2/g)
d	The distance between the plates of a supercapacitor (m)
Q	Charge, stored in the supercapacitor electrodes (C)
U	Voltage of the supercapacitor (V)
E_s	Electrode surface
\parallel	Electrical double-layer
K^+ and A^-	Cations and anions of the electrolyte
P	The power density (kW/kg)
i	Current (A)
τ	Time (s)
U_{\max}	Maximum voltage (V)
U_{\min}	Minimum voltage (V)
m	Mass or volume of the electrolyte (kg or L)
R_{sup}	Internal resistance of a supercapacitor (Ohm)
R_{load}	Load resistance (Ohm)
η	Efficiency
E	Energy (J)
s	Sweep rate in (V/s)
D	Outside diameter (nm)
d	Inside diameter (nm)
l	Length (cm)
ρ	Density (g/cm^3)
C_{sp}	Specific capacitance ($\mu\text{F}/\text{cm}^2$)
r_1	Inside radius (cm)
r_2	Outside radius (cm)
S	Surface area (cm^2)
V	Volume (cm^3)

1 INTRODUCTION

One of the modern areas of research in the field of rechargeable electrical energy storage devices is the research concentrating on the development of electrochemical supercapacitors. There are also other names for supercapacitors such as ultracapacitors or electrochemical double-layer capacitors.

Supercapacitor is a device in which quasi-reversible electrochemical charge-discharge processes take place. The shapes of galvanostatic charging and discharging curves of these processes are close to linear [1].

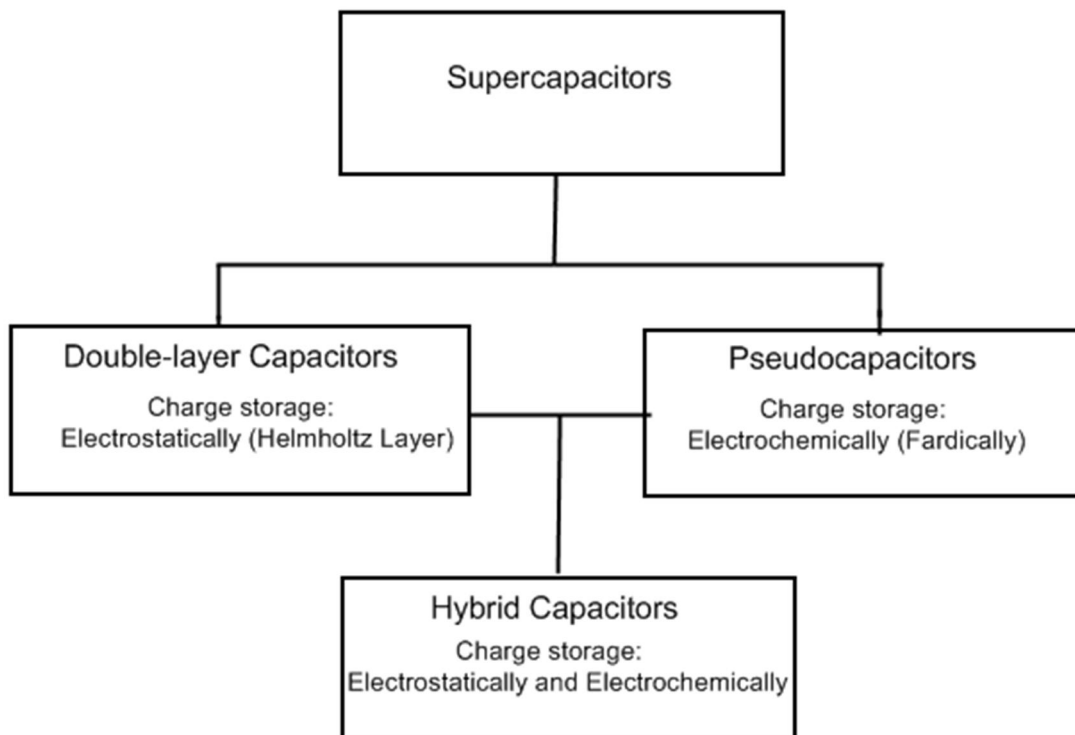


Fig. 1 Hierarchical classification of supercapacitors and related types (modified from [35])

Electrochemical double-layer supercapacitors have an intermediate position between rechargeable batteries, which can store a high amount of energy, and dielectric capacitors,

which have high output power. Supercapacitors are widely suggested for automobile energy efficiency improvement which can take place e.g. in recuperation during braking. Energy storages also facilitate engine starting and electric stabilization of the system. They are also used in the industry in forklifts and elevators and also in consumer electronics e.g. as computer components. Modern supercapacitors have high cycle life – about 700000 cycles, which is from 5 to 20 years of work depending strongly on the level of load. They have low-cost calculated per one cycle of use. Usually companies give value of the cycles number before decreasing of the capacitance on 20% and increasing of the internal resistance on 100%, Also, this number depends on operation power and temperature. They also have ability to work under extreme conditions e.g. at amplitudes of currents and voltage drops in extreme temperature conditions. They are also mad of environmentally-friendly materials. Supercapacitors that best meet these requirements use activated carbon as a primary electrode material and a water solution as an electrolyte.

1.1 History

The possibility of storing electrical energy in an electric double layer which is formed in a solid submerged in the electrolyte has been known since the nineteenth century. The first report about an electrical device based on the double-layer storage was made in 1957 by H.I. Becker from General Electric (U.S. patent 2800616). However, Becker's device was impractical and it was not commercialized. Later Becker appreciated large values of capacitance which were achieved by Robert A. Rightmire, a chemist from the Standard Oil Company of Ohio (SOHIO).

Fig. 1.

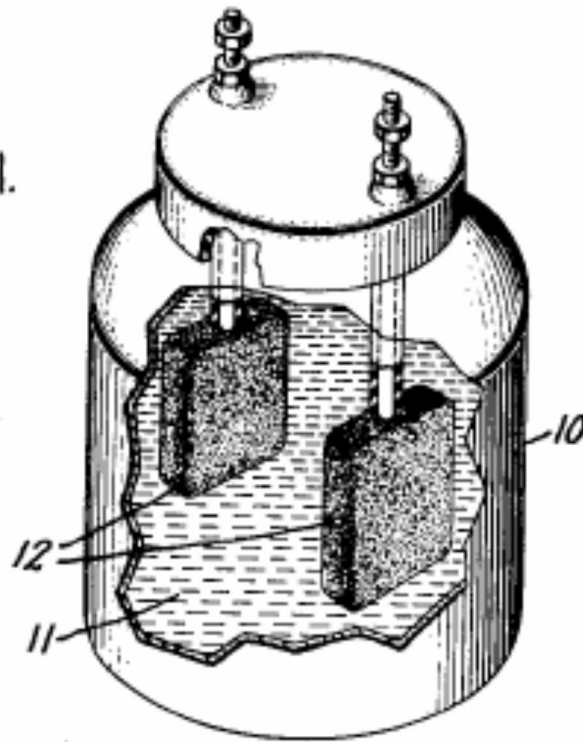


Fig. 2 The capacitor patented by General Electric (10- can, 11- electrolyte, 12- electrodes) [5]

In 1970 SOHIO (USA) presented an industrial supercapacitor which was based on high-surface area carbon electrodes and tetra-alkyl ammonium salt electrolyte. Because of cutting of financing in 1971 SOHIO shared a license with NEC (Nippon Electric Company). NEC gave to the device the name supercapacitor and successfully introduced it to the market. Independently of foreign developers in 1974 under the leadership of Dr. Alexander Ivanov supercapacitors were created in the USSR. During the period from 1975 to 1981 Conway in collaboration with the other researchers developed the new type of the supercapacitor, which was based on pseudocapacitance principles [2]. In this supercapacitor a redox process took place mainly in the surface layers of the electrode. To provide the fast Faraday reaction there was used a redox system based on mixed ruthenium oxide (RuO_x). Sulphuric acid was used to ensure high specific capacitance ($> 700 \text{ F/g}$) and low internal resistance. Further researches were focused on developing electrodes which were based on NiO_x , MnO_2 [3] and with intercalated lithium (LiMnO_2) [4].

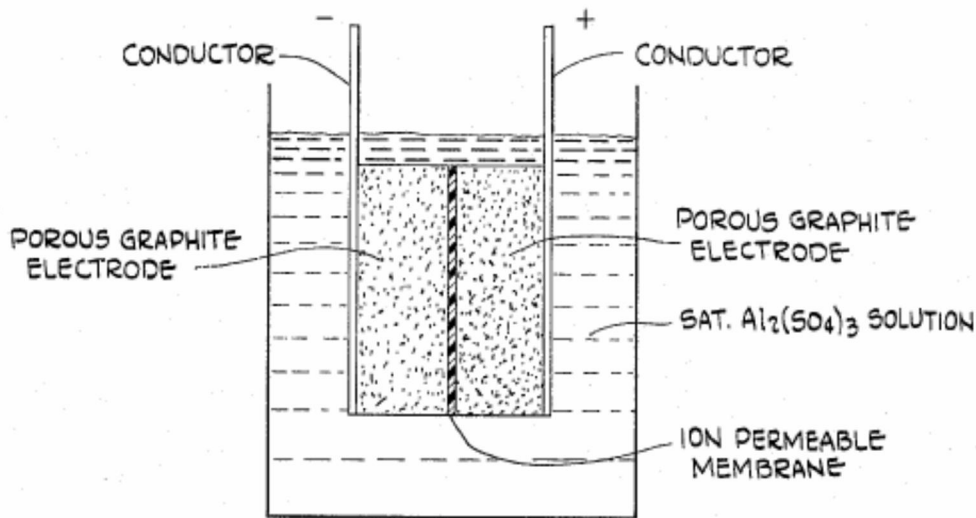


Fig. 3 An electrolytic energy storage device patented by SOHIO [6]

In the 90s years of the 20th century researches in the field of supercapacitors began to increase rapidly because of the need of power sources for hybrid electric vehicles. The United States Department of Energy (DoE) in 1998-2003 initiated a short-term, and after 2003 a long-term research on this topic. Nowadays, manufacturers produce so called “Big” industrial supercapacitors which can store tens of kilojoules of energy. They also produce systems which can store more than 1 MJ of energy.

Currently, a number of companies around the world produce supercapacitors in a commercial capacity. Japanese companies NEC and Panasonic have been producing supercapacitors components since the 1980's. In the United States components are produced by Epcos, ELNA, AVX, and Cooper, while Evans and Maxwell produce integrated modules which include voltage balancing circuitry. Kold Ban International sells a supercapacitor module developed specially for starting internal combustion engines in cold weather. Cap-XX from Australia and Ness Capacitor Co. from Korea offer a range of components. Tavrma (Canada) produces a range of modules. Russian company ESMA manufactures a wide variety of electrochemical double-layer capacitors modules for applications in power quality, electric vehicles, and for starting internal combustion engines.

Table 1 Commercially available capacitor properties [36]

Manufacturer	Capacitance (F)	Voltage (V)	Equivalent Series Resistance (m Ω)
Power Star China	50 300 600	2.7 2.7 2.7	1
Panasonic	0.022-70	1-5.5	200-350
Maxwell	63 94	125 75	18 15
Vinatech	10-600 3-350	2.3 2.7	20-400 8-90
Nesscap	33 51	15 340	27 19

The specific capacitance of commercial supercapacitors usually varies between 3.8 F/g (Nesscap 50 F cell) to 2 F/g (Nesscap 5 F cell). Vinatech cells show approximately similar results. Electrochemical supercapacitors are a special group of energy storage devices, which occupies an intermediate position between conventional capacitors and batteries, as shown on the Ragone chart (Fig. 4).

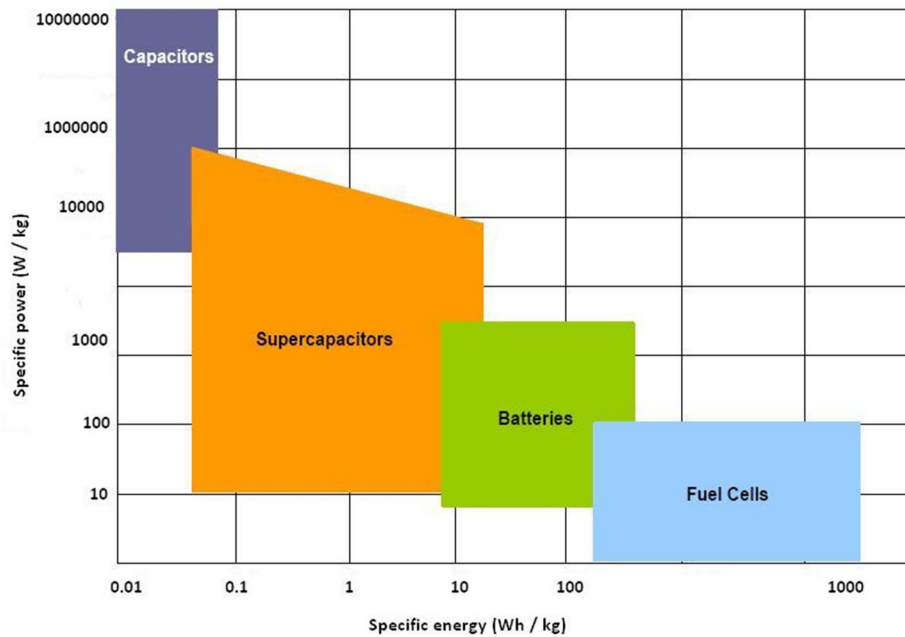


Fig. 4 Ragone chart for various energy storage devices (modified from [7])

The specific energy of supercapacitors is close to the specific energy of rechargeable batteries and the specific power is close to the specific power of conventional capacitors. The advantage of supercapacitors over rechargeable batteries is the ability to work at low temperatures without significant reduction in performance. Another advantage is much higher amount of cycles (more than 10 years or 100,000 full charge-discharge cycles) and higher energy output rate. Compared to conventional capacitors supercapacitors have higher capacitance and pulse duration. For example in the power range of a sound amplifier up to 1000 W, which has traditionally used aluminium capacitors, supercapacitors show higher voltage at the end of the 100 millisecond discharge, and, therefore, more power. Table 1 shows a comparison of the properties, performance and efficiency between supercapacitor, dielectric capacitor and rechargeable battery.

Table 2 Comparison of Capacitor, Supercapacitor and Battery [36]

Parameters	Dielectric Capacitor	Supercapacitor	Battery
Charge Time	$10^{-5} - 10^{-3}$ sec	1 – 30 sec	3 – 4 hrs
Discharge Time	$10^{-5} - 10^{-3}$ sec	1 – 30 sec	1 – 5 hrs
Energy Density (W·h / kg)	< 0.1	1 –10	20 – 100
Power Density (W / kg)	> 10 000	1000 – 2000	50 – 200
Cycle life	> 500 000	> 100 000	500 – 2000
Charge / Discharge Efficiency	~ 1.0	0.90 ~ 0.95	0.7 ~ 0.85

1.2 Principles of work

Operation principles of EDLC are based on the electrical double layer. Helmholtz's model has been developed over the years to explain the phenomena of the electrical double layer. The electrical double layer is formed by opposite charges at the interface between two phases – the electrode / electrolyte. Those two phases have different natures of conductivity (electrons and ions) as well as different physical states (solid and liquid). As well as in traditional capacitors, in double-layer supercapacitor electrostatic storage of charges is used. During charging and discharging there is no electrochemical reaction, but a process of charging and discharging of the electrical double layer takes place.

Extremely high capacitance of this electrochemical double-layer capacitor, can reach up to 250 farads per gram of active substance because of two factors:

- Very small distance between the plates of the supercapacitor, which is equal to the thickness of the electrical double layer (depends on the size of ions and concentration of the electrolyte).
- The largest possible contact area between the materials, which is achieved using nanostructured porous material with a surface area up to 2600 m²/g immersed in conductive liquid.

The specific capacitance (capacitance C per mass m) can be calculated by

$$\frac{C}{m} = \frac{\varepsilon \cdot S'}{d} \quad (1)$$

ε – Dielectric constant

S' – Specific surface area (m²/g)

d – The distance between the plates of a supercapacitor (m)

In an electrical circuit a supercapacitor can be represented by a series connection of C_1 and C_2 (the double-layer capacitances of the anode and cathode). The implementation of the idea of using the electrical double layer in the supercapacitor faced difficult problem of the current

collection from both electrical layers. The current collection from the activated carbon can be relatively easily implemented using metal current collectors (their electrical conductivity is close to the electrical conductivity of a coal). However, current collection from the electrical layer which is formed in the liquid is very problematic (it is almost impossible to find the material for current collectors which has the same electrical conductivity as the liquid). Otherwise, another double layer is formed on the surface of the liquid and current collectors or another capacitor, with the characteristics that would negate the benefits of a supercapacitor.

To solve this problem current collection from the liquid is not used at all. Because of this reason a system of two pairs of contacting materials which are divided by an ion-conducting separator is used. In this system, two series-connected supercapacitors are formed. From the technical point of view one of the plates is a virtual one (liquid). In this case current collection is carried out by metallic layers which are in contact with the electrode layers formed in the porous material. Figure 5 shows a schematic diagram of a supercapacitor.

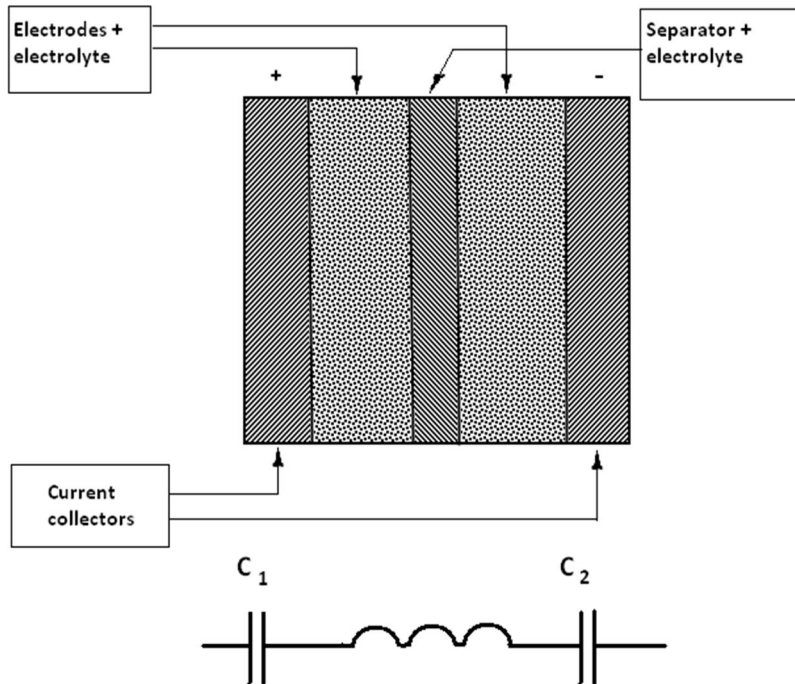


Fig. 5 The schematic diagram of a supercapacitor and its equivalent electrical circuit

The simplest supercapacitor consists of two porous polarizable electrodes, a separator which is saturated with an electrolyte and two current collectors. An electrode saturated with an electrolyte consists of activated carbon on a suitable substrate for example stainless steel or aluminium. The thickness of the activated carbon layer varies between 0.1 and 5.0 mm. The particle size of the activated carbon is in the range of 1 – 50 microns, the size of the active pores is 0.7 – 16 nm.

Usually in industrially produced supercapacitors aqueous solution of alkali (decomposition voltage is 1.23 V and electrical conductivity is 1.0 S / cm) or organic electrolytes (decomposition voltage is 2.7 V and electrical conductivity 0.01 S / cm) are used.

One of the most common types of separators is asbestos paper. This type of separator meets the requirements for electrical, mechanical, operational and cost characteristics but is difficult from the environmental point of view as asbestos fibres are known to be very dangerous to human respiratory system. However, small carbon particles are as dangerous but they can be annihilated easily by burning.

When a potential difference is applied to current collectors the positive electrode attracts negative ions and the negative electrode attracts positive ions from the electrolyte. Porous dielectric separator between the electrodes allows the electrolyte ions to pass through it, but the separator does not allow a short circuit between the electrodes.

The absence of electrochemical reactions and polarization related to these reactions in charging and discharging processes makes supercapacitors “very fast”. In this case the only issue is the Ohmic resistance. At the same time, the motion of ions in the solution and the formation of the electrical double layer is a longer process than the motion of electrons and holes in a solid (traditional capacitors). Therefore supercapacitors are "slower" devices compared to conventional capacitors.

1.3 Classification of supercapacitors

In recent years, due to the large variety of materials and processes used in the industry there are discrepancies in the classification of electrochemical supercapacitors. The easiest way to

identify a supercapacitor is to look the shape of constant current discharge curve. If it has linear form with an ohmic voltage drop at the beginning, this is a supercapacitor (Unlike batteries, the voltage in any capacitor drops significantly during discharging process [35]). All other forms belong to different types of chemical sources of current. The most successful is the classification adopted in the United States (J. Miller, JME Inc.). According to this classification all electrochemical capacitors are divided into 4 classes, called generations because, in addition, they indicate the sequence of development. The first generation includes the earliest types of supercapacitors.

- The first generation: electrochemical supercapacitors which have positive and negative electrodes made of activated carbon and aqueous electrolyte solutions (KOH, H₂SO₄, etc.).
- The second generation: electrodes are made of activated carbon with non-aqueous electrolyte solutions (ethylene carbonate, acetonitrile, etc.)
- The third generation: one electrode is made of activated carbon with aqueous electrolytes (NiOOH / KOH / C, PbO₂ / H₂SO₄/C, etc.).
- The fourth generation: one of the electrodes is made of activated carbon and another working in non-aqueous electrolytes (graphite, LiMnO₂). Activated carbon is carbon processed to have numerous small pores that increase the surface area of the specimen.

Electrochemistry of processes and the type of electrolyte divide electrochemical supercapacitors by power and energy. Thus the first, the third and part of the second generation represent more powerful electrochemical supercapacitors compared to the fourth generation ones. The first generation supercapacitors are the most powerful (up to 15 kW / kg in a pulse) but the specific energy is limited (1 W·h / kg). The fourth generation has the highest energy density (more than 10 W·h / kg), but the power of these devices is below 1 kW / kg.

Classification can also be based on the principle of determination of the main current-generating process. According to this classification, all supercapacitors can be divided into three groups: based on the electrical double-layer, based on pseudocapacitance and hybrid supercapacitors. Electrochemical capacitors of the third and the fourth generation are often called as "hybrid" or "asymmetric". "Hybrid" supercapacitors are supercapacitors with ideally polarizable carbon electrode and non-polarizable or slightly polarizable cathode or anode. In

this type of supercapacitors on one of the electrodes (anode and cathode) electrochemical reaction takes place. Capacitance of those supercapacitors is two times higher than in double-layer supercapacitors, since the capacity of non-polarizable electrode is limited by electrochemical reaction. However, this reaction imposes diffusion and kinetic limitations on the rate of charging and discharging of 'hybrid' supercapacitors. Therefore, in the magnitude of specific energy and power, temperature range and number of cycles hybrid supercapacitors are closer to batteries.

The most studied electrode materials of supercapacitors which are based on the pseudocapacitance are:

- Electrically conductive oxides or oxide films hydrates of metals: RuO_2 [8], IrO_2 [9], MnO_2 [10], MoO_3 , WO_3 , Co_3O_4 [11].
- Electrically conductive polymers, such as polythiophene [12], polypyrrole [13], polyaniline [14].

The most studied materials for double-layer supercapacitor electrodes are different types of carbon materials such as carbon aerogels [15], activated carbon [16], and carbon nanotubes (CNT) [17]. However, in real supercapacitor electrodes with highly developed surface a mixed mechanism of charging is usually observed. In the general case in double-layer supercapacitors based on carbon material there is always a contribution of pseudocapacitance (1 – 5%) because of functional groups on the surface. At the same time in rechargeable batteries the contribution of the electric double layer capacitance is 5 – 10% [1]. Pseudocapacitance may be the result of hydrogen atoms adsorption or the redox reaction of particles.

1.4 Application of supercapacitors

Recently significant advances have been made in improving both energy and power density of supercapacitors and new applications for EDLCs are being developed at an increasing rate. The following are a number of possible applications for the EDLC as an energy storage device.

Supercapacitors have long been in use as short-term backup supplies in consumer electronics. Many devices now also include digital components with memory, and even a very short interruption in the power supply would otherwise cause a loss of stored data. In such situations a supercapacitor can serve as the power supply for a brief period of time, by that retaining information.

Battery is the common alternative to the supercapacitor in this application. Their disadvantage is relatively short product lifetime, and therefore a need to be replaced regularly. Due to their long lifetime supercapacitors are therefore a good choice as backup power supply.

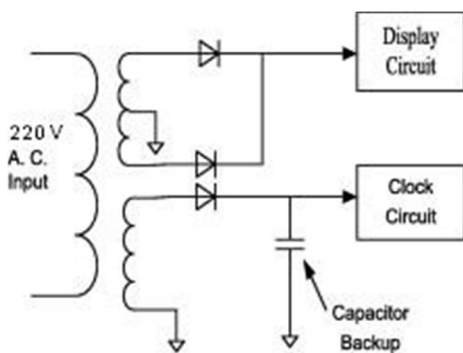


Fig. 6 Scheme for memory backup of clock memory using supercapacitor [18]

Lots of attention is drawn to EDLCs because of the possibility to use the technology in electric vehicles. The biggest advantage is energy saving because of supercapacitors energy efficiency and because of the possibility of recuperating energy lost during braking. Many of the present power sources being chosen for use in electric vehicles (EVs) do not satisfy the power requirements of vehicle acceleration. Fuel cells represent very promising technology due to their extremely high energy density. However, at the moment fuel cells are limited in their power characteristics. A combination of fuel cell and supercapacitor technology can meet both the power and energy requirements of an EV.

The high-energy density device such as a fuel cell can provide the average load requirements with the help of a combined power source configuration. The high-power device such as a supercapacitor module can meet peak load requirements that result from accelerating or climbing up hills. In addition, regenerative braking becomes possible with utilization of su-

percapacitors. It is possible to store some of the energy of an already moving vehicle because the EDLC bank can be recharged, and therefore it is possible to increase the fuel efficiency of the EV.

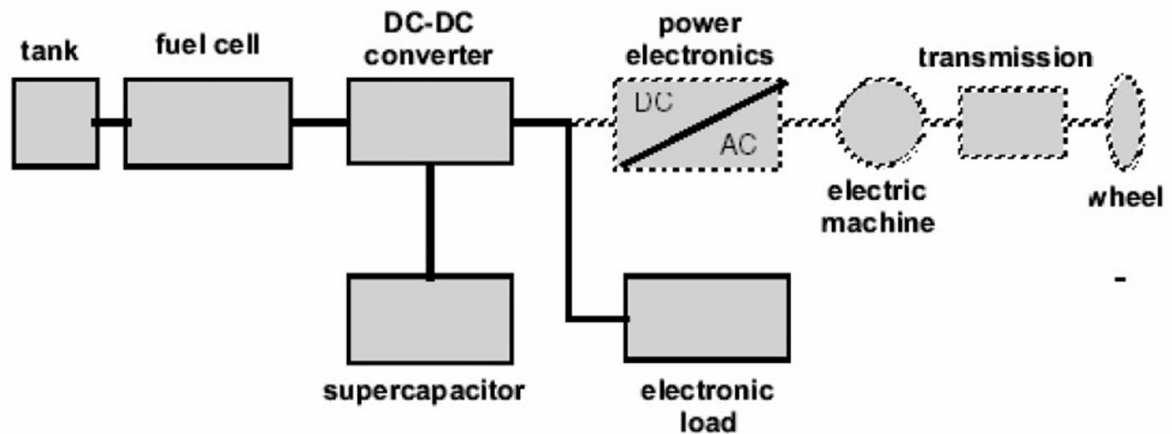


Fig. 7 Electric drive train using a fuel cell and supercapacitors [19]

Systems designed to improve the reliability and quality of power distribution can use EDLCs as the energy storage device. In order to compensate for voltage fluctuations static condensers (Statcons) and dynamic voltage restorers (DVRs) are used. This systems aim is to inject or absorb power from a distribution line. As a result, there is a need in such systems in a DC energy storage device of some sort from where energy can be drawn and in where energy can be stored.

Energy density of the DC storage device determines the length of voltage disturbance that can be effectively compensated. The vast majority of voltage perturbations on the distribution bus are short-lived, most not lasting more than ten cycles [20]. Therefore the limited storage capability of the supercapacitor does not cause a problem. The EDLC has the advantage of possessing a fast discharge time. That means the storage device based on supercapacitors is able to respond quickly to voltage disturbances. In general, batteries are not suitable for short-duration, fast response applications such as the Statcon or DVR. The device lifetime will be shortened considerably and if the battery is fully drained.

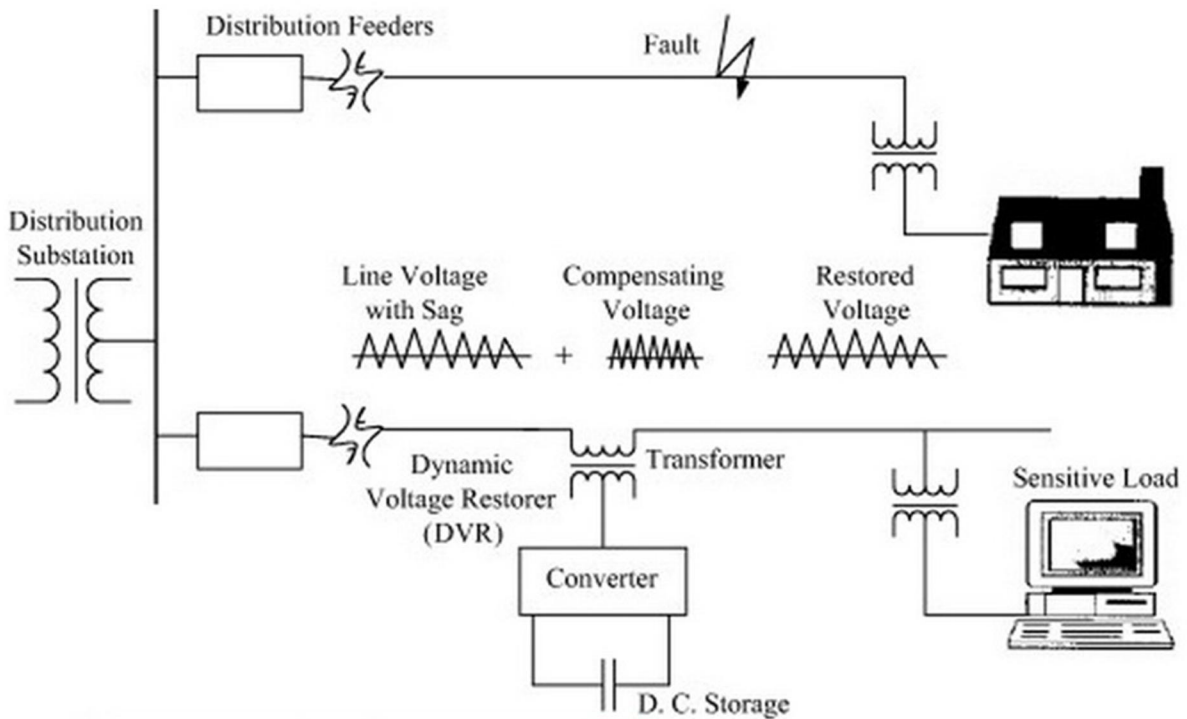


Fig. 7 Improved power quality on distribution side by DVR [20]

In addition, in portable electronic equipment with moderate energy demands supercapacitors are well suited to act as rechargeable stand-alone power sources. If a device uses battery power supplies it has long recharge times and it needs to be charged overnight. This is considered to be a limitation of the current technology. However, the main advantage of supercapacitors is the opportunity to create devices that can be recharged quickly, perhaps in just a few seconds. It is possible to perform repeated charging and processes without significant losses in efficiency. For example, it would therefore be possible to create a highly efficient and quickly rechargeable safety light by using the latest light-emitting diodes (LEDs). There will be no need to constantly replace the batteries of handheld remote controls.

Renewable sources of energy that are inconstant sources such as wind or solar radiation require energy storage to ensure that energy is available at all times. In that case EDLCs have a number of advantages over the widely used rechargeable batteries. When a battery works in pair with a photovoltaic panel (PV) it gets charged and discharged every day and this continuous charging and discharging has a detrimental effect on batteries resulting in their needing to be replaced every 3-7 years [21]. In their turn, supercapacitors can withstand a large number

of charge and discharge cycles without suffering significant losses in performance. Therefore, supercapacitors only need to be replaced every 20 years, which is the lifetime of the PV panels [21]. Thus lifecycle costs are reduced through the removal of frequent maintenance activities.

The primary concern in renewable power generation is energy efficiency, and supercapacitors have a higher charging efficiency compare to batteries. For Instance, in a lead-acid battery up to 30 % of the energy can be lost during charging. On the other hand, supercapacitors may lose only 10 % [21]. Another advantage of supercapacitors is the ability to operate efficiently of a wider range of temperatures. Some power stations which are utilizing RES may be located in cold climates and if batteries are used for energy storage additional cost and energy consumption is required to maintain the temperature at close to room level with the help of auxiliary systems.

The major disadvantage of supercapacitor technology for application in RES is limited energy density. As a result EDLCs are rarely chosen as an option because the capital costs of energy storage is more excessive compare to batteries. However, in recent years, the prices have been significantly reduced.

1.5 Outline of the Thesis

Electrochemical double-layer capacitors represent the main subject of study of this Master's Thesis. The Master's Thesis is divided into five chapters. In the first chapter the reader is given basic information about supercapacitors, the history of their development, basic principles of work and possible ways of application. The second part of the Master's Thesis provides information about construction of supercapacitors and materials which are used in their production. In the third part power, capacitance and energy of EDLCs is discussed. In the next part author represents current experimental techniques and applies them to test multiwalled carbon nanotubes (MWCNT) as the material for electrodes and analyzes obtained experimental data. The conclusion and summary is presented in the last chapter.

1.6 Contribution of the Thesis

In this Master's Thesis the author describes materials which are currently used in supercapacitors. In the experimental part he gives the detailed description of supercapacitors energy density measuring methods. In addition the author utilizes galvanostatic method and cyclic voltammetry method to measure the energy density of multiwalled carbon nanotubes and analyzes the obtained data.

2 ELECTRICAL DOUBLE-LAYER CAPACITORS AND THEIR CONSTRUCTION

Electrochemical double-layer supercapacitors consist of porous electrodes based on carbon. The electric charge of an EDLC is determined by the capacitance of the electrical double layer and is stored mainly due to electrostatic interaction.

$$C = \frac{Q}{U} \quad (2)$$

Q - Charge, stored in the supercapacitor electrodes

U - Voltage of the supercapacitor

The specific capacitance C' is defined as

$$C' = \frac{C}{m} = \frac{Q}{U \cdot m} \quad (3)$$

The energy W stored in a capacitor is

$$W = \frac{1}{2} C \cdot U^2 \quad (4)$$

and the specific energy $W' = W/m$ is

$$W' = \frac{W}{m} = \frac{C \cdot U^2}{2 \cdot m} \quad (5)$$

If we have one gram of carbon and can reach e.g. 250 F/g and 2.7 V the specific energy should be $\frac{1}{2}CU^2/m = 911 \text{ J/g} = 253 \text{ Wh/kg}$. Obviously the casing and conductors occupy most of the space.

As an example let us assume that the surface area of a single electrode is 1 cm^2 .

Then, $m_{\text{supercapacitor}} = m_{\text{separator}} + 2 \cdot m_{\text{electrode}} + 2 \cdot m_{\text{current collector}} + m_{\text{case}} = 0.095 + 2 \cdot 0.15 + 2 \cdot 0.028 + 0.4 = 0.851 \text{ g}$.

$m_{\text{current collector}} = V_{\text{current collector}} \cdot \rho_{\text{current collector}} = S \cdot \delta \cdot \rho_{\text{current collector}} = 1 \cdot 0.005 \cdot 4.5 = 0.028 \text{ g}$.

$m_{\text{separator}} = m_{\text{separator}} + m_{\text{electrolyte}} = V_{\text{separator}} \cdot \rho_{\text{separator}} + V_{\text{electrolyte}} \cdot \rho_{\text{electrolyte}} = S \cdot N_{\text{separator}} \cdot \delta \cdot \rho_{\text{separator}} + S \cdot N_{\text{separator}} \cdot \delta \cdot \rho_{\text{electrolyte}} = 1 \cdot 0.5 \cdot 0.05 \cdot 2.6 + 1 \cdot 0.5 \cdot 0.05 \cdot 1.2 = 0.095 \text{ g}$.

$m_{\text{electrode}} = m_{\text{electrode}} + m_{\text{electrolyte}} = V_{\text{electrode}} \cdot \rho_{\text{electrode}} + V_{\text{electrolyte}} \cdot \rho_{\text{electrolyte}} = S \cdot N_{\text{electrode}} \cdot \delta \cdot \rho_{\text{electrode}} + S \cdot N_{\text{electrode}} \cdot \delta \cdot \rho_{\text{electrolyte}} = 1 \cdot 0.683 \cdot 0.1 \cdot 2.2 + 1 \cdot 0.317 \cdot 0.1 \cdot 1.2 = 0.15 \text{ g}$.

$m_{\text{case}} = V_{\text{case}} \cdot \rho_{\text{case}} = 0.34 \cdot 1.4 = 0.4 \text{ g}$.

Electrode: Activated carbon, thickness: $\delta = 1 \text{ mm}$, Density: $\rho = 2.2 \text{ g/cm}^3$, Porosity: $N = 0.683$.

Current collector: Titanium, thickness: $\delta = 0.05 \text{ mm}$, Density: $\rho = 4.5 \text{ g/cm}^3$.

Separator: Asbestos, thickness: $\delta = 0.5 \text{ mm}$, Density: $\rho = 2.6 \text{ g/cm}^3$, Porosity: $N = 0.5$.

Electrolyte: Propylene carbonate, Density: $\rho = 1.2 \text{ g/cm}^3$.

Case: Polyvinyl chloride, $\rho = 1.4 \text{ g/cm}^3$.

The specific capacitance (including the mass of the parts) of the capacitor with $m = 0.851 \text{ g}$, will be $250 \cdot 2 \cdot 0.15 / 0.851 / m = 88 \text{ F/g}$. The specific energy should be $\frac{1}{2}CU^2/m = 320 \text{ J/g} = 88 \text{ Wh/kg}$. Propylene carbonate can be used as the electrolyte to get 2.7 V cell voltage.

The electrochemical process in an EDLC can be represented as follows [22]:

Positive electrode: $E_S + A^- \leftrightarrow E_S^+ \parallel A^- + e^-$

Negative electrode: $E_S + K^+ + e^- \leftrightarrow E_S^- \parallel K^+$

Overall reaction: $E_S + E_S + K^+ + A^- \leftrightarrow E_S^- \parallel K^+ + E_S^+ \parallel A^-$

E_S – Electrode surface

\parallel – Electrical double-layer

K^+ and A^- – Cations and anions of the electrolyte

During the charging process electrons are transferred from the positive electrode to the negative electrode through an external source of power, at the same time ions from the electrolyte move to electrodes. During discharging process electrons move from the negative electrode to the positive electrode through the load resistance, and the ions move from the double-layer to the electrolyte. Thus, in the process of charging and discharging a change in the charge density at the interface of the electrode and the electrolyte takes place. Theoretical understanding of the specific capacitance (per unit of real surface of the electrode) of EDLCs is based on the famous classical theories of the double layer (Helmholtz, Gouy-Chapman, Stern and Grahame and others).

To obtain a high capacitance in double-layer supercapacitors it is necessary to use electrodes with high specific surface area. Energy characteristics of supercapacitors are highly dependent on the electrolyte used.

2.1 Types of electrode materials

The surface characteristics of the electrode greatly influence the capacitance of the cell because double-layer charge storage is a surface process. Currently the most widely used electrode material is carbon, but metal-oxides and conducting polymers are nowadays studied as well.

From the very beginning of the development of electrochemical capacitors carbon has been utilized as a high surface area electrode material. Thanks to its low cost, availability, and long history of use it is still an attractive option. Carbon has a number of forms such as foams, fibres, and nanotubes.

The specific capacitance is not always directly proportional to the carbon electrode's surface area. Frequently, a type of carbon with a larger surface area will have a lower specific capacitance than a type with a lower surface area. This happens because the process used to prepare the carbon affects the actual double-layer capacitance.

The porous structure of the electrode surface and accessibility of the pores to the electrolyte is influenced by the treatment of activated carbon materials. Pore size greatly affects the mobility of the ions within the pores which is different to the mobility of ions in the bulk of the electrolytic solution. Pores do not contribute to double-layer capacitance, if the pores are too small to allow easy access to electrolyte ions. Thus, the pore size must be selected to match the electrolyte and thus provide guarantee the pore size distribution is optimal based upon the size of the ions [15]. In Figure 8 the relation between pore diameter and specific capacitance is clearly shown. Small pores become entirely inaccessible to the ions at high frequencies.

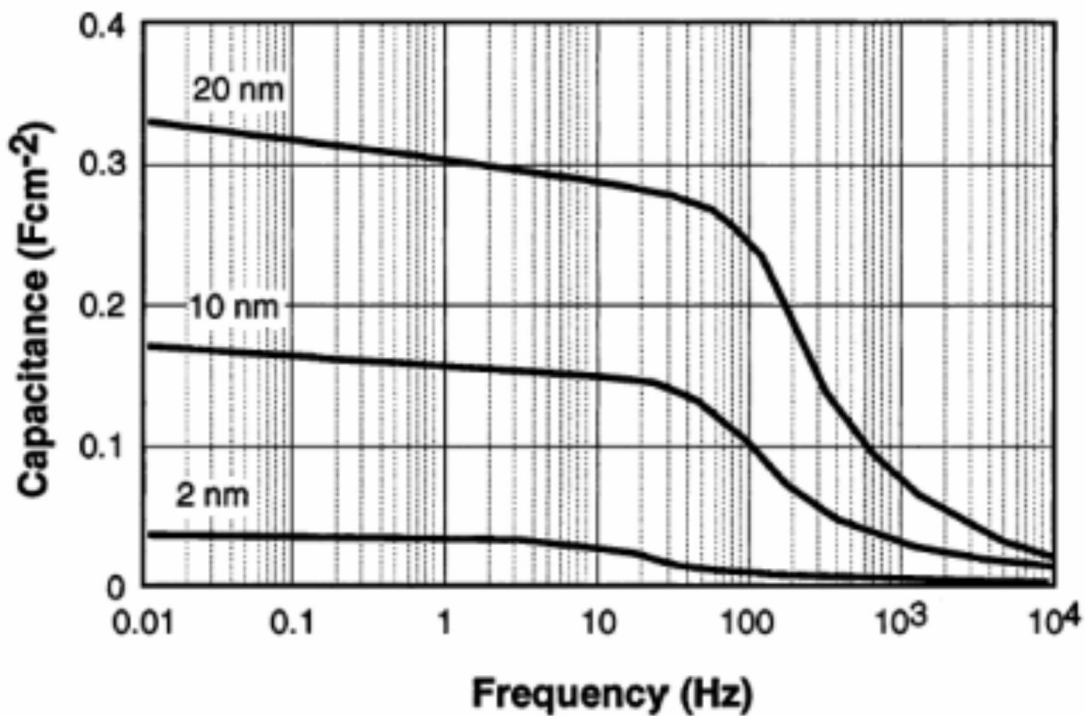


Fig. 8 Pore diameter effect on specific capacitance [7]

The conductivity of the electrode strongly affects the power density of a supercapacitor. The conductivity is inversely proportional to the particle size. This means that a material made of smaller particles has higher surface area and in the same time it has larger resistance. The use of activated carbons with more large pores will improve power density. However, due to reduced surface area, energy storage will be limited. Conductivity is also affected by use of binding material (PVDF- Polyvinylidene fluoride). With a decreased percentage of binder power performance gets higher [15].

On the surface of activated carbons pseudocapacitive effects usually take place. If the carbon is treated to increase the surface functionality, the level of pseudocapacitance can be enhanced.

Besides activated carbons, electrodes can also be produced from carbon aerogels. Aerogels present a suspension of carbon nanoparticles within a gel. Aerogels have a high surface-area and good conductivity. It is possible to use aerogels without binding material. Preparation process controls particle size. Larger accessible pore surface-area is a result of smaller particles [15].

Another prospective material for carbon electrodes is nanotubes. Preliminary researches suggest that a higher capacitance is the result of tangled networks with an open central canal (Figure 9) [15].

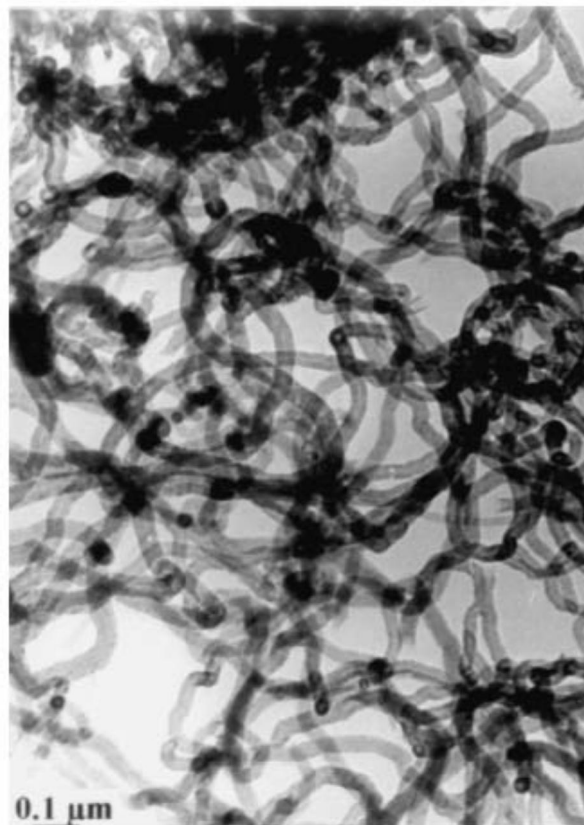


Fig. 9 Tangled network of carbon nanotubes [15]

Conducting polymers offer a new possibility for supercapacitors electrodes. The storage of charges is performed through redox processes. Ions are transferred to the polymer backbone when oxidation occurs, (also referred to as ‘doping’). The ions are released back into the solution when reduction occurs (also referred to as ‘dedoping’) (Fig. 10). Charging in conducting polymer films takes place not just on the surface as in the case with carbon but throughout the bulk volume of the film. High levels of specific capacitance can be achieved due to this fact.

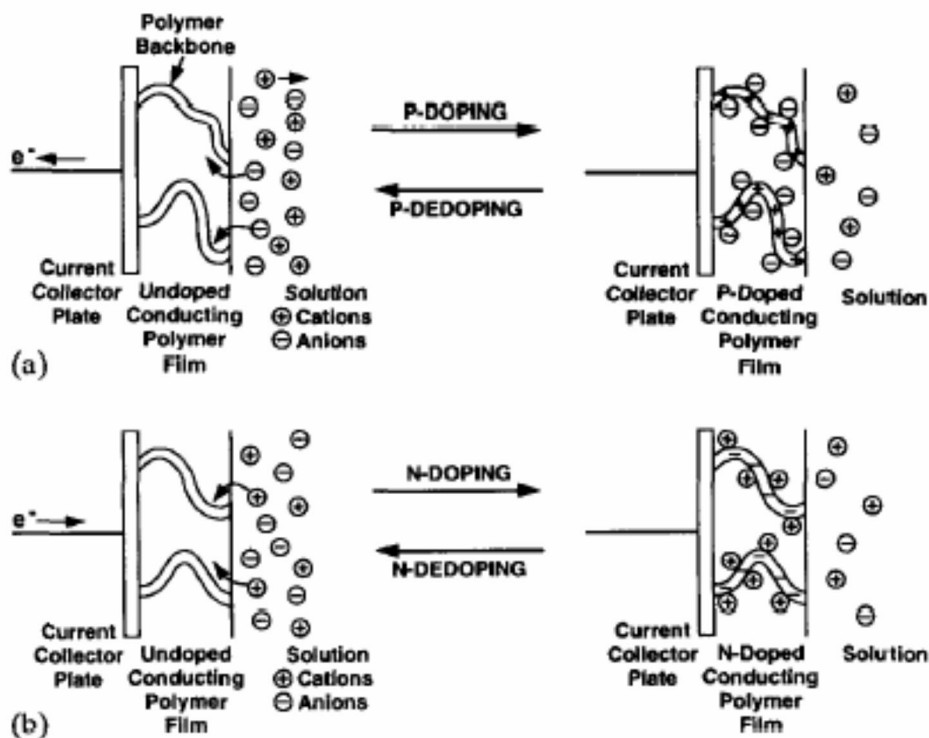


Fig. 9 Charging process of conducting polymer electrodes [23]

High specific capacitance and low resistance makes metal-oxides attractive alternatives as electrode materials. Usage of metal-oxides makes it easier to construct high-energy, high-power supercapacitors. For military applications extensive research into rutheniumoxides has been conducted. Prototype cells with an energy density of $8.5 \text{ W}\cdot\text{h} / \text{kg}$ and a power density of $6 \text{ kW} / \text{kg}$ was assembled by the US Army Research Lab [24].

Research institutions have concentrated on searching for other, cheaper, materials to use instead of ruthenium-oxides, but the choice has traditionally been limited by the use of concen-

trated sulphuric acid as an electrolyte. It was believed that H sorption defined high capacitance and fast charging. In that case a strong acid was necessary to provide good proton conductivity. A narrow range of electrode materials was possible because most metal-oxides break down quickly in acidic solutions. As a result for use with metal-oxides such as manganese-oxides aqueous solutions such as potassium chloride have been considered.

Achievable cell voltage is limited because metal-oxide electrodes can only be used with aqueous electrolytes. Thus, benefits in power density from lower resistance are often offset by losses because of the lower operating voltage.

Considerable potential is shown by hybrid electrode configuration. This configuration consists of two different electrodes made of different materials. In composite electrodes one type of material is incorporated into another one within the same electrode.

Researchers from the University of Bologna conducted a course of experiments. They found that a sufficiently high polymer concentration could not be realized in the negative electrode. However, the positive polymer electrode was successfully constructed. As the negative electrode activated carbon was used. As a result this hybrid configuration outperformed a cell comprised of two carbon electrodes (Fig. 10) [25].

Another interesting option is to combine polymers with carbon substrates to form composite electrodes. Carbon nanotubes coated with conducting polymers showed good results. Specific capacitance was approximately 180 F/g [26, 27]. Due to the charging taking place largely throughout the bulk of the material (along the surface of the nanotubes and along the backbone of the polymer) the improved levels of energy storage are achieved. The pseudocapacitance arising from the redox processes in the polymer makes additional contribution to capacitive characteristics.

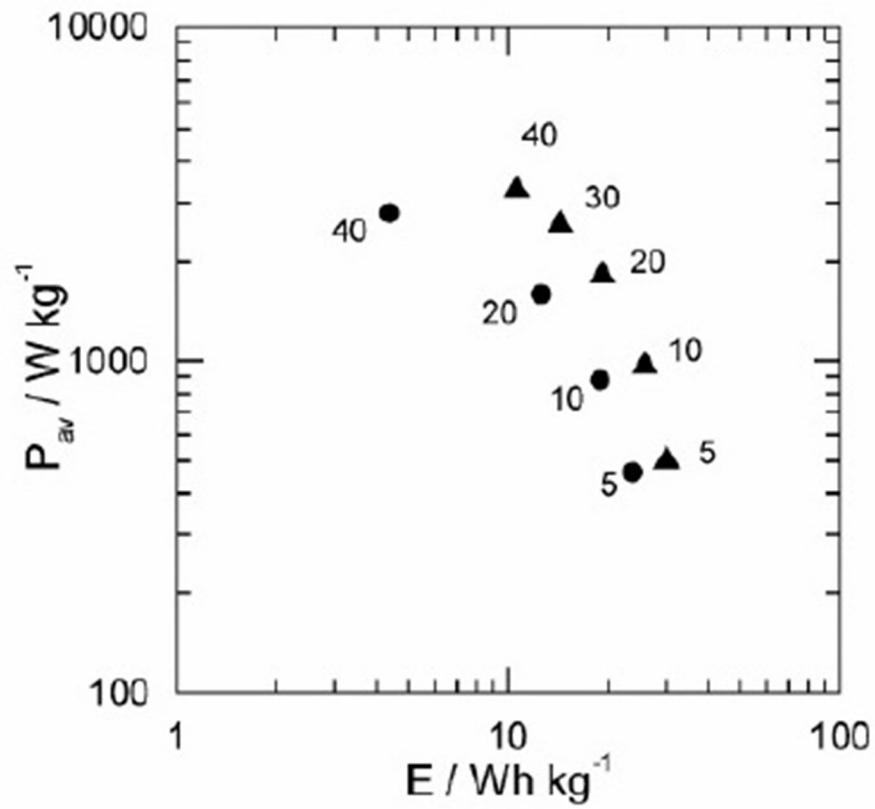


Fig. 10 Ragone plot of hybrid (▲) and carbon (●) supercapacitors (the values represent current densities in mA/cm²) [25]

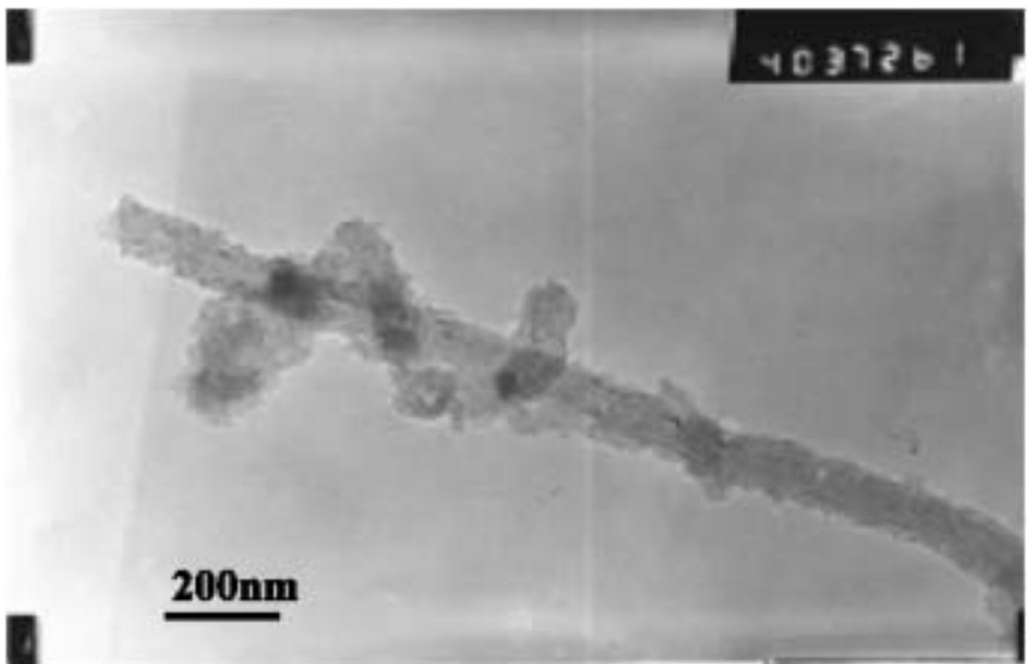


Fig. 11 Carbon nanotube coated in polypyrrole [28]

2.2 Carbon nanotubes as electrode material

The specific capacitance values of the carbon nanotubes usually range from 20 F/g to > 300 F/g. The first report about the supercapacitor electrodes prepared from MWCNT was made by Niu [29] with specific capacitance, power density and energy density values of 113 F/g, 8 kW/kg and 0.56 Wh/kg, respectively (as electrolyte H₂SO₄ aqueous solution was used). Ma [30] also reported about MWCNT supercapacitor electrodes with relatively low specific capacitance values of 15-25 F/g (also in H₂SO₄ solution). The SWCNT electrodes in the form of paper show a specific capacitance value of 40 F/g in 6 M KOH aqueous solution, and 20-40 F/g in NaCl aqueous electrolyte [31]. Shiraishi achieved similar results in 1.0 M LiClO₄/propylene carbonate electrolytes [32]. Liu [33], however, reported that the specific capacitance of SWCNTs in acetonitrile electrolyte with 0.1 M tetra-n-butylammonium hexafluorophosphate is approximately 280 F/g.

Large specific surface area of activated carbon (~2000 m²/g) is generally produced with physical and chemical activation. These methods were also used to treat carbon nanotube based electrodes to increase the specific surface area by introducing micropores to improve the capacitance. Physically activated and chemically activated carbon nanotube electrodes have significantly higher specific surface area as well as the specific capacitance compared to non-activated electrodes. In addition to pore structures and specific surface area, another important property that affects the capacitance behaviour is wetting capability. For this reason, hot nitric acid, fluorine, and ammonia plasma functionalized carbon nanotube electrodes have been tested to estimate capacitance performance. However, unstable capacitance and increased current leakage were caused by the pseudofaradaic reactions induced by the surface functional groups [35].

Generally, SWCNTs have been shown to have higher specific capacitance, mainly because of their large surface area. However, Frackowiak found that MWCNTs could generate capacitance twice as high compared to SWCNTs under certain circumstance [27]. He suggested that the higher capacitance of MWCNTs in his research was explained by the presence of mesopores due to the open central canal and the accessible network of entangled nanotubes, facilitating the transport of the ions from the solution to the charged interface. Capacitance of car-

bon nanotubes also depends on the surface condition of the nanotubes. Carbon nanotubes chemically modified by strong acid oxidation have performed a well defined pseudocapacitance behaviour because of the Faradaic redox reactions of their rich surface functionality [15].

Other common electrode materials for supercapacitors are conducting polymers, such as polyacetylene, polypyrrole, polyaniline, polythiophene, and their derivatives. When CNTs are modified with conducting polymers the capacitance of the composite is increased due to redox contribution of the conducting polymers. In the CNT/conducting polymer composite, the conducting polymer serves as an electron donor, while CNTs are electron acceptors. A charge-transfer complex is formed between aniline monomer and CNTs in their ground state. There were a number of reports about CNT/conducting polymer composite studies for electrochemical capacitor application.

2.3 Types of electrolytes

Electrolytes which are used in double-layer capacitors should have the highest possible voltage of dissociation and be resistant to temperatures from -25 to +70 ° C. The electrolytes used in supercapacitors can be aqueous, organic or solid.

Traditional aqueous electrolytes are characterized by high conductivity, have a higher total capacitance than the non-aqueous electrolytes. Another advantage of aqueous electrolytes is that requirements to cleaning and drying during manufacturing process are less strict. Moreover, the price of water electrolytes is usually much lower than the price of organic electrolytes. The main disadvantages of aqueous solutions are:

- Low discharge voltage (~1 V)
- Narrow range of working temperatures
- High corrosivity

The most commonly used aqueous electrolytes in supercapacitors are 30 % KOH [44] or 1 M H₂SO₄. Currently, work is underway to improve water electrolytes. Improved electrolytes can be divided into three classes:

The first class is the ammine solutions [45], which are produced by interconnecting some salts with ammonia gas, resulting in formation of a liquid with high conductivity at room temperature. Due to their high electrical conductivity, voltage stability, and temperature range, these solutions ($[\text{NH}_4\text{NO}_3] \cdot 1.3 [\text{NH}_3]$, $[\text{NaI}] \cdot 3.3 [\text{NH}_3]$, $[\text{LiClO}_4] \cdot 4 [\text{NH}_3]$) are good options for use as electrolytes in double-layer capacitors.

The second class includes electrolyte solutions based on sulfur dioxide. Sulfur dioxide, which has a gaseous state at room temperature, is used as a solvent for the electrolyte. Sulfur dioxide dissolves certain salts to form liquid electrolytes at room temperature. These solutions have higher conductivity than the corresponding ammine solutions, but they also have higher corrosiveness. These electrolytes are produced when sulfur dioxide is used to dissolve chemical compounds of AlCl_3 with lithium, calcium, sodium and strontium [46]. These electrolytes can be represented as: $\text{Me}[\text{AlCl}_4]_x \text{SO}_2$, where x is 2.5 - 6.0, and Me is metal selected from the group of Li, Na, Ca and Sr.

The third class represents electrolytes made from molten salts. Molten salts electrolytes are produced from ionic salts (ionic salts are liquid at temperatures from 450°C and higher) [47]. These electrolytes have the highest values of ion conductivity among all electrolytes. Molten salts electrolytes can be represented in this form: $[\text{AlCl}_3] \cdot \text{MX}$, where M is alkali metal and X is either chlorine or bromine. The main disadvantage of these electrolytes is that they require high operating temperatures, and many of them are highly corrosive.

To achieve higher voltage non-aqueous liquid electrolytes are used. Usually these electrolytes are organic. They have high dissociation voltage ($> 2.3 \text{ V}$) and wide range of operating temperatures. For organic electrolytes (usually ammonium salts [48]) these solvents are mainly used: propylene carbonate (PC) [49, 50], γ -butyrolactone, N-N-dimethylformamide, sulfolene, 3-methylsulfolene [51]. In fact electrolytes based on aprotic solvents (acetonitrile or propylene carbonate) can achieve only 2.3 - 2.7 V. This phenomenon can be explained by dissociation voltage of the electrolyte. The disadvantages of organic non-aqueous electrolytes are low electrical conductivity, explosion risk, toxicity. The need for careful isolation from external impacts increases the cost of supercapacitors. Conductivity of organic electrolytes is 50 times lower than conductivity of aqueous electrolytes [1]. Conductivity affects the re-

sistance in the porous layer. As a result the maximum output power of a supercapacitor is reduced.

Further increase of a supercapacitor voltage, as well as replacement of toxic, explosive and corrosive compounds can be provided by utilization of ionic liquids. In addition, ionic liquids have much higher dissociation voltage and they are more environmentally friendly.

Ionic liquids are molten salts of organic acids which are liquid at room temperature. Supercapacitor based on N-Butyl-N-Methyl pyrrolidinium bis(trifluoromethanesulfonyl)imide showed good characteristics: high working voltage (3.6 V), good cycling (after 16000 cycles energy density and power density decreased less than 50 %), starting values of energy density and power density were 12 W·h/kg and 6 kW/kg respectively [52].

2.4 Types of separators

Large share of the commercial available separators are designed mainly for utilization in batteries. Therefore, an accurate assessment of the separator is required to achieve the outstanding performance of EDLCs. Polymer (typically PP) or paper separators are typically used in case of organic electrolytes. . It is possible to use glass fiber separators and ceramic separators with aqueous electrolytes [53]. The separator allows the transfer of the charged ions but makes impossible the mechanical contact between the electrodes. Mechanical contact between the electrodes causes short-circuit and failure (fire or explosion hazard).

In order to construct a competitive EDLC it is necessary to satisfy all the following requirements [53]:

- high ionic conductivity of the electrolyte
- high ionic conductivity of the separator
- high electronic resistance of the separator
- high electronic conductivity of the electrode
- large electrode surface
- low separator and electrodes thickness

Table 3 shows an overview over material specifications for the optimal performance of EDLCs with organic electrolyte (based on model calculations).

Table 3 Optimal parameters of a supercapacitor [53]

Active layer thickness	100 μm
Volumetric and Specific Capacitance	100 F/cm^3 25 F/g
Electrolyte	0.05 S/cm
Cell Voltage	2.5 V
Current Collector Thickness	25 μm
Separator Porosity	50 %
Separator Thickness	25 μm
Distributed Resistance in Pores	10 \times electrolyte*

* the resistance of the separator is ten times the resistance of the electrolyte

3 POWER, CAPACITANCE AND ENERGY OF SUPERCAPACITORS

The most important characteristics of a supercapacitor are capacitance, power and energy. In the most common form electrostatic capacitance of a supercapacitor was defined by Eq. (2)

If we want to calculate capacitance of galvanostatic mode, we should use the following equation to calculate the capacitance:

$$C = \frac{I \cdot \tau}{U_{\max} - U_{\min}} \quad (3)$$

I – Current (A)

τ – Time (s)

U_{\max} – Maximum voltage (V)

U_{\min} – Minimum voltage (V)

It should be mentioned that each electrode of double-layer capacitor can be considered as a capacitor with the corresponding capacitance. In the elementary supercapacitor total capacitance will be determined as the apparent capacitance of two series-connected capacitors (C_1 and C_2). Therefore, it is required to make electrodes of the same weight. Total capacitance of an EDLC will be determined according to:

$$\frac{1}{C} = \frac{1}{C_1} + \frac{1}{C_2} \quad (4)$$

A supercapacitor elementary equivalent circuit can be represented in the form of two series-connected capacitors (Fig. 12).

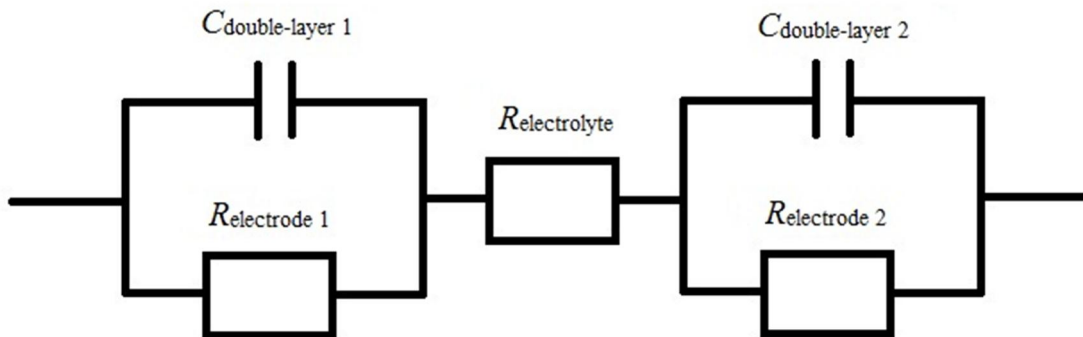


Fig. 12 Equivalent electrical circuit of a supercapacitor with two different or similar layers

The energy accumulated by a supercapacitor during charging or discharging is arises due to the separation of charges in the electrolyte under the influence of the electrostatic potential.

The amount of this energy was given by Eq. (4)

It is convenient to use specific values (per unit of mass of the capacitor) for comparison purposes. Moreover, energy can be also expressed in watt hours. In that case, the specific energy W' can be expressed this way:

$$W' = \frac{C \cdot U^2}{2 \cdot 3600 \cdot m} \quad (6)$$

m – Mass of the electrolyte (kg)

Equation (4) can be obtained by integrating:

$$W = \int_0^Q U dQ = \int_0^Q \frac{Q}{C} dQ = \frac{1}{C} \int_0^Q Q dQ = \frac{Q^2}{2 \cdot C} = \frac{C^2 \cdot U^2}{2 \cdot C} = \frac{CU^2}{2} \quad (7)$$

The diagram of an ideal supercapacitor charge is shown in Figure 13.

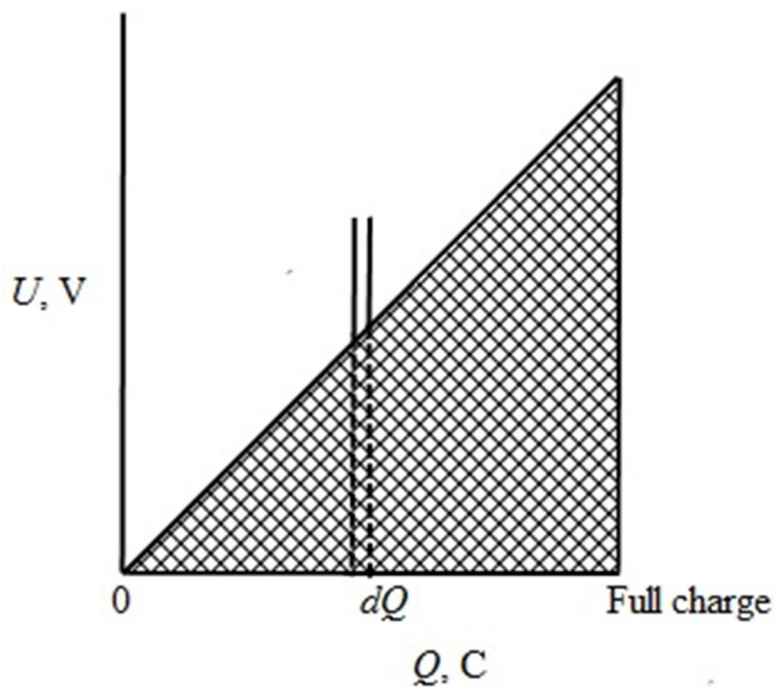


Fig. 13 The diagram of an ideal (super)capacitor charging

The power density (P , kW/kg), which can be obtained while discharging a double-layer capacitor from nominal voltage (U_{nom}) to half of nominal voltage ($U_{\text{nom}}/2$), average voltage ($3/4U_{\text{nom}}$) depends on efficiency and can be presented by the equation [54]:

$$P = \frac{U^2 \cdot (1 - \eta)}{R_{\text{sup}} \cdot m} = \frac{(3/4U_{\text{nom}})^2 \cdot (1 - \eta)}{R_{\text{sup}} \cdot m} = \frac{9U_{\text{nom}}^2 \cdot (1 - \eta)}{16R_{\text{sup}} \cdot m} \quad (8)$$

P – The power density (kW/kg)

R_{sup} – Internal resistance of a supercapacitor (Ohm)

m – Mass or volume of the electrolyte (kg or liter)

η – Efficiency (Usually 0.95)

The efficiency of a supercapacitor is mainly defined by internal resistance and can be roughly calculated according to the formula:

$$\eta = \frac{R_{\text{load}}}{R_{\text{load}} + R_{\text{sup}}} \quad (9)$$

R_{load} – Load resistance (Ohm)

However, in some cases developers and manufacturers of supercapacitors specify the maximum power density for the efficiency of 50% (when the internal resistance of an EDLC and the load resistance are equal) and for full discharge of a supercapacitor from the nominal voltage to 0 V. In this case the maximum power density is defined by:

$$P = \frac{U^2 \cdot (1 - \eta)}{4R_{\text{sup}} \cdot m \cdot 100} \quad (10)$$

From the above equations we can see that the power density and the efficiency of a supercapacitor are defined by its internal resistance. Thus, researchers' efforts are largely focused on developing new ways to reduce the internal resistance. Internal resistance is a key characteristic of a double-layer capacitor which determines many of its advantages over other sources of

power. It should be mentioned that great attention is paid to increasing of supercapacitors' power density. In addition, for successful entry to the market of power sources supercapacitors should have competitive prices.

4 TESTING METHODS AND EXPERIMENTS

It is necessary to be able to evaluate the performance of an EDLC quantitatively in order to make comparisons between different devices and technologies, and also to be sure that a particular device is suitable for a certain application. There are a number of methods for determining performance of a supercapacitor. In this chapter two main methods will be represented.

4.1 Cyclic voltammetry method

Cyclic voltammetry provides a measure of a supercapacitor's charge-response with regard to a changing voltage, and is therefore a means of evaluating capacitance. Voltammogram can be obtained by the simple process.

Cyclic voltammetry tests are performed by applying a series of changing voltages at a constant sweep rate (dU/dt) with simultaneous recording of the response current. Then, the capacitance can be calculated [55] by:

$$C = \frac{I}{s} \quad (11)$$

I – Current (A)

s – Sweep rate in (V/s)

Voltammetry is usually graphed as capacitance vs. voltage instead of current vs. voltage. Despite the fact that an ideal capacitor with no resistance would have the voltammogram with rectangular shape, the majority of real EDLC have the voltammograms with the shape of a parallelogram with irregular peaks (Fig. 14). If a double-layer capacitor has pseudocapacitive addition, prominent peaks occur within voltage window.

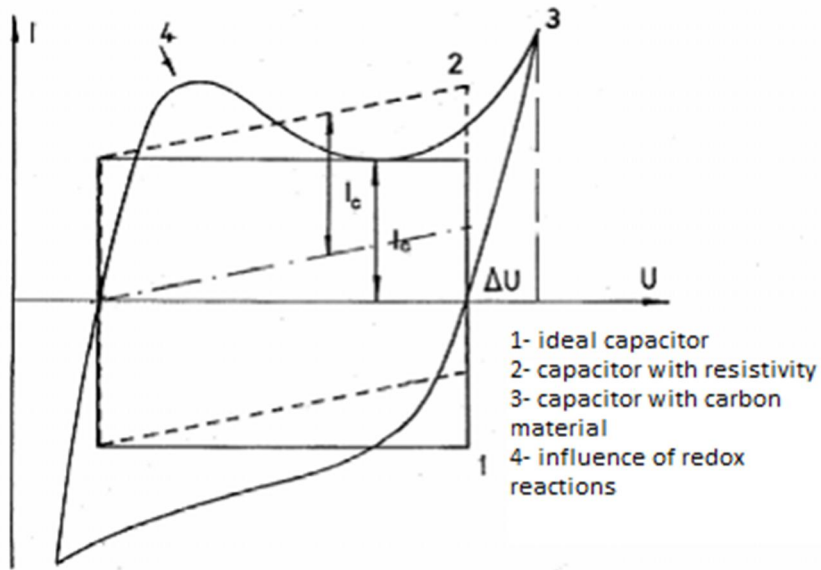


Fig. 14 Comparison of ideal and real cyclic voltammograms [15]

Charging and discharging at higher power levels correspond to faster sweep rates. Multiple plots which are obtained at different sweep rates are usually displayed on the same graph to demonstrate the influence of power levels on the charging characteristics (Fig. 15).

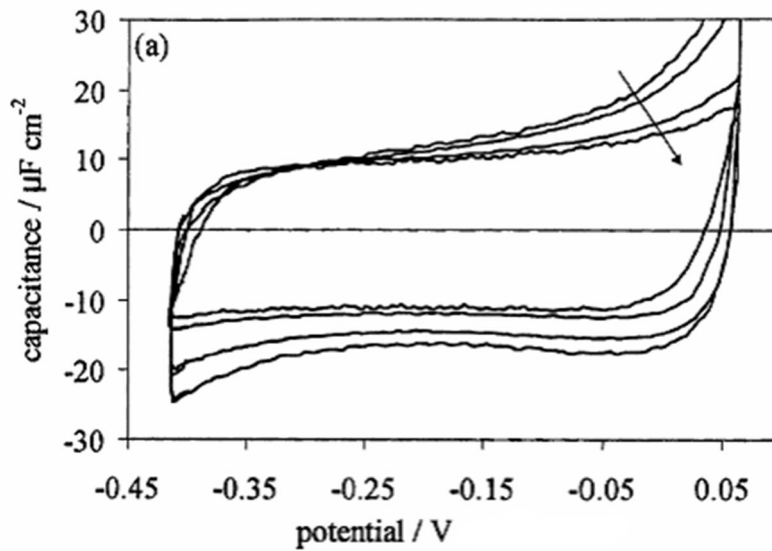


Fig. 15 Cyclic voltammograms at different sweep rates [55]

4.2 Galvanostatic method

Capacitance of a supercapacitor can also be evaluated by constant-current charging. The result of charging or discharging the cell at a constant current is a voltage response. The signal is applied to the system and causes the potential to scan from the starting potential to the final potential and back again. Different currents can be chosen resulting in different current densities that can be used to calculate specific capacitance.

A typical constant current charge and discharge chart of an ideal supercapacitor is characterized by linear charging and discharging curves as shown on the figure 16. However, a supercapacitor which is characterized by pseudocapacitance has non-linear charge and discharge curves.

Then, capacitance is calculated by the same formula (11) as in the case of cyclic voltammetry.

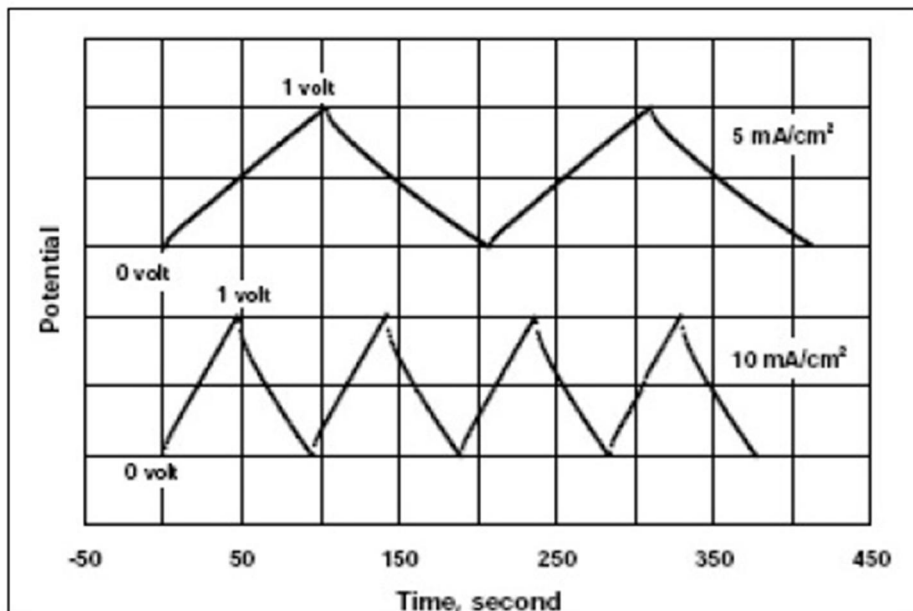


Fig. 16 Typical charge and discharge curves for a supercapacitor [55]

4.3 Testing nanotubes

For this experiment multiwalled carbon nanotubes produced by Chinese company Hongwu Nanometer were taken.

Known properties:

Purity: 98%

Outside diameter: $D = 60 \text{ nm}$

Inside diameter: $d = 40 \text{ nm}$

Assumed properties:

All values are assumed from numerous past experiments which were conducted in Russian Academy of Sciences A. N. Frumkin Institute of Physical Chemistry and Electrochemistry.

Length: $l = 1 \text{ cm}$

Density: $\rho = 2 \text{ g/cm}^3$

Specific capacitance: $C_{\text{sp}} = 5 \text{ }\mu\text{F/cm}^2$

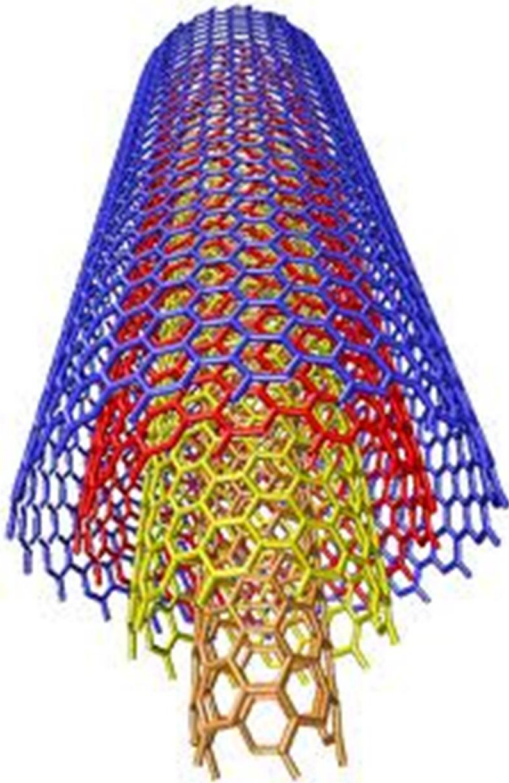


Fig. 17 Schematic view of multiwalled carbon nanotube [56]

Calculations:

Inside radius: $r_1 = 20 \cdot 10^{-7} \text{ cm}$

Outside radius: $r_2 = 30 \cdot 10^{-7}$ cm

Surface area: $S = 2 \cdot \pi \cdot r_1 \cdot l + 2 \cdot \pi \cdot r_2 \cdot l = 2 \cdot \pi \cdot 20 \cdot 10^{-7} \cdot 1 + 2 \cdot \pi \cdot 30 \cdot 10^{-7} \cdot 1 = 3.14 \cdot 10^{-5}$ cm²

In this specific case we need the volume V between tubes to calculate the mass. In any type of carbon nanotubes the charge is stored on the surface

Volume: $V = 2 \cdot \pi \cdot l \cdot (r_2^2 - r_1^2) = 2 \cdot \pi \cdot 1 \cdot ((30 \cdot 10^{-7})^2 - (20 \cdot 10^{-7})^2) = 3.14 \cdot 10^{-11}$ cm³

Capacitance: $C' = (C_{sp} \cdot S) / (\rho \cdot V) = 2.5$ F/g

Items used:

Cell: In order to conduct the experiment properly a cell, which is a model of double layer supercapacitor should be taken (a photo of the cell is shown in Figure 18). As we see a two electrodes scheme is used.

Counter electrode: The counter electrode is prepared from carbon material of high capacitance (absorbent carbon). It was cut from carbonaceous fabric. It is important to prepare it in shape and size of the cell (circle). The main requirement to the counter electrode material in case of the two electrode scheme is the capacitance much higher than in the testing material. The material was bought additionally. It consists of absorbent carbon and the fabric. It does not contain CNTs. The capacitance of the material usually is at least 30 F/g.

Working electrode: There was no special process of electrodes preparations. Nanotubes were just poured on the separator. 28 mg were taken and weighted by standard laboratory scales. 28 mg of the material which were poured on the separator formed the layer. When the cell was closed the contact of the material and current collector was ensured.

Separator: Separator was a hydrophilic porous teflon (should be used in case of acid). For example, in case of an alkali or any other non-aggressive electrolyte polypropylene could be used. The thickness of the separator was approximately 1 mm.

Electrolyte: 0.5 M H_2SO_4 . The amount of electrolyte should be large enough to get the electrodes and the separator wet. Different types of electrolytes could also be used but only sulfuric acid was tested.



Fig. 18 Testing cell photo, made in the laboratory

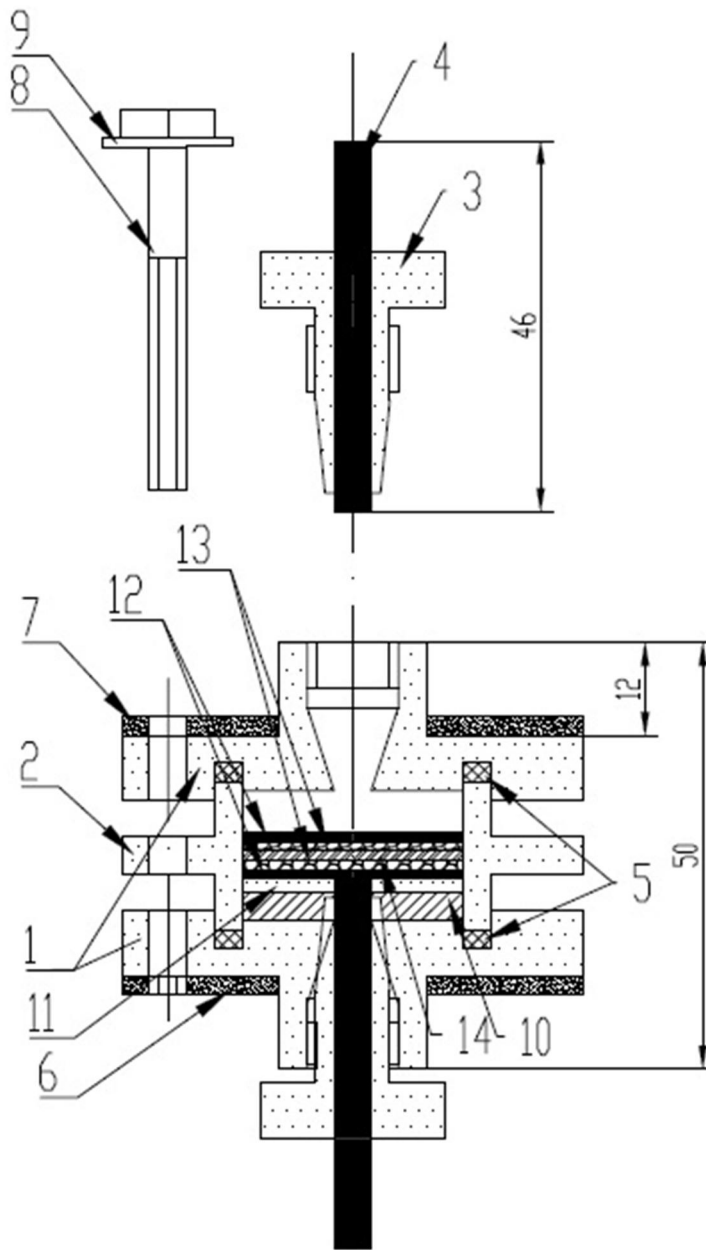


Fig. 19 Drawing of the partially assembled electrochemical cell (1 - Teflon cell covers, 2 – Teflon case, 3 – Teflon conical screw-plugs, 4 – Graphite current suppliers, 5 – Rubber sealing rings, 6 – Force plate – a nut, 7 – Force plate – a washer, 8 – Bolt M6 in length of 45 mm, 9 – Washer, 10 – Rubber sealing washer, 11 - Teflon washer, 12 – Graphite contact disk, 13 – Electrode from carbonaceous fabric, 14 – Separator)

Working electrode is the electrode with the testing material. Counter electrode is the electrode with carbon material of high capacitance. However, the counter electrode material capacitance

must be higher than the working electrode material capacitance in order to conduct measurements correctly. In fact, its capacitance is so big that $\frac{1}{C_{\text{counter}}} + \frac{1}{C_{\text{test}}} \approx \frac{1}{C_{\text{test}}}$.

It is possible to use the counter electrode material in commercial supercapacitors and for testing purposes. Its usability depends on if the sample of activated carbon has a satisfactory capacitance. According to evaluative calculations the approximate weight of the counter electrode is 300 times the weight of the working electrode. So, in this case the high mass of the counter electrode is the fact providing a high enough capacitance for the counter electrode.

It is naturally possible to prepare two similar electrodes and avoid therefore the use of the counter electrode.

Testing:

First of all, the half of the cell with the counter electrode was assembled according to Figure 19. Secondly, carbon nanotubes were poured on the separator. Then, electrolyte must be filled in. Finally, the cell must be closed.

Measurements:

Cycling of the cell was done with the cycler which was working in the mode of potentiostat (in case of cyclic voltammetry) and in the mode of galvanostat (in case of constant current charging and discharging).

Firstly, the cell must be connected to the cycler by crocodile clips (see Fig. 18).

Secondly, process of cycling (charging and discharging) should be done. Personal computer with special soft is required for that purpose. After setting parameters (voltage window (mV), cycling rate (mV/s) in case of voltammetry and in case of galvanostatic method the value of the current (mA) and charging time (s)) the process of cycling must be started. The more cycles are done the better, but usually 10-15 cycles are enough. Important fact that on the first cycles there could be processes that will not appear during the next processes should be taken into consideration (for instance wetting of the material). All data is collected to the .dat file. Next, this file was opened by "Origin" program. "Origin" presents the data in the form of a

table, which is used for plotting the graph. The same sequence of actions should be done in case of galvanostatic method.

Analysis of the results:

Results for cyclic voltammetry are shown in Figure 20. Different voltage windows are shown by different colors. Left low corner of each line is a result of high oxidation but level of oxidation has reduced after few cycles.

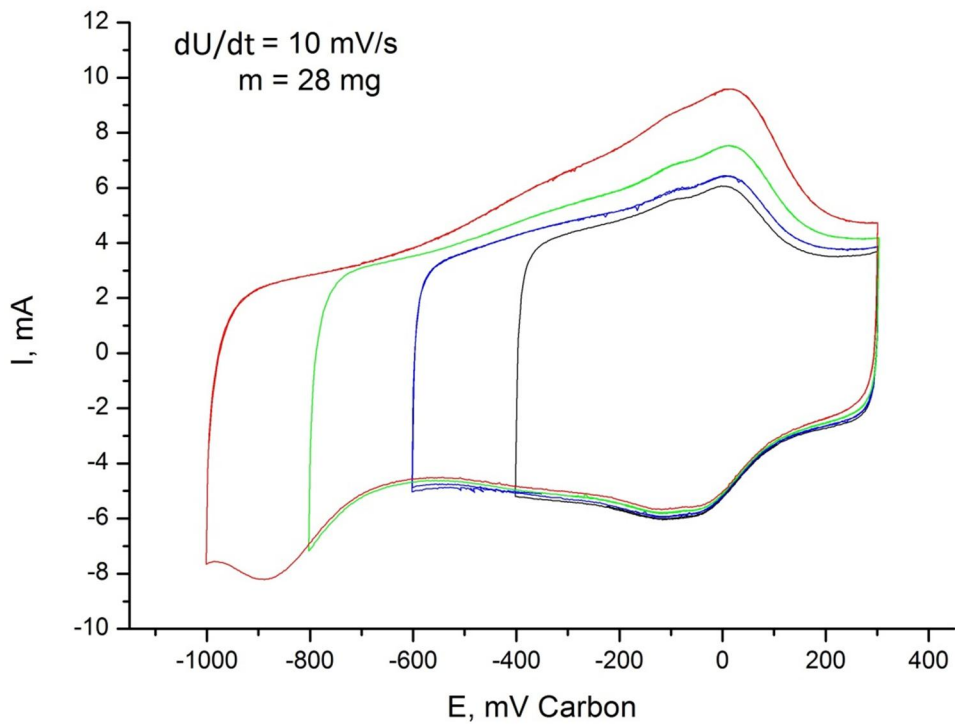


Fig. 20 Cyclic voltammogram.

In figure 20 we can see the measured current versus the voltage. The specific capacitance is calculated from the obtained data with the help of the equation:

$$C' = \frac{Q}{U \cdot m} = \frac{I \cdot \tau}{U \cdot m} = \frac{6}{10 \cdot 0.028} \approx 17 \text{ F/g} \quad (12)$$

The result must be divided on the amount of grams in order to obtain specific values. Different cycling rates are shown by different colors.

Result for the capacitance is taken as an average for upper left quarter of coordinate plane. In our case the capacitance is approximately 17 F/g which is a poor result. The area which is surrounded by the curve shows the amount of the energy which is accumulated. Non standard shape of the curve can be explained by the presence of the pseudocapacitance. As the result we have peaks in the lower left corner (accumulated energy) and in the upper right corner (discharge of the accumulated energy).

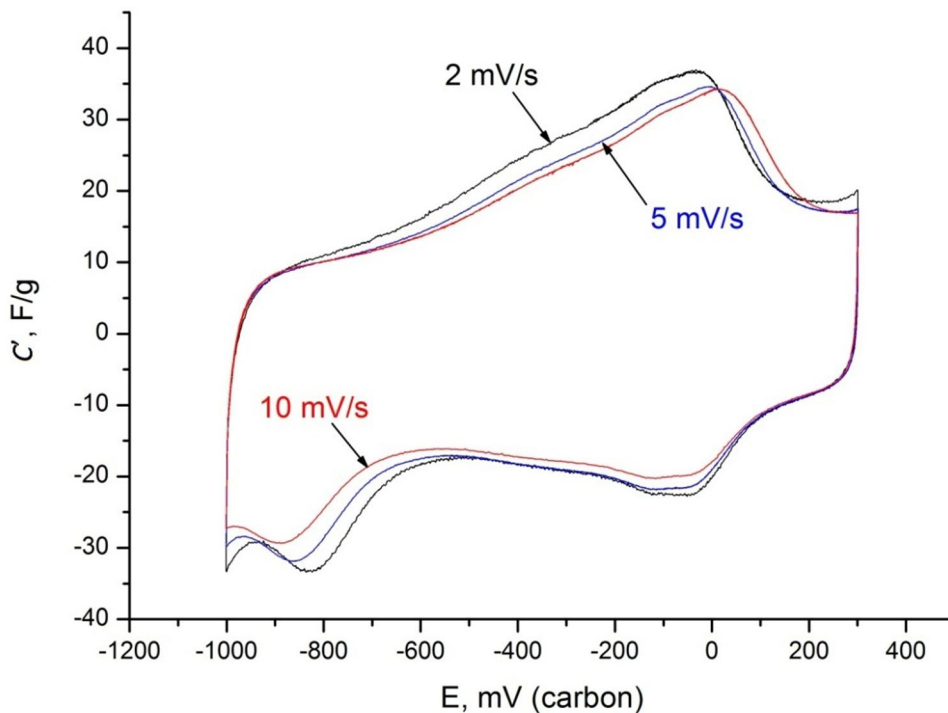


Fig. 21 Cyclic voltammogram

Figure 22 shows the result for galvanostatic method. Different charging times are shown by different colors.

Capacitance for galvanostatic method can be calculated from the same equation.

$$C' = \frac{\tau \cdot I}{U \cdot m} = \frac{220 \cdot 0.002}{1 \cdot 0.028} = 15.7 \text{ F/g} \quad (12)$$

We can claim that the capacitance does not change much from cycle to cycle.

From the shape of the galvanostatic lines we can see that the material has pseudocapacitance (lines are not straight). The surface area above the the curves corresponds to the energy of the discharge Presence of the pseudocapacitance can explain why the experimental capacitance is higher than the theoretical.

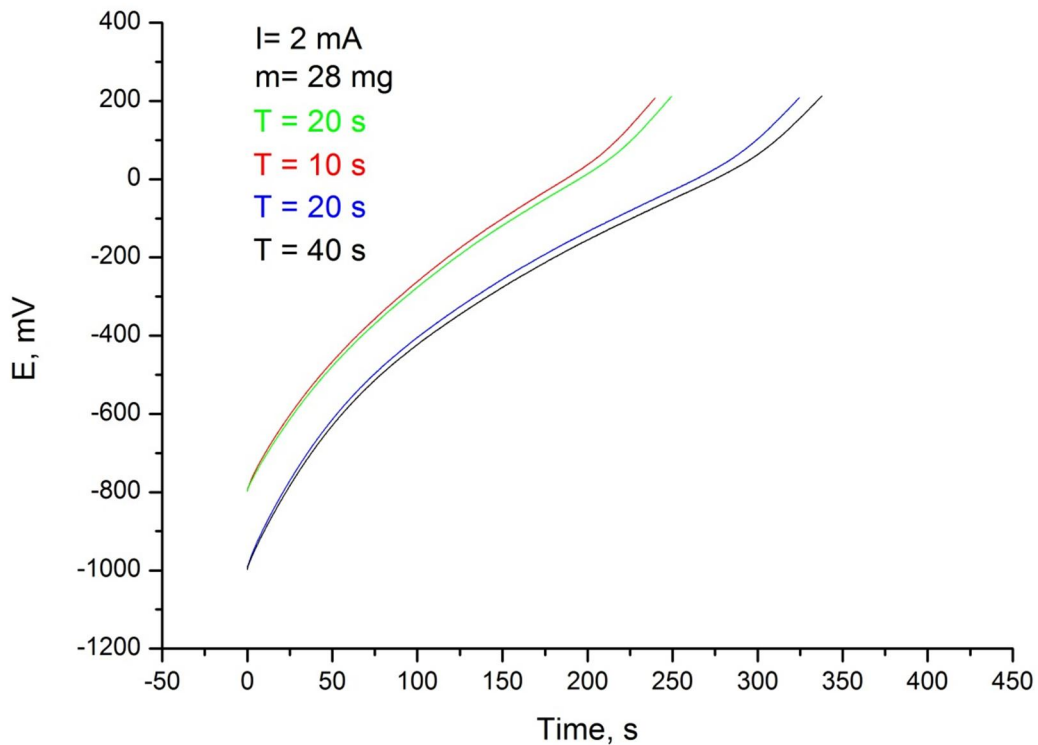


Fig. 22 Galvanostatic curves with the charging time T as a parameter

5 CONCLUSION AND FUTURE WORK

The aim of this study was to make an overview of electrochemical double-layer capacitor technology as it exists today. This research provides basic information about all aspects of supercapacitors. The study describes the history of development efforts and also covers the

scientific background of double-layer capacitor technology. Possible applications of EDLC technology have also been described and the wide range of possibilities that exist was also introduced to the reader.

The EDLC technology is very prospective. In a short time supercapacitors can become viable alternative to batteries. New ways how supercapacitors could be used effectively can also be discovered. Because of the advantages of charging efficiency, long lifetime, fast response, and wide operating temperature range, it is possible to apply EDLCs to any application that requires energy storage. However, the limitations of current technology must be taken into account. Commercial EDLC devices have been available for many years and they are still improving. As devices of higher energy density and higher power become available on the market, more new applications are found and demand will rise dramatically. Increased levels of interest in the technology then lead to increased development and research efforts, which will result in better devices being manufactured. As manufacturing quantities and demand both increase costs will go down.

One of the most important things is to remember about the differences of battery, capacitor and supercapacitor technologies and to understand in which applications each technology should be used.

One chapter of this research is devoted to the methods of testing and analyzing properties of the materials which are used in supercapacitors. Galvanostatic method and cyclic voltammetry method are described. Multiwalled carbon nanotubes were taken as an example and detailed description of measuring specific capacitance and the analysis of obtained data are provided. In the future the description can be used to measure properties of different electrode materials. Different combinations of electrode materials and electrolytes can also be evaluated.

Finally, it should be noted that supercapacitors are a part of the new advanced energy storage devices that will become a useful tool to develop highly efficient electrical and electronic systems and increase energy efficiency.

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