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SUPERCAPACITORS FOR ENERGY STORAGE

SUPERKAPACITORY PRO AKUMULACI ENERGIE

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BAKALÁŘSKÁ PRÁCE

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Superkapacitory pro akumulaci energie

POKYNY PRO VYPRACOVÁNÍ:

Sestavte přehled použití superkapacitorů v zařízeních pro akumulaci energie. Na základě získaných znalostí navrhnete zařízení pro akumulaci energie s kapacitou nejméně 1 Wh při jmenovitém napětí 24 V. Porovnejte toto zařízení se standardně používanými akumulátory z hlediska předpokládané ceny, životnosti a elektrických parametrů.

DOPORUČENÁ LITERATURA:

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Abstract

This bachelor thesis focuses on problematics of supercapacitors. The first chapter deals with principles of operation of a supercapacitor. The basic principle, used materials and main advantages and disadvantages are described. Furthermore, are described applications of a supercapacitor technology in various branches of industry. The following chapter outlines another type of energy storage also with their advantages and disadvantages, what is more, a brief table comparing main parameters is presented. The last chapter focuses on the theoretical design of supercapacitor module.

Abstrakt

Tato bakalářská práce je zaměřena na problematiku superkapacitorů. První kapitola se zabývá principem funkčnosti superkapacitoru. Jsou představeny základní funkční principy, použité materiály, hlavní výhody a nevýhody superkapacitoru. Dále jsou představeny možnosti využití superkapacitoru v různých průmyslových odvětvích. Následující kapitola nastiňuje ostatní způsoby ukládání energie i s jejich výhodami a nevýhodami, která je doplněna o srovnávací tabulku s parametry. Poslední kapitola je zaměřena na teoretický návrh modulu superkapacitorů.

Key words

Supercapacitor, energy storage, EDLC, supercapacitor module, usage of supercapacitor, materials,

Klíčová slova

Superkapacity, ukládání energie, EDLC, modul superkapacitorů, použití superkapacitoru, materiály

Poděkování

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V Brně dne

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(podpis autora)

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1. Supercapacitors

1.1. Introduction

Modern world requires a lot of energy. The power of various applications rises at a huge rate which corresponds with energy consumption. Therefore, we are looking for means of a fast and effective energy storage. Currently the vast amounts of ways to restore lost energy exist, for example, recuperation of braking energy in vehicles. Problem is that even though we are increasing power capabilities, we are still using old energy storage devices. Conventional battery charging cycles are very slow, while we need to store energy quickly and effectively. Also, actual numbers of cycles are limited by chemical reactions which hold a charge which leads to further problems in long-term runs.

Supercapacitors could be possible answers to problems mentioned above. These devices are able to be charged and discharged very quickly and their lifetime is not limited by a number of charging cycles. This technology is almost a half century old but only began to develop in recent years, when demand on energy saving is on the rise. Supercapacitors might be applied in various industries. From heavy industry, where it is used to save recuperated energy from a crane, through public transport where it can reduce the energy consumption of trams to Formula 1, where pilots can use stored power in supercapacitors via KERS system to gain the critical advantage on the long straights. The main aim of this thesis is to explain problematic of supercapacitors. The principle of operation, electrical parameters, linking rules and applications are discussed. Furthermore, other methods of electrical energy storage are described and compared to a supercapacitor. In the end, a design of supercapacitor module with rated voltage 24 V and energy capacity of 1 Wh is presented.

1.2. History

The capacity of an electrical charge in the interface between a metal and an electrolytic arrangement has been examined by scientists since the nineteenth century, however the commonsense utilization of double-layer capacitors just started in 1957,

when a patent was set by General Electric for an electrolytic capacitor utilizing permeable 4 carbon electrodes

Later, in 1966, The Standard Oil Organization, Cleveland, Ohio (SOHIO) patented a stored energy in the doublelayer interface . As of now SOHIO recognized that "the 'double layer' at the interface carries on like a capacitor of moderately high specific capacity." SOHIO went ahead to patent a circle formed capacitor in 1970 using a carbon paste absorbed an electrolyte. By 1971, a resulting absence of sales drove SOHIO to surrender development and license the innovation to NEC. NEC went on to deliver the commercially successful double-layer capacitors under the name "supercapacitor."

These low voltage gadgets had a high inner resistance and were in this manner essentially intended for memory backup applications, discovering their way into different customer apparatuses . By the 1980's various organizations were creating electrochemical capacitors. Matsushita Electric Modern Co., (also called Panasonic in the Western world), had built up the "Gold capacitor" since 1978. Like those delivered by NEC, these gadgets were additionally expected for use in memory reinforcement applications . By 1987 ELNA had started creating their own double-layer capacitor under the name "Dynacap" . The first high-power double-layer capacitors were created by PRI. The "PRI Ultracapacitor," created from 1982, consolidated metal-oxide cathodes and was intended for military applications, for example, laser weaponry and rocket guidance systems . News of these gadgets set off a review by the United States Department of Energy (DoE) with regards to hybrid electric vehicles, and by 1992 the DoE Ultracapacitor Improvement Program was in progress at Maxwell Research facilities[1]

1.3. Principle of operation

The principle of operation of supercapacitor depends on energy storage and distribution of the ions originating from the electrolyte to surface region of the electrodes. In light of the energy storage mechanism supercapacitors are arranged into three classes: Electrochemical double-layer capacitors, pseudocapacitors, and hybrid supercapacitors as appeared in figure underneath.[3]

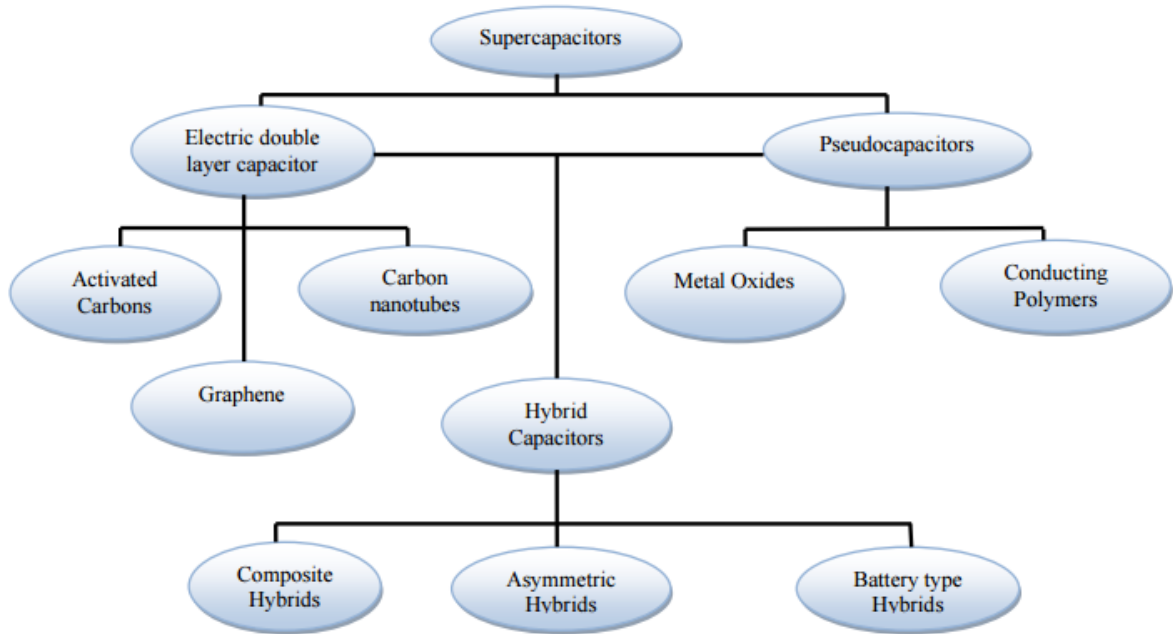


Figure 1 Taxonomy of supercapacitors [2]

1.4. Electric double layer capacitor

EDLCs are built utilizing two carbon based materials as electrodes, an electrolyte and a separator. EDLCs can either store charge electrostatically or by means of non-faradic process, which includes no exchange of charge amongst electrode and the electrolyte. The guideline of energy storage utilized by EDLCs is the electrochemical double-layer. At the point when voltage is applied, there is an amassing of charge on electrode surfaces, because of the distinction in potential there is an attraction of opposite charges, these outcomes to IONS in electrolyte diffusing over the separator and onto pores of the opposite charged electrode. To maintain a strategic distance from recombination of ions at electrodes a double layer of charge is framed.

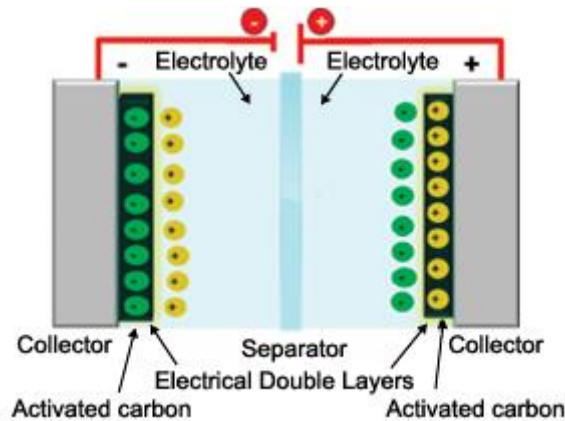


Figure 2 Scheme of EDLC [18]

The double layer, joined with the expansion in specific surface area and separations between electrodes diminished, enables EDLCs to achieve higher energy density Also, due to the EDLCs storage mechanism this takes into account quick energy take-up, delivery and better power performance. Due to non-faradic process, that is not a chemical reaction. It disposes of swelling seen in an active material which batteries show amid charging and discharging.[2]

List of contrasts between EDLCs and batteries

- EDLCs can withstand a great many cycles not at all like batteries that can withstand a couple thousands,.
- Energy storage mechanism does not include solvent of the electrolyte; in a Li-ion batteries it contributes to solid electrolyte inner phase when high-potential cathodes are utilized or graphite anodes. Because of the electrostatic surface charging mechanism,
- EDLCs devices encounter a limited energy density, which is the reason today's EDLCs research is fundamentally centered around expanding energy performance and enhancing temperature range where batteries can't work.
- Performance of EDLC can be balanced relying upon the sort of electrolyte utilized.

1.4.1. Pseudocapacitors

Contrasted with EDLCs, that store charge electro-statically. Pseudocapacitors store charge by means of faradic process which includes the exchange of charge amongst electrode and electrolyte. At the point when a potential is applied to a pseudocapacitors reduction and oxidation happens on the electrode material, which includes the passage of charge over the double layer, bringing about faradic current going through the supercapacitor cell. The faradic process involved in pseudocapacitors enables them to achieve greater specific capacitance and energy densities contrasted with EDLCs. Cases are metal oxides, conducting polymers. Which prompts enthusiasm for these materials yet due the faradic nature, it includes reduction-oxidation reaction simply like on account of batteries; consequently they likewise endure absence of stability amid cycling and low power density.[2]

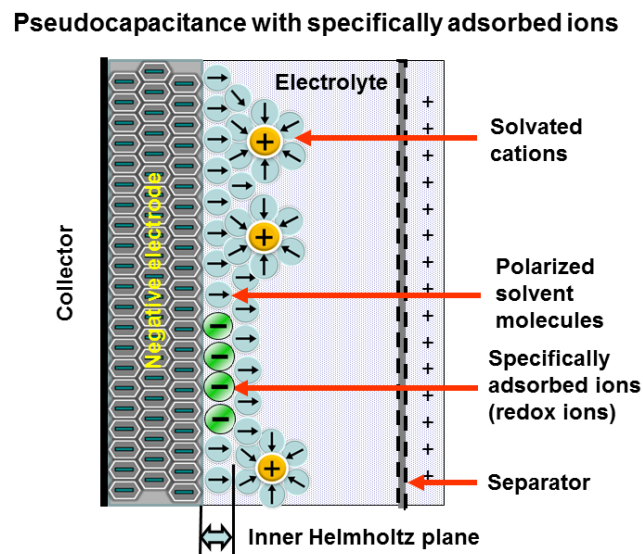


Figure 3 Scheme of a pseudocapacitor [19]

1.4.2. Hybrid capacitors

As was introduced, EDLCs offer great cyclic stability, great power performance while on account of pseudo capacitance it offers great specific capacitance. On account

of hybrid system it offers a mix of both, that is, by consolidating the energy source of battery-like electrode, with a power source of capacitor-like electrode in a same cell.

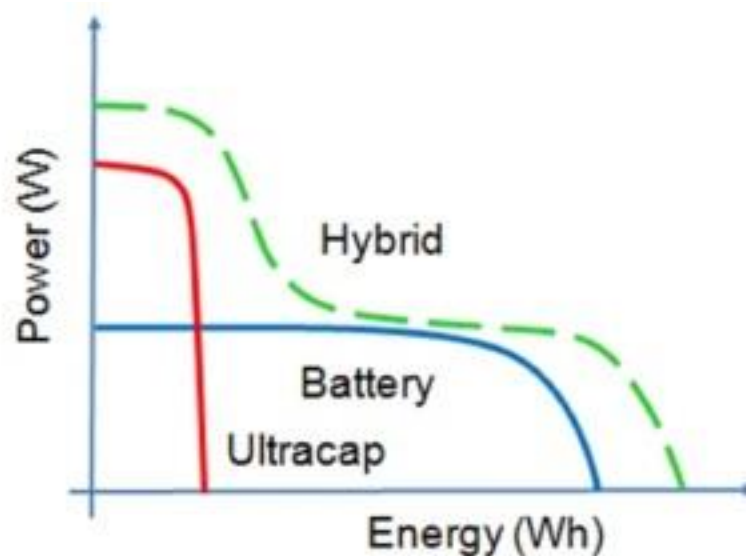


Figure 4 Plot of hybrid supercapacitor energy to power comparison [20]

With a right electrode mix it is conceivable to expand the cell voltage, which thus prompts an improvement in energy and power densities. A several combination have been tried in the past with both positive and negative electrodes in aqueous and inorganic electrolytes. For the most part, the faradic electrode outcomes in an expansion of energy density at the cost of cyclic stability, which is the fundamental disadvantage of hybrid gadgets contrasted with EDLCs, it is basic to abstain from transforming a decent supercapacitor into a standard battery. Currently, scientists have focused on the three distinct sorts of hybrid supercapacitors, which can be recognized by their electrode setups: Composite, Asymmetric and Battery-type.[2]

1.5. Materials used for supercapacitors

Among the parameters that depend on the kind of electrode materials utilized as a part of supercapacitors are capacitance and charge storage.

1.5.1. Carbon materials

Carbon materials in their different forms are the most utilized electrode materials in the manufacture of supercapacitors.

Reasons for usage of carbon materials

- high surface area
- low cost
- accessibility
- built up electrode production technologies.

The storage mechanism utilized via carbon materials is electrochemical double layer framed at the interface between the electrode and electrolyte. Henceforth, the capacitance for the most part depends at the surface area open to electrolyte ions. Critical components which impact the electrochemical performance are specific surface area, pore shape and structure, pore size distribution, surface usefulness and electrical conductivity.

Having a high specific surface area on account of carbon materials, brings about a high capability for charge aggregation at the interface of electrode and electrolyte. While enhancing specific capacitance for carbon materials, aside from pore size and high specific surface area, surface functionalization must be considered. Cases of carbon materials utilized as electrode materials are activated carbon, carbon aerogels, carbon nanotubes, graphene along with others.[2]

1.5.2. Activated carbon

The most broadly utilized electrode material is activated carbon (AC) and that is because of its vast surface area, great electrical properties and moderate cost. AC can be delivered by either physical or chemical initiation from different sorts of carbonaceous materials (e.g. wood, coal nutshell.). The physical enactment includes the treatment of carbon precursors at a high temperature (700-1200 °C) in the presence of oxidizing

gasses like steam, CO² and air. On account of chemical activation it is done at a lower temperature (400-700 °C) utilizing activating agents, for example, sodium hydroxide, potassium hydroxide and zinc chloride.

Contingent upon the activating methods and the carbon precursors utilized, AC have various physiochemical properties with well developed surface areas of up to 3000 m²/g. Permeable structure of AC acquired utilizing activation process had a wide pore size distribution that comprises of micropores (50 nm) . Various specialists have tried the connection between specific capacitance and specific surface area (SSA) of AC and it appears there is a discrepancy between them. Having a high SSA of around 3000m²/g, a moderately little capacitance was acquired. This shows not all pores are effective amid charge aggregation.

Subsequently, despite the fact that the SSA in EDLC is a critical parameter with regards to performance, some different viewpoints are also considered in carbon materials that impact electrochemical performance to extraordinary degree like pore size distribution . Also, over the top activation brings about extensive pore volume, which thus prompts disadvantages like low conductivity and material density, which will prompt a low energy density and loss of power capability. Endeavors have been made to see the impact of various electrolytes on the capacitance performance of AC. It was observed that the capacitance of AC is higher in fluid electrolytes (extending from 100 F/g to 300 F/g) when contrasted with natural electrolytes. [2]

1.5.3. Carbon nanotubes

With the discovery of CNT there has been a huge headway in the science and building of carbon materials. The component that determines the power density in a supercapacitor is the general resistance of the components. A lot of consideration is been given to CNT as supercapacitor anode material because of its novel pore structure, great mechanical and thermal stability and superior electrical properties . Carbon nanotubes are created through catalytic decomposition of a few hydrocarbons and by deliberately manipulating diverse parameters, it ends up plainly conceivable to produce nano structures in different compliances and furthermore control their crystalline structure .

Carbon nanotube not at all like other carbon based electrodes, have mesopores that are interconnected, this takes into account a continuous charge distribution that uses the majority of the open surface range. CNTs have a lower ESR than activated carbon in light of the fact that the electrolyte particles can diffuse into the mesoporous arrange. CNT can be ordered as single-walled carbon nanotubes (SWCNTs) or multi-walled carbon nanotubes (MWCNTs), both are for the most part explored as supercapacitor electrode materials. With regards to high power electrode materials CNT are respected because of their great electrical conductivity and promptly accessible surface area. Furthermore, they give a decent support to active materials because of their high mechanical resilience and open tubular system. For the most part, CNT have little SSA.[2]

1.5.4. Graphene

Graphene has appreciated huge late consideration . Graphene a one atom thick layer 2D structure has developed as a one of a kind carbon material that has potential for energy storage gadget applications on account of its brilliant qualities of high electrical conductivity, chemical stability , and substantial surface area . As of late, it was proposed that graphene can be utilized as a material for supercapacitor applications, since when graphene is utilized as supercapacitor electrode material it doesn't rely on upon the distribution of pores at solid state, when contrasted with other carbon materials, for example, activated carbon or carbon nanotube.

Among all carbon materials utilized as electrode materials electrochemical double layer capacitors, recently created graphene has higher particular surface area (SSA) around $2630\text{m}^2/\text{g}$. On the off chance that the whole SSA is completely used graphene is equipped for accomplishing a capacitance of up to 550 F/g . Another advantage of utilizing graphene as electrode material is that both major surfaces of graphene sheet are outside and are promptly available by electrolyte. There are a wide range of techniques as of now being explored for the production of various sorts of graphene, for example, chemical vapor deposition, micromechanical peeling, arch discharge method, unzipping of CNTs, epitaxial development, electrochemical and chemical methods and

intercalation methods in graphite . With a specific end goal to use the highest surface capacitance and specific surface. [2]

1.5.5. Metal oxide

Metal oxides show another option for materials utilized as a part of electrode creation in supercapacitor in light of the fact that they display high specific capacitance and low resistance, making it more straightforward to build supercapacitors with high energy and power. The usually utilized metal oxides are nickel oxide (NiO), ruthenium dioxide (RuO_2), manganese oxide (MnO_2), iridium oxide (IrO_2). The lower cost of creation and utilization of a milder electrolyte make them a possible option . [2]

1.6. The connection of supercapacitors

The connection of supercapacitors is based on same rules as the connection of any other large voltage power sources. Main aim is to ensure low electrical resistance of all conducting connections as well as mechanical rigidity of its joints which must withstand incidental mechanical shocks or eventual thermal expansion

Various methods are used for connection of supercapacitors. The most used are connection through buss bars. The main advantage of such connection is its simplicity followed by easy dismantling. Increased resistance and the possibility of loosen joints can be considered as a drawback. Welding or soldering are some of the methods to ensure lowest possible resistance which occurs by connecting of supercapacitors. Both cases represent unbreakable connection, therefore it is crucial to use such methods in the case where disassembly of a supercapacitor module is no longer required.[3]

1.6.1. Serial connection of supercapacitors

One of the biggest disadvantages of supercapacitors is their low nominal voltage which is around 2.5 V. Such voltage is unsatisfactory for the most application therefore, is necessary to establish the serial connection of supercapacitors to achieve desired voltage. Due to the fact that each capacitor has a low tolerance of capacitance and

resistance is, therefore, crucial to balance in supercapacitor in the manner that nominal voltage is not exceeded. [4]

1.6.2. Active balancing

Active balancing is working in the real-time and balances voltage depending on the actual situation on one or between two neighbouring elements. It is a comparator with an exact reference which in need switches discharging resistance on to capacitors clamps. Such solution is used in application which quickly switches between charge and discharge cycle i.e. cars, trams. [3]

1.6.3. Passive balancing

The most frequent utilization of passive balancing is based on usage of a resistor. Concept of resistive balancing uses resistor in parallel connection with supercapacitor

The range of resistance is based on leakage current and desired speed of voltage balancing. (Time may vary in hours or days) This method is used in applications with slow dynamics of Exchange of electrical energy e.g. backup resources. The disadvantages of such solution are increased losses and reduced efficiency.

Determination of the right number of supercapacitors depends on the intended application. Each application has different factors that need to be considered. The most crucial factors are:

- Maximum and minimum voltage
- Magnitude of average current or power
- Magnitude of power or current peaks
- Temperature

All of factors mentioned above must be considered when designing module of supercapacitor [4]

1.6.4. Supercapacitor linking rules

These rules must be followed when connecting supercapacitors

- Low resistance of joints: surface of connected parts must be clean, bolt joints tightened, contact area must be as large as possible
- Surface treatment: Oxidation affects the resistance of joints, therefore joints must be treated with an electrical conductive paste
- Thermal expansion: Loosen joints can occur when connecting materials with different thermal expansion which could result in increased electrical resistance, increased heating that will result in reduced quality of supercapacitor
- Interconnecting wire area: The area of the connecting wires must be designed to the highest expected currents with a safety factor of 1.5. Such connections should be dimensioned against occasional short circuit.
- Electrical insulation: additional insulation in between supercapacitors. A material and thickness must be designed with regard to the purpose of a supercapacitor.
- Galvanic corrosion of joints: Usage of material with lowest possible galvanic activity with aluminium is recommended when coupling supercapacitors. Corrosion occurs due to different electrochemical potentials of used materials.
- Mechanical stress: joints and the whole structure must be designed to withstand possible mechanical stress and shakes to prevent damaging of insulation
- Thermal resistance: the correct temperature for the normal supercapacitor functionality should range from $-40\text{ }^{\circ}\text{C}$ to $60\text{ }^{\circ}\text{C}$, therefore it is necessary to add a cooling device that will spread heat to surroundings. The lower temperature of supercapacitor will increase life time. Operation temperature should not drop below $-40\text{ }^{\circ}\text{C}$ otherwise will electrolyte freeze. Also, temperature should not exceed limits when is supercapacitor in idle [4]

1.7. Humidity

The supercapacitor cells are able to operate effectively at high levels of humidity. During operation, no special precautions are required other than to prevent condensation

and the collection of condensation that can interfere with the operation of any electrical device. However, storage humidity can have a negative effect on the supercapacitor. Those parts are shipped in vacuum packed containers in order to exclude moisture exposure to the parts when the parts are stored. The terminal pins of the cells are susceptible to oxidation and eventually corrosion due to high levels of humidity over prolonged periods of time. [3]

1.8. Pressure

Supercapacitor cells are able to tolerate low pressure operation without any negative effects or impacts. Operating at high pressure is also tolerated well up to nominal pressures above atmospheric. However, when high pressure is exceeding certain limits, negative effects may occur i.e. deformation of nanostructures or the whole module might be damaged.[3]

1.9. Polarity

Unlike many batteries, an anode and a cathode of a supercapacitor are comprised of the same material. If the positive and negative terminal and casing are also comprised of similar materials, then theoretically the supercapacitor has no true polarity. For manufacturing and consistency purposes terminals are marked with a polarity. It is recommended practice to maintain the polarity although catastrophic failure will not occur if the supercapacitor is reversed charged for some reason. However, if the supercapacitor has been conditioned for a charge in a certain direction and then is changed, the life will be reduced due to this conditioning. [3]

1.10. Charging

Since the energy storage mechanism of the supercapacitor is not a chemical reaction, charging/discharging of the supercapacitor can occur at the same rate. Therefore, the rated current for the supercapacitor applies for both charge and discharge. The efficiency of charge and discharge are in practical terms the same. A variety of methods are possible for charging of the supercapacitors. This may be either through

constant current or constant power charging via a DC source or through AC charging methods. [3]

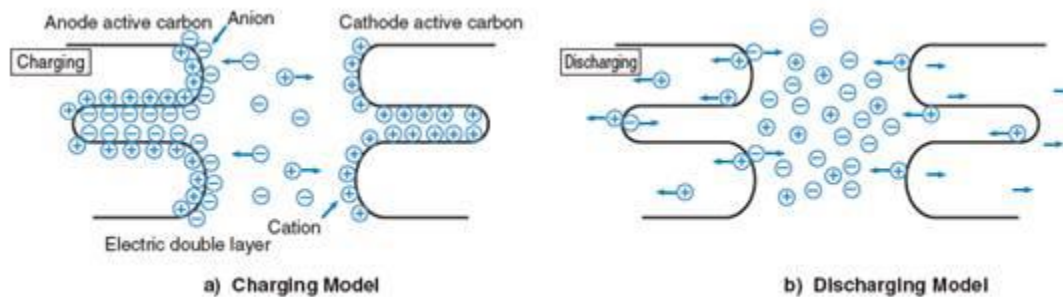


Figure 5 Charge and discharge model [21]

1.11. The efficiency

The efficiency of energy stored in a supercapacitor as well as an energy drained mainly depends on the efficiency of power transfer between a point of energy drain, a source of energy and a supercapacitor. Mainly it is the efficiency of an inverter, which is usually present and to whom is supercapacitor connected. A further aspect is ohmic losses during transfer of electric energy. Super capacitor's efficiency is very large (up to 98%) [3]

1.12. The lifetime

The lifetime of a supercapacitor is much longer compared to other energy storage devices. Some manufacturers claim that their supercapacitor is able to withstand up to 1 million cycles. Furthermore, when the supercapacitor reaches such limit it will continue working, but with aggravated attributes (reduced capacity, increased inner equivalent serial resistance). Next factors affecting lifetime are temperature and an operational voltage. [3]

1.13. Advantages of supercapacitors

- Almost unlimited recharge cycle
- Very low impedance
- Small recharge time

- Ability to deliver huge power
- High efficiency of the charging / discharging cycle >95%
- If is maximum voltage limited supercapacitors are impossible to overcharge
- Wide working temperature range -40 °C to 65 °C [6]

1.14. Disadvantages

- Expensive in comparison to conventional energy storage devices
- Low energy density
- Voltage drops during discharge – a converter required
- Low maximum voltage (0,9 V aqueous electrolyte / 2,7 V organic electrolyte)
- Huge self-discharge in comparison to standard accumulators
- Serial connection is complicated [6]

1.15. Specifications

Supercapacitors, as any other electrical component, have also parameters specifying properties. Manufacturer provides datasheet which carries component parameters. Furthermore, it is also possible to find various methods of measurement or typical applications. [5]

Description of supercapacitor parameters:

- **Capacity:** An electrical charge stored at a given electrical potential

$$C = \frac{Q}{U}$$

- **Voltage:** Maximum operating voltage for one cell. Rated voltage is dependent at temperature
- **Inner resistance:** It is a resistance involving all secondary resistances, such as: imperfection of manufacturing process, material, etc. It is one of two of main parameters indicating life of the supercapacitor.
- **Leakage current:** A stable parasitic current that discharges the supercapacitor even at idle

- **Thermal range:** Range of operating temperatures which would not affect its abilities
- **Maximum Continues current:** Current that can fed device without increasing device temperature beyond the supported range
- **Maximum peak current:** peak current of supercapacitor which does not affects lifetime
- **Lifetime:** until capacity is below 80% or inner resistance is doubled
- **Number of cycles:** In range of 500K to 1M of cycles [5]

1.16. Usage of supercapacitors

Supercapacitors are more popular each day and are being implemented at various applications which need to store electrical energy. The main field of application is propulsion devices. Thanks to its ability, supercapacitors allow us to store a vast amount of power in very short time which then can be very quickly used. This is useful when recuperating energy losses, mostly from braking. Huge opportunity for manufacturers is in public transport, where trams or buses have to accelerate and break very often. But we can find examples of usage of supercapacitors in racing. Formula 1 uses KERS system, which gives racers huge boost on straight lines for a short period of time. Below are listed examples of usage by supercapacitor manufacturer Maxwell [7]

1.17. List of examples of usage of supercapacitors

- Reliably crank semi-trucks when batteries are drained or in cold weather
- Provide voltage stabilization in star/stops system and cranking power in automotive systems
- Serve as an energy storage in regenerative braking systems
- Capture energy from regenerative systems and assist acceleration in trains and trams. Provide energy when overhead wiring systems are not available
- Function as safe systems to open doors in the event of power failure in aircrafts
- Capture energy and provide burst to assist in lifting operation
- Provide power backups for data centers in the event of failure

- Start-up back up power systems such as diesel generators or fuel cells
- Energy storage for firming the output of renewable installations and increasing grid stability [7]

2. Other types of storage of electrical energy

Means of storage

- Electrostatic field
- Flywheel
- Electrochemical transformation

2.1. Division of chemical sources

2.1.1. Primary cells

These are cells, which can't be recharged after discharging. They are commonly called batteries and can be used only once [8]

2.1.2. Secondary cells

Contrary to primary cells, these cells can accept electrons and recharge by adding external current. Electrical energy, which is used for charging, is accumulated in form of chemical energy. [8]

2.1.3. Lead-acid battery

The most generally utilized rechargeable battery is the lead–acid battery. The cathode is made of PbO_2 , the anode is made of Pb , and the electrolyte is sulphuric acid. Lead–acid batteries have quick reaction times, little day by day self-discharge rates, generally high cycle efficiencies and low capital expenses

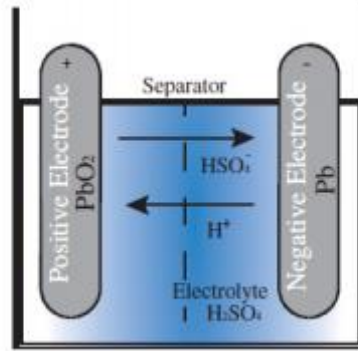


Figure 6 Illustration of a lead-acid battery[8]

Main advantages of Lead-acid batteries are:

- An acceptable energy and power density for stationary applications
- A complex cell management is not necessary
- Can be implemented in large scale storage
- A short amortization period and a low firstly investment regarding the barriers,

Main disadvantages of Lead-acid batteries:

- This technology has not enough research capability
- Limited cycle life
- The charging and discharging ability are not symmetrical.

Some progressed lead–acid batteries have achieved faster reactions than flywheels and supercapacitors and a few of them are in the development stage, for example, Ecoult UltraBattery brilliant frameworks and Xtreme Power progressed lead–acid "Dry Cell". [8]

2.1.4. Li-Ion battery

In a Li-Ion battery, the cathode is made of a lithium metal oxide, for example, LiCoO₂ and LiMO₂, and the anode is made of graphitic carbon. Graphite is promptly accessible naturally or as a by-product of oil, yet the cost fluctuates, contingent upon the heat-treatment process, in any case, the graphite framework has a constrained limit of around 310 mAh/g.

Then again, soft carbons (500-1000 °C) give a reversible capacity of about 700 mAh/g and hard carbons (± 1100 °C) give a reversible limit of 600 mAh/g, however with little irreversible limit capacity loss and polarization. In the commercial cells, very established graphite, for example, mesocarbon microbeads (MCMB) (3000 °C), normal graphite and nongraphitizing carbons have been mostly utilized. There are other intermetallic materials that have been explored as alternatives for high specific capacity, for example, Si, Sn or SnO^2 . A scheme of the cell structure is appears in the figure beneath.

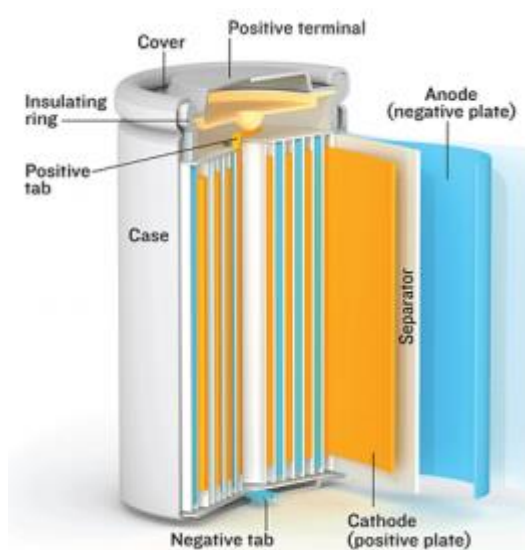


Figure 7 Cross section of a Li-Ion cell [8]

These days, Li-ion batteries are generally stretched out for portable hardware applications because of their good performance and energy density and additionally their advances in system design and assembling. In addition, this innovation has points of interest as well as a few difficulties:

- Li-Ion batteries have an inherent risk of fire, heat generation and thermal runaway in the presence of flammable organic electrolyte solvents because the Li-graphite electrode operates at a potential close to that of metallic lithium. To minimize this risk, lithium ion batteries are equipped with a monitoring unit to avoid over-charging and over-discharging.

- To prevent voltage deviations among each individual cell, it can be implemented a voltage balance circuit, which could also monitor the voltage level.
- Reduce the high cost. This is not a problem in small portable electronic applications but is critical in scale-up applications, as HEVs, PHEVs or EVs. Moreover, in some cases, an on-board computer is necessary, which implies an additional cost and the high cost is mainly attributed to the materials cost
- While promising progress has been achieved with the high-capacity alloy anodes, structural stability issues ascribed to large-volume expansion (300-400 vol %) during alloying with lithium still remain. [8]

2.1.5. NiCad

These batteries have been in business use since around 1915. A NiCad battery utilizes nickel hydroxide and metallic cadmium as two electrodes and an aqueous alkali arrangement as the electrolyte.

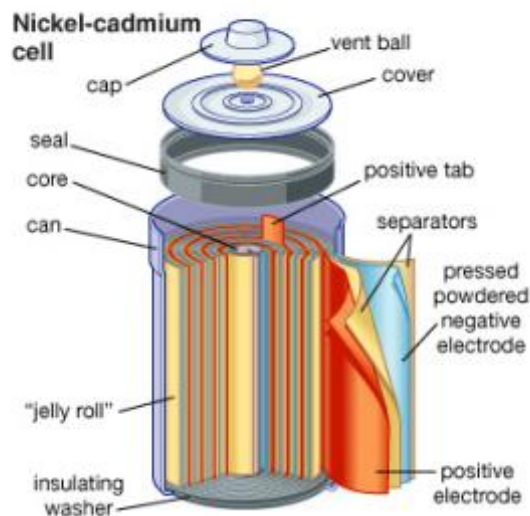


Figure 8 Cross section of NiCad cell [8]

The main advantages:

- Relatively high robust reliabilities.
- Low maintenance requirements.
- It is a very successful battery product because of the capacity of performing well in a large low-temperature range (from -20°C to 40°C)

The main disadvantages:

- Cadmium and nickel are toxic heavy metals, resulting in environmental hazards
- The battery suffers from the memory effect, the maximum capacity can be dramatically decreased if the battery is repeatedly recharged after being only partially discharged [8]

2.1.6. NaS

A NaS battery utilizes liquid sodium and liquid sulphur as two electrodes, and utilizes beta alumina as the solid electrolyte.

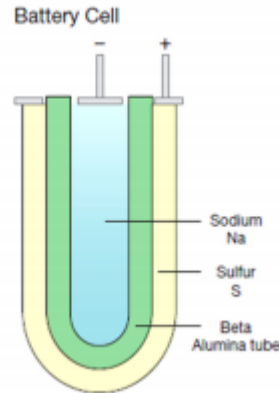


Figure 9 NaS battery cell [8]

The main advantages:

- A relatively high energy densities (150–300Wh/L).
- Almost zero daily self-discharge.
- Highly energy efficient (89–92%).
- Higher rated capacity than other types of batteries (up to 244.8MWh).
- High pulse power capability.
- Inexpensive materials.
- Non-toxic and high materials recyclability (99%).

The main disadvantages:

- High annual operating cost (80 \$/kW/year).
- The chemical reactions require a temperature of 300–350 °C to ensure the electrodes are in liquid states, which leads to a high reactivity and, because of that, an extra system required to ensure its operating temperature (which implies an extra cost too)
- Suitable only for large-scale stationary applications.[8]

2.2. Flywheels

Flywheels utilize rotational mechanical movement of a mass around a settled pivot as an instrument to store kinetic energy. In a flywheel electric energy storage framework the turning mass is coupled by means of an electric motor (engine/generator) and a power inverter to an outside electric circuit. At the point when electric power is connected to the motor utilizing it as an engine to make a torque accelerating the turning mass, the flywheel storage is charged.

On the other hand, when the turning mass conveys a torque to the motor utilized as a generator to give electric power to the outer circuit, the flywheel storage is released. To a great extent the flywheel mass, geometry and speed decide the energy storage ability, while engine/generator and power gadgets determine the power capacity. As of now, the biggest single flywheel storage frameworks have a limit of up to 360 MJ of energy and rated power of 5 MW. The proportion of these numbers yields a least

required time allotment for about entire charge or release of somewhat more than one minute.

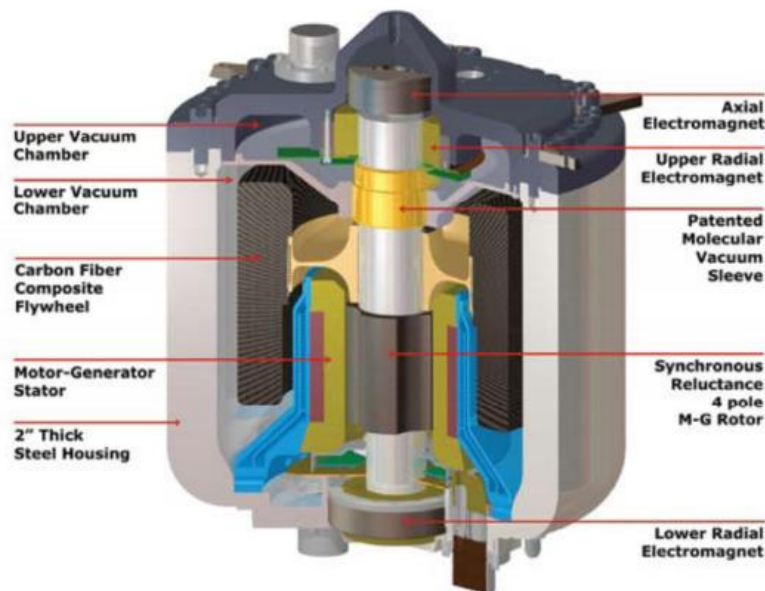


Figure 10 Cross section of flywheel [22]

The easiest technique to utilize the flywheel system is to utilize a standard engine with a generally high characteristic pivoting mass. The inertia of this pivoting mass is as of now utilized as a part of generators in large power plants today. The same applies to numerous industry drive applications worked today. Fluctuations in the electrical framework can in this manner be compensated by misusing the energy limited in this turning mass and its latency. In these straightforward flywheel applications, ordinarily the rotational speed amid operation is a great deal not as much as the basic speed of rotor defragmentation, so no extra preventive measures are required. Conversely, for superior flywheels, the requests for high proficiency require high rotor radius, high material density and particularly fastest possible rotational speed without the hazard to violate operational security.[9]

Benefits of flywheels:

- High power density nearly independent of stored energy level.
- High energy density.
- Proven technology of motors, inverters and rotating masses.

- Long service (15 years).
- Wide range of operating temperature.
- Unlimited charging cycles (if good maintenance provided).
- Relatively high round-trip efficiency.
- Real time monitoring of its charge.
- Short recharge time.
- Scalable technology and universal localization.
- Environmental friendly materials, low environmental impact.

Disadvantages:

- Potential failure of different components (bearings, vacuum pump, cooling fans, control sensors).
- High complexity of durable and low loss bearings.
- Stress and fatigue limits for the mechanical parts, material limits at around 700 m/s tip speed.
- Gyroscopic forces during operation in case of varying angular orientation.
- Hazardous failure modes requiring extensive burst protection.
- Lower energy density.
- Small applications might have deeper impact on environment (e.g., < 50 kW).
- High standby losses.[9]

2.3. Comparison of supercapacitors and other electrical energy storages

	SUPERCAPACITORS	FLYWHEELS	LEAD- ACID	LI-ION	NAS	NI-CAD
CHARGE TIME	Milliseconds to hours	Seconds to hours	Minutes - hours	Minutes- hours	Minutes- hours	Minutes- hours
DISCHARGE TIME	Milliseconds to hours	Seconds to hours	Seconds - hours	Minutes- hours	Seconds- hours	Seconds- hours
ENERGY WH/KG	1 to 10	10-100	10 to 100	10-100	10-100	10-100
LIFETIME	100000+cycles	15 years	500-1000 cycles	1000+ cycles	2500 cycles	2500 cycles
SPECIFIC POWER	0-300 kw	0-20 mw	0-20 mw	0-100 kw	50 kw-80 mw	0-40 mw
EFFICIENCY	>95%	>85%	>35%	>95%	>90%	>95%
COST [\$/KWH]	300-2000	1000-5000	200-400	600-2500	300-500	;800-1500

Table 1 Table of energy storage parameters [5,6,8,17]

2.4. The Ragone plot

The Ragone plot is used to compare the performance of a range of electrochemical and electromechanical devices.[10]

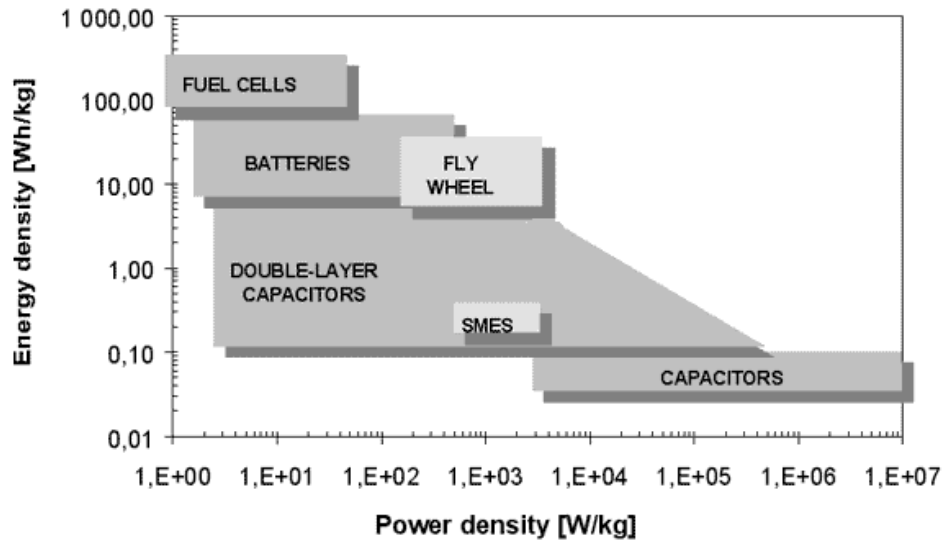


Figure 11 The Ragone plot [17]

3. Module design

3.1. Equations for calculations

[11]Supercapacitors are very useful and in many applications unbeatable way of storage of an electric energy. Even though supercapacitor has a large capacity, it is limited by small voltage, usually between 2,3 V and 2,7 V. Therefore it is crucial to connect supercapacitors in series, which allows adding voltage up to required value.

In case of serial connection capacitance is calculated by an equation:

$$\frac{1}{c} = \frac{1}{c_1} + \frac{1}{c_2} + \frac{1}{c_3} + \dots + \frac{1}{c_n} \quad (F)$$

Voltage is calculated by an equation:

$$U = U_1 + U_2 + U_3 + \dots + U_n \quad (U)$$

Where n is number of connected supercapacitors

An equation for the stored energy in joules is calculated:

$$E_{\text{stor}} = \frac{CV^2}{2} (j)$$

However we must calculate with unused energy after discharge. Discharging will be done at a quarter of rated voltage. Therefore an equation for the unused energy is:

$$E_{\text{left}} = \frac{C}{2} * \left(\frac{U}{4}\right)^2 (j)$$

Total useable energy in Wh is then calculated by an equation

$$E_{\text{use}} = \frac{E_S - E_L}{3600} (Wh)$$

An equation for calculation resistance of each resistor connected to supercapacitor in parallel

$$R = \frac{V_{\text{cap}}}{10 * I_{\text{leak}}}$$

3.2. Calculations

The assignment says to design a supercapacitor module with a rated voltage 24 V and a capacity at least 1 Wh. However, to simplify module and to reduce prize will module be designed to half voltage 12 V. Resistors will be used to passively balance supercapacitors.

BOOSTCAP 0370 P270 will be used as a fundamental cell for a module. Main parameters of this cell are: voltage 2,7 and capacity: 370F. Five of these cells will be connected in series to achieve required voltage and capacity with sufficient reserve for potential losses.

3.3. Capacitor cell specifications

PRODUCT SPECIFICATIONS

ELECTRICAL		BCAP0310
Rated Capacitance ¹		310 F
Minimum Capacitance, initial ¹		310 F
Maximum ESR _{DC} , initial ¹		2.2 mΩ
Test Current for Capacitance and ESR _{DC} ¹		31 A
Rated Voltage		2.70 V
Absolute Maximum Voltage ²		2.85 V
Absolute Maximum Current		250 A
Leakage Current at 25°C, maximum ³		0.45 mA
TEMPERATURE		
Operating temperature range (Cell case temperature)		
Minimum		-40°C
Maximum		65°C
Storage temperature range (Stored uncharged)		
Minimum		-40°C
Maximum		70°C

Table 2 Capacitor cell parameters [16]

3.4. Calculations

Capacitance

$$\frac{1}{C} = \frac{1}{310} + \frac{1}{310} + \frac{1}{310} + \frac{1}{310} + \frac{1}{310}$$

$$C = \frac{5}{310}$$

$$C = 62 \text{ (F)}$$

Voltage

$$U = 2,7 + 2,7 + 2,7 + 2,7 + 2,7 \text{ (V)}$$

$$U = 13,5 \text{ (V)}$$

Resistor

$$R = \frac{2,7}{10 * 0,15 * 10^{-3}}$$

$$R = 1800 \text{ } \Omega$$

Usable energy

$$E_{\text{stor}} = \frac{62 * 144}{2} \text{ (j)}$$

$$E_{\text{stor}} = 4464 \text{ j}$$

$$E_{\text{left}} = \frac{32}{2} * \left(\frac{12}{4}\right)^2 \text{ (j)}$$

$$E_{\text{left}} = 288 \text{ (j)}$$

$$E_{\text{use}} = \frac{4464 - 288}{3600}$$

$$E_{\text{use}} = 1,16 \text{ (Wh)}$$

3.5. Block diagram and a price table

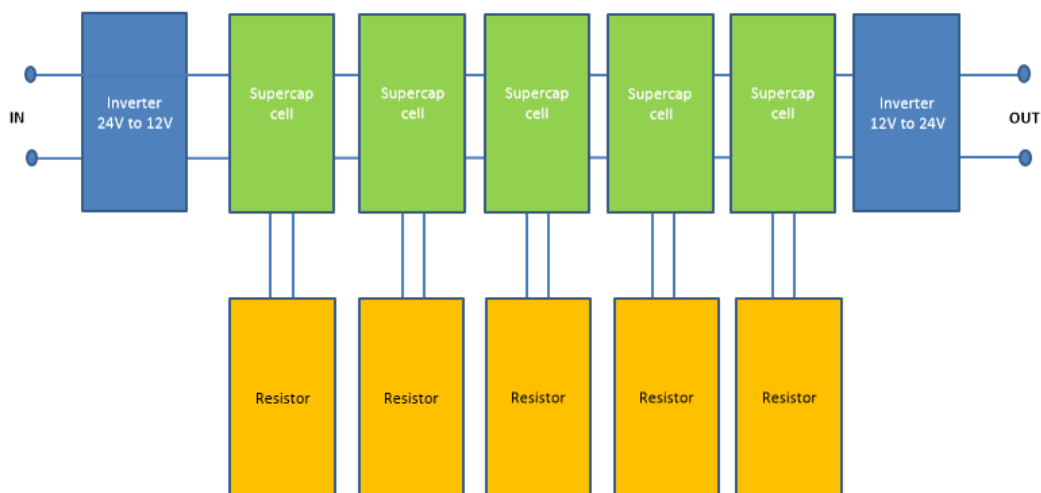


Figure 12 Block diagram of a module

Component	Name	QTY	Price/pcs
Cell	<i>Maxwell BCAP0310</i>	5	303,-
Resistor	<i>1k8 ohm 1% Royal Ohm</i>	5	1,-
Inverter 24V to 12 V	<i>DC 24V to DC 12V Car Power Supply Inverter Converter Step- down Transformer 30A</i>	1	170,-
Inverter 12V to 24 V	<i>Step-up Module DC 12V to 24V 10A 240W Car Power Supply Inverter Converter</i>	1	600,-
Others	<i>Connecting materials, case, etc.</i>	1	200,-
		Total	2490,-

Table 3 A price table [12,13,14,15]

4. Conclusion

The aim of this thesis was to assemble an overview of the use of super-capacitors in the energy storage devices and to suggest the energy storage device. The technology of the supercapacitor is relatively old, however, its potential is not fully used yet. Customer will encounter such technology very rarely. It might be said that this technology is only for a big corporation which works on implementation in industrial use or for aficionados who are able to design such device for their own use with specified parameters they need.

In fact, all types of storage of electrical energy have its pros and drawbacks. Battery systems are suitable for applications where their energy density in a small package is needed. However, they lack higher power output and their lifetime is limited by used technology of charge storage. Namely limited number of cycles or memory effect which reduces capacity. On the other supercapacitor is the exact opposite. Due to high charging and discharging currents, it is able to quickly acquire energy and then release it in same fast manner. Also, lifetime is definitely higher thanks to charge storage technology without chemical reaction. Some companies claim to have 500000+ cycles on their supercapacitor cells without any capacity losses. However, low energy density might be a problem. Moreover, to achieve the capacity of a common battery, a supercapacitor module would need to be a lot larger. A further cause of problems when implementing a supercapacitor-based energy storage device might be its high price, which, despite the new production technologies, is still very high. Flywheels, in comparison with supercapacitors, offer similar electrical parameters. They can also offer very high power in very short time. Their lifetime is also very long, but it hugely depends on a mechanical maintenance of its critical parts. However, flywheels are usually designed to large-scale applications and it is inconvenient to design them to fit into our pockets.

Suggested supercapacitor module might be used as a car battery. It has significantly longer lifespan than a regular car battery. Yet there is a problem with its capacity, which is considerably smaller, and its price approximately 2490 Czech crowns, which can't compete with a common car battery price of 1000 Czech crowns. Another

issue is its size. To achieve the capacity of a car battery, it would have to be considerably larger.

All in all, supercapacitor might offer a bright future of storage of electrical energy. It can offer interesting ways of application with increasing demand for saving energy. Various applications exist where quick energy storage and usage is needed. But we will have to wait to buy supercapacitor devices in common supermarkets. It mainly depends on price per 1 kW/h and ingenuity of pioneers who can get such technology in our pockets or at least backpacks.

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