

**Development of a new hybrid supercapacitor with  
improved cycling ability**

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## Abstract

Electrochemical energy storage is an old branch of energy storage that started at the end of XVIII century with first example of battery. New batteries like lithium-ion can have very high energy densities comparing to other ones but on the other hand batteries cannot have high power densities. Last 50 years have given some breakthroughs in the electrochemical energy storage technologies that lead to invention of supercapacitor. Supercapacitors compared to batteries can have very high power densities but not energy densities. Nowadays markets are looking for devices that could fill the gap between batteries and supercapacitors.

Charge2Change (C2C) is a spin off company founded by IST researchers and holds a patent for the fabrication of electrodes for Faradic supercapacitors. The company succeeded to develop a series of prototypes at lab scale, using small electrodes (few  $\text{cm}^2$ ), and is now launching the pilot scale phase. For this purpose the company outsourced the scale up and production of electrodes with  $50\text{cm}^2$  area, using the technology developed. The main goal is to produce a hybrid device for electrochemical energy storage, between a battery and a supercapacitor. This hybrid is composed of a carbon based electrode (supercapacitor type electrode), which stores charge using the electrochemical double-layer and a metallic oxide/hydroxide electrode (battery type electrode) that stores energy via redox processes. One of the electrodes used for the assembling of the hybrid device is based on transition metallic oxides/hydroxides of Ni-Co coatings with a 3D dendritic structure and were manufactured directly on thin stainless steel current collectors, in a one single and fast step with the need of introducing binders and foreign additives. Stainless steel was chosen because it is cheap, mechanically stable and corrosion resistant material, being very attractive for electrodes fabrication. Ni-Co electrodes were produced through a very simple, low cost and environmental friendly process called electrodeposition.

The main objective of the thesis was to design and test a new energy storage device, an hybrid between a battery and supercapacitor, to evaluate its performance and to compare it with currently available electrochemical devices, namely lead acid batteries and electrochemical double layer supercapacitors. Work done in the thesis included preparation of the testing setup, testing of electrodes quality, determination of energy and power densities, construction of respective Ragone plot for different setups to compare with recently available technologies and capacitance fading test of different setups to check the behaviour of electrodes.

Obtained results showed that the hybrid technology is very promising and can easily compete with supercapacitors and batteries widely available on the market.

key words: supercapacitor, battery, hybrid, energy storage

## Resumo

O armazenamento de energia electroquímica é um ramo antigo de armazenamento de energia, que começou no final do século XVIII, com o primeiro exemplar de uma bateria. Novas baterias, como a de ião-lítio, possuem elevada densidade energética quando comparadas a outras tecnologias mas, por outro lado, não detêm uma densidade de potência elevada. Nos últimos 50 anos observaram-se alguns avanços na área de armazenamento de energia electroquímica que conduziram à invenção de supercondensadores. Estes, comparados com baterias, revelam uma densidade de potência elevada mas baixa densidade energética. Actualmente os mercados estão a apostar na investigação de tecnologias que combinem as vantagens de baterias e supercondensadores.

Charge2Charge (C2C) é uma spin-off fundada por investigadores do IST e detém a patente para a fabricação de eléctrodos de supercondensadores Farádicos. A empresa foi bem sucedida no desenvolvimento de vários protótipos a nível laboratorial, com pequenos eléctrodos (alguns  $\text{cm}^2$ ) e está agora a iniciar a fase piloto. Neste intuito, a empresa subcontratou para o scale up e produção dos eléctrodos, com  $50\text{cm}^2$  de área, usando a tecnologia desenvolvida. O principal objectivo é produzir um equipamento híbrido para armazenamento de energia electroquímica, combinando baterias e supercondensadores. O híbrido é constituído por um eléctrodo de carbono (típico de supercondensadores), que armazena a carga através de uma camada electroquímica dupla e um eléctrodo metálico de óxido/hidróxido (típico de baterias) que armazena energia via processos redox. Um dos eléctrodos usado na elaboração do híbrido é baseado na transição metálica óxidos/hidróxidos revestidos por Ni-Co com uma estrutura dendrítica 3D e é fabricado directamente em finos colectores de corrente de aço inox, num passo único e rápido, havendo necessidade de introduzir aglutinantes e aditivos externos. Foi escolhido aço inox por apresentar baixo custo, estabilidade mecânica e resistência à corrosão, tornando-o um material atractivo para o fabrico de eléctrodos. Os eléctrodos de Ni-Co foram produzidos por um processo simples, de baixo custo e ecológico denominado electrodeposição.

O principal objectivo desta tese foi projectar e testar um novo equipamento de armazenamento de energia, um híbrido que combina a tecnologia de baterias e supercondensadores, avaliar a sua performance e compará-la a equipamentos já existentes de armazenamento electroquímico, nomeadamente baterias ácido chumbo e supercondensadores electroquímicos de camada dupla. O trabalho realizado durante a tese consistiu na preparação da configuração de testes, teste da qualidade dos eléctrodos e determinação das densidades energéticas e de potência, construção do respectivo gráfico de Ragone para diferentes configurações para comparar com tecnologias disponíveis recentemente e testar a diminuição da capacitância de diferentes configurações de modo a analisar o comportamento dos eléctrodos.

Os resultados obtidos demonstram que a tecnologia híbrida é promissora e uma concorrente viável aos supercondensadores e baterias amplamente disponíveis no mercado.

Palavras-chave: supercondensadores, baterias, híbrido, armazenamento de energia

## Abstrakt

Elektrochemiczne magazynowanie energii jest dojrzałą dziedziną, której początki sięgają końca XVII wieku i zaczęły się od pierwszego prototypu baterii. Nowe baterie takie jak baterie litowo-jonowe posiadają bardzo wysoką gęstość energii porównując z innymi rodzajami jednak baterie te charakteryzują się bardzo niskimi wartościami gęstości mocy. Ostatnie 50 lat przyniosło wiele przełomów w technologiach magazynowania energii elektrochemicznej, które doprowadziły do wynalezienia superkondensatora. Superkondensatory w porównaniu do baterii posiadają bardzo dużą gęstość mocy i stosunkowo małą gęstość energii. W dzisiejszych czasach na rynku poszukuje się urządzeń, które potrafiłyby wypełnić lukę pomiędzy bateriami i superkondensatorami.

Charge2Change (C2C) jest firmą założoną przez badaczy z IST, która posiada patenty na produkcję elektrod dla superkondensatorów faradycznych. Firma z powodzeniem stworzyła serię prototypów w skali laboratoryjnej używając małych elektrod (kilka  $\text{cm}^2$ ) i aktualnie przygotowuje się do stworzenia prototypu w większej skali (elektrody o powierzchni  $50\text{cm}^2$ ). Głównym celem C2C jest stworzenie hybrydy pomiędzy baterią i superkondensatorem. Hybryda miałaby się składać z jednej elektrody węglowej (typ superkondensatora) i drugiej elektrody opartej na tlenkach/wodorotlenkach metali (typ baterii). Jedną z elektrod, która zostanie użyta do stworzenia hybrydy wyprodukowana została metodą elektrodpozycji przekształcając tlenki/wodorotlenki metali Ni-Co w trójwymiarowe rozgałęzione struktury wprost na cienkiej folii ze stali nierdzewnej. Stal nierdzewna została wybrana ponieważ jest tania, mechanicznie stabilna i odporna na korozję.

Głównym celem pracy było zaprojektowanie i przetestowanie nowego urządzenia do magazynowania energii w postaci elektrochemicznej, hybrydy pomiędzy baterią i superkondensatorem aby sprawdzić jej wydajność i porównać z szeroko dostępnymi technologiami takimi jak baterie ołowiowo-kwasowe i kondensatory dwuwarstwowe. Prace przeprowadzone zawierały przygotowanie stanowiska testowego, sprawdzanie jakości elektrod, określenie gęstości energii oraz mocy, stworzenie wykresu Ragone'a dla różnych ustawień aby porównać hybrydę ze współcześnie dostępnymi technologiami, a także przeprowadzenie testu zaniku pojemności.

Uzyskane wyniki pokazały iż stworzona hybryda jest bardzo obiecującą technologią, która z łatwością może rywalizować z bateriami i superkondensatorami.

słowa kluczowe: superkondensator, bateria, hybryda, magazynowanie energii

## List of content

---

<b>1</b>	<b>Introduction.....</b>	<b>11</b>
<b>1.1</b>	<b>Energy storage.....</b>	<b>12</b>
1.1.1	Mechanical energy storage.....	13
1.1.2	Chemical energy storage.....	16
<b>2</b>	<b>Application and maturity of different energy storage technologies. ....</b>	<b>23</b>
<b>3</b>	<b>Electrochemical Energy Storage.....</b>	<b>27</b>
<b>3.1</b>	<b>Batteries and supercapacitors.....</b>	<b>27</b>
<b>4</b>	<b>Charge 2 Change .....</b>	<b>30</b>
<b>4.1</b>	<b>Aim of the thesis.....</b>	<b>32</b>
<b>5</b>	<b>Methodology.....</b>	<b>33</b>
<b>5.1</b>	<b>Description of the experiment.....</b>	<b>33</b>
5.1.1	Electrode quality test.....	34
5.1.2	NiCo-NiCo and NiCo-C electrode test.....	35
5.1.3	Capacitance fade.....	37
<b>5.2</b>	<b>Calculations.....</b>	<b>38</b>
<b>6</b>	<b>Results .....</b>	<b>41</b>
<b>6.1</b>	<b>Electrode Test1 and Test2.....</b>	<b>41</b>
<b>6.2</b>	<b>Capacitance fade experiment.....</b>	<b>51</b>
<b>7</b>	<b>Summary .....</b>	<b>53</b>
<b>8</b>	<b>Suggestions for future work .....</b>	<b>55</b>
	<b>References .....</b>	<b>56</b>

## List of Figures

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Fig.1 Above ground pumped hydro (energy storage) [6].	13
Fig. 2 Above ground pumped hydro (energy release) [6].	14
Fig.4 Different land-based reservoirs for compressed air storage [8].	15
Fig. 5 Schematic conversion of carbonaceous feedstock and its further use [9].	16
Fig.6 Small scale hot water storage [10].	17
Fig.7 Schematic molten salt power tower [12].	17
Fig.8 Schematic of battery charging (left) and discharging (right) [13].	18
Fig.9 Schematic working principle of lithium-ion battery [14].	19
Fig 10 Electrostatic (left) and electrolytic (right) capacitor [18].	20
Fig.11 Model of electrical double-layer supercapacitor [18].	21
Fig.12 Fuel cell working principal [9].	22
Fig.13 Development path of energy storage technologies with respect to capital and risk [21].	23
Fig.14 Application of Energy Storage technologies [22].	24
Fig.15 Cost of different Energy Storage technologies with respect to response [23].	25
Fig.16 Future pathway of electrochemical energy storage [24].	26
Fig.17 Ragone plot for different Energy Storage technologies [25].	27
Fig.18 Electrochemical Energy Storage technologies application [27].	28
Fig. 19 Cross-section of Ni-Co structures [29].	30
Fig. 20 Ragone plot for C2C comparison.	31
Fig. 22 Schematic view of NiCo-C prototype.	32
Fig. 23 Example of charge/discharge curves of two identical NiCo-NiCo plates under an applied current of 0,04 A.	33
Fig. 24 Test-bench and VoltaLab PGZ 100 potentiostat.	34
Fig. 25 Experimental set-up.	35
Fig. 26 VoltaLab software set-up.	35
Fig. 27 NiCo-NiCo (left) and NiCo-Carbon (right) tested plates.	36
Fig. 28 Assembly of NiCo-NiCo plates (left) and already assembled NiCo-NiCo and NiCo-C plates.	36
Fig. 29 NiCo-NiCo Test2 set-up.	37
Fig. 30 NiCo-C Test2 set-up.	37
Fig. 31 Charge/discharge curves of capacitance fade experiment in VoltaLab software.	38
Fig. 32 Illustrative charge/discharge curve illustrating the ohmic drop and the potential window to extract the capacitance.	39
Fig. 33 Example of a discharge curve for the NiCo-NiCo electrodes.	39
Fig. 34 Charge/Discharge curves for NiCo-NiCo Test1.	41
Fig. 35 Charge/Discharge curves for NiCo-C Test1.	42
Fig. 36 Charge/Discharge curves for NiCo-C in higher potential window Test1.	42
Fig. 37 Evolution of resistance with respect to the applied current in Test1.	42



<i>Fig. 38 Charge/Discharge curves for NiCo-NiCo Test2.....</i>	<i>43</i>
<i>Fig. 39 Charge/Discharge curves for NiCo-C Test2.....</i>	<i>43</i>
<i>Fig. 40 Charge/Discharge curves for NiCo-C 1.6V Test2. ....</i>	<i>44</i>
<i>Fig. 41 Evolution of resistance with respect to the applied current in Test2. ....</i>	<i>44</i>
<i>Fig. 42 Ragone plot Test1.....</i>	<i>50</i>
<i>Fig. 43 Ragone plot Test2.....</i>	<i>51</i>
<i>Fig. 44 Capacitance fade results.....</i>	<i>52</i>
<i>Fig. 45 Ragone plot with calculated value after capacitance fade test.....</i>	<i>52</i>
<i>Fig. 46 Ragone plot with obtained results compared to other technologies.....</i>	<i>54</i>

## List of Tables

---

<i>Tab. 1 Battery market. [24].</i>	26
<i>Tab. 2 Supercapacitors market [24].</i>	26
<i>Tab.3 Comparison of chosen parameters [26].</i>	28
<i>Tab. 4 Comparison of C2C with other technologies.</i>	31
<i>Tab. 5 Results of average Specific Energy and Power for NiCo-NiCo.</i>	45
<i>Tab. 6 Results of average Specific Energy and Power for NiCo-C.</i>	45
<i>Tab. 7 Results of average Specific Energy and Power for NiCo-C 1.6V.</i>	46
<i>Tab. 8 Results of maximum Specific Energy and Power for NiCo-NiCo.</i>	47
<i>Tab. 9 Results of maximum Specific Energy and Power for NiCo-C.</i>	47
<i>Tab. 10 Results of maximum Specific Energy and power for NiCo-C 1.6V.</i>	48
<i>Tab. 11 Charge/discharge times and efficiency of NiCo-NiCo Test1 and Test2.</i>	49
<i>Tab. 12. Charge/discharge times and efficiency of NiCo-C Test1 and Test2.</i>	49
<i>Tab. 13 Charge/discharge times and efficiency for NiCo-C in higher potential window for Test1 and Test2.</i>	50

# 1 Introduction

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The demand for primary energy sources is increasing rapidly from one year to another. Data show that in year 2000 the demand for primary energy sources was around 10.000 Mtoe and until 2011 this demand has increased up to 13.000 Mtoe and is still increasing. This has an enormous impact on environment because fossil fuels hold more than 81% share of the fuel mix for primary energy demand [1]. On the other hand fossil fuels resources are not uniformly spread worldwide and are depleting quite fast. It is foreseen that world reserves of coal are sufficient to meet 113 years of global production. Oil and natural gas reserves will be able to meet global demand for around 50 years [2]. This is a big threat for energy security of many countries. Many of those countries are trying to develop renewable sources of energy like biomass, wind, solar or hydropower. These are more environmentally friendly solutions and can secure the energy demand, but they cannot be implemented so rapidly. This challenge needs more evolution than revolution. Energy from renewable resources may be easy to adapt, but we cannot fully rely on it because of renewable energy intermittent nature.

Energy storage is one of the key solutions that will lead to the implementation of sustainable energy systems. Energy storage technologies can store the excess of energy that is produced by renewable sources and deliver when needed. Additionally energy storage technologies have the potential to boost the transportation sector particularly that of electric and hybrid vehicles, into a more sustainable model, that allows reducing substantially greenhouse gases emissions. Another market in which energy storage technologies, mostly electrochemical energy storage technologies, play a major role is the electronic devices market. The consumable electronic devices market that has increased significantly through last years and would not be able to “survive” without energy storage.

Electrochemical energy storage is an old branch of energy storage that started at the end of XVIII century with first example of battery. Through 200 years battery technologies have evolved and many types of batteries, starting from primary (one-time use) batteries used in many everyday applications, through lead acid batteries that are very important in transport as well as in many stationary applications for energy storage, up to new lithium-ion batteries.

At this moment the market of portable electronic devices is being boosted by the new generation of lithium-batteries. This is due to its high energy density, good cycling abilities and small dimensions comparing to other technologies. Lithium-ion batteries are also used in the electric vehicle applications allowing competing on the market with internal combustion engine vehicles.

Last 50 years have given some breakthroughs in the electrochemical energy storage technologies. In 1972 the Japanese company from Osaka, Matsuhita Electric Industrial Co, used a high specific surface carbon based material to construct electrochemical capacitor. This led to invention of a capacitor with the highest capacitance known at that time. This capacitor was called supercapacitor. Nowadays supercapacitors are characterised by higher power density compared to batteries and they can receive/deliver high amounts of energy in very short time periods. Additionally supercapacitors are characterized with very high cycling ability when compared to batteries and this fact makes them attractive for long lasting applications.

Presently supercapacitors are used for energy storage in wind power stations due to the ability of fast response to changes in load, in household equipment and electronic tools for sudden power requirements, in automotive industry where they are combined with batteries or other applications as aeronautical, space or military [3].

The performance of a supercapacitor depends mostly on the performance of the electrodes and electrode performance depends mostly on the electrode active material. Presently, commercial supercapacitors are essentially made of electrodes that contain carbon-based materials with high specific area to increase the electrochemical (double layer) performance. The technology of an electrochemical double layer (EDL) carbon-based supercapacitor is very simple and reliable, but it also presents some drawbacks. Powdered carbon materials have high specific area when dried, however to be assembled on the current collector there is need to introduce foreign agents, namely organic binders. The wet mixture (carbon powder plus binders) forms a paste that is “painted” on the metallic current collectors. The procedure is simple and cheap but presents three major disadvantages: the organic binder increases the material resistivity; the adhesion to the current collector is typically very poor and there is a high risk of material loss and electrode malfunction; this kind of assembly is prone to electrolyte contact with the collector that may induce corrosion. All together these factors decrease the performance of supercapacitor. Therefore there is the need to develop new strategies to improve the lifetime and reliability of supercapacitors.

In this thesis new hybrid electrochemical energy storage device, between a battery and supercapacitor, was tested in order to check its performance and to compare it with currently available electrochemical devices, particularly with lead acid batteries and electrochemical double layer supercapacitors.

## **1.1 Energy storage**

Energy storage is not a new invention. It accompanied human kind from its beginning and plays an important role in our daily life. It started with the storage of wood for heating and cooking purposes and now is essential in everyday technologies to run portable devices like laptops, tablets, mobile phones, vehicles etc.

Storage of energy can be divided into various classes. The most often used classification is into chemical and non-chemical energy storage. Non-chemical storage technologies cover mechanical energy storage, whereas chemical energy storage covers thermochemical and electrochemical energy storage. The next section briefly explains the basics of the most important energy storage technologies used nowadays.

## 1.1.1 Mechanical energy storage

Mechanical energy storage is associated with motion and position of an object (storing medium). We can derive three ways of mechanical energy storage based on the common forms of energy: potential, kinetic and internal.

### 1.1.1.1 Potential energy storage

Potential energy can be stored in a weight of a working system. In order to store energy the working system has to be raised until a specific height (for example using the excess of energy released from an operation). When there is a need for energy consumption, the working system can do work by returning to its initial state [4].

Pumped hydro storage is the most efficient and mature way of large-scale energy storage nowadays. It holds more than 95% of the shares in the energy storage mix all around the world and it provides around 180 GW of rated power [5]. The principle is quite simple. Pumped energy storage uses two reservoirs at two different elevations. During the periods of lower electricity demand water from the lowest reservoir is pumped into the highest reservoir and the energy is stored. When there is a demand energy peak, water is released from the highest reservoir to do work in the turbine and to produce electricity. Fig.1 and 2 show the basics of pumped hydro energy storage.

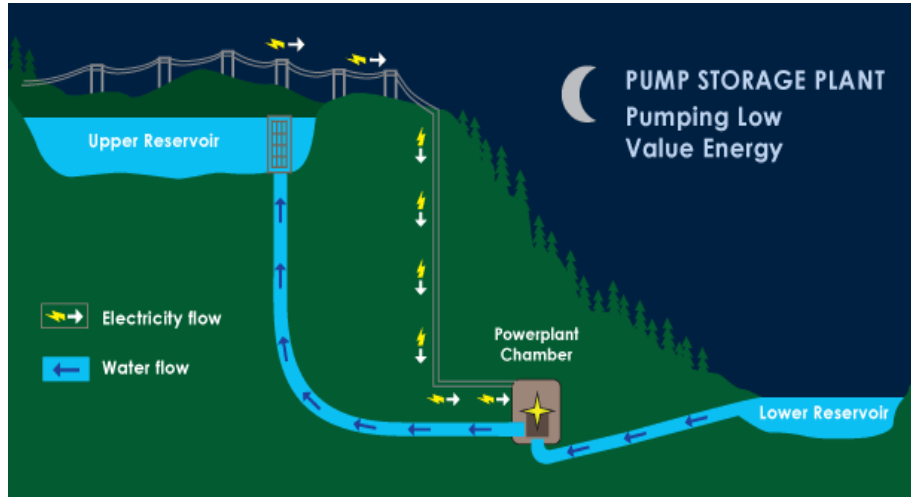


Fig.1 Above ground pumped hydro (energy storage) [6].

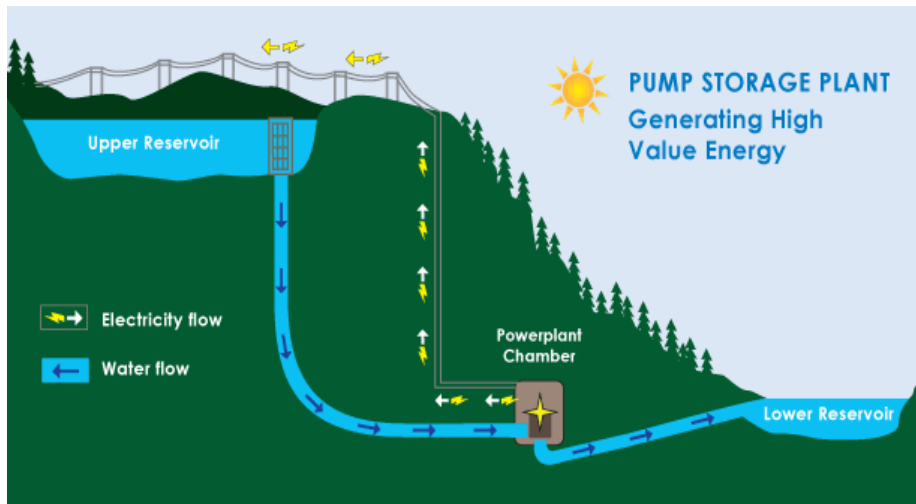


Fig. 2 Above ground pumped hydro (energy release) [6].

### 1.1.1.2 Kinetic energy storage

Flywheels are amongst the most used technologies for kinetic energy storage and attract a lot of attention from researchers. They were traditionally used for short-term energy storage in steam engines, internal combustion engines and turbines. More recently flywheels are being introduced in electrical vehicles as additional energy storage systems. In general a flywheel is a mass rotating about an axis that has very fast response on receiving and delivering the energy. The working principle of flywheels is as follows: when there is an excess of energy, the motor is charging the flywheel, while operating increasing its kinetic energy and when energy is needed motor becomes a generator and releases the stored energy. Flywheels have high power and energy density and the lifetime of a flywheel does not depend on charge/discharge, but on the other hand, they have very short discharge time, and may undergo high mechanical stresses and fatigue limits. Fig.3 shows a schematic view of a flywheel system equipped with a motor/generator.

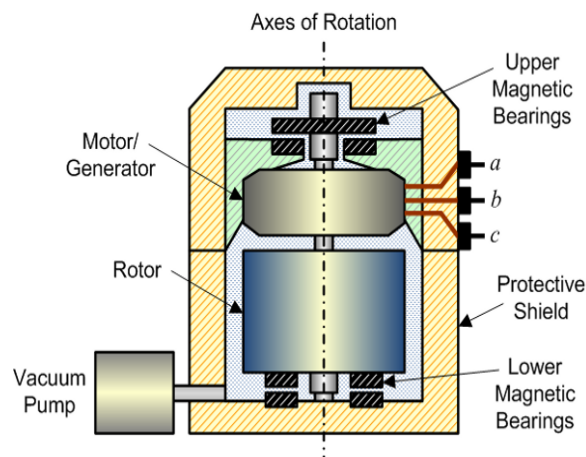


Fig. 3 Structure of conventional flywheel [7].

### 1.1.1.3 Internal energy storage

Compressed air energy storage is a well-known technology that uses internal energy storage and can be divided into three main parts: diabatic, adiabatic (isentropic) and isothermal. Diabatic compression dissipates a lot of heat into the atmosphere as waste. In order to recover energy, while expanding, the air must be re-heated. For re-heating purposes there is the need to use fossil fuel. This leads to low efficiencies of energy storage and when the cost of fuel raises the costs of recovered electrical energy and environmental benefits rise as well. Unfortunately, so far, this is the only system that has been implemented commercially.

Adiabatic compression does not require additional fossil fuel based re-heating and can achieve efficiencies up to 70%. In that case high efficiency can be obtained if the heat produced, while compressing the air is recovered, and then released to heat compressed air before expanding.

Isothermal compression storage is an emerging technology that intends to overcome the limitations of diabatic and adiabatic compression, but it is still in the development phase without any relevant industrial application.

The most recent compressed air energy storage systems make use of land-based reservoirs that can be divided into two different types:

- constant volume reservoirs, such as salt caverns or abandoned mines,
- constant pressure reservoirs, such as aquifers or water compensated hard rock caverns.

Examples of different land-based reservoirs are shown on Fig.4.

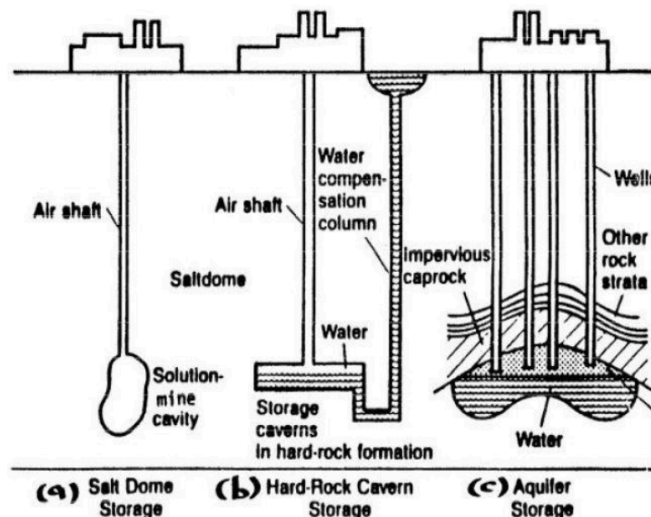


Fig.4 Different land-based reservoirs for compressed air storage [8].

In general compressed air energy storage systems operate under conditions of constant volume. The process of charging/discharging of high pressure is highly unstable because of the changing pressure ratios. This results in decreased efficiencies in what concerns compression and expansion.

## 1.1.2 Chemical energy storage

Chemical energy is the energy that is stored in the bonds of chemical compounds; thus the chemical energy stored in this way can be released when the chemical reactions occur, often producing heat (thermochemical energy) or electricity (when the processes involve electrochemical reactions).

### 1.1.2.1 Thermochemical energy storage

Thermochemical energy storage includes both storage associated with chemical reactions and physical transformations.

Production of synthetic gas has become one of the most popular approach for chemical reactions use. Synthetic gas or syngas can be one of the bases to produce hydrogen, methanol, ammonia or synthetic fuels through Fischer-Tropsch synthesis (gasoline and diesel). Syngas is a mixture of carbon monoxide, carbon dioxide, and hydrogen and it can be produced from coal, biomass, natural gas, waste or any carbonaceous feedstock available. Production of synthetic gas takes place in a gasifying unit, under high temperature and pressure, using oxidants such as  $O_2$  or steam [9,10]. Fig.5 shows the schematic conversion of carbonaceous feedstock into syngas and its further use.

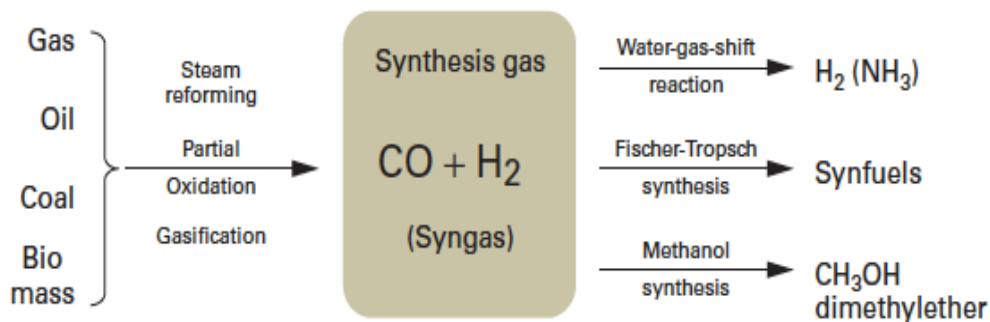


Fig. 5 Schematic conversion of carbonaceous feedstock and its further use [9].

Physical transformation of energy can be divided mainly into two parts:

- storage as a sensible heat, that is a result of cooling or heating of a storage medium,
- latent heat storage that occurs through phase change of storage material.

Because of its high heat capacity and low cost, water is one of the most preferable mediums for thermal energy storage using sensible heat. Fig.6 shows a small-scale hot water storage system that can be used for household purposes. The schematic view depicted in Fig.6 shows that a solar collector collects solar radiation energy, while the sun is shining. The captured radiation heats the working fluid (usually glycol), which then flows through a storage tank and exchanges heat with cold water increasing its temperature [10].



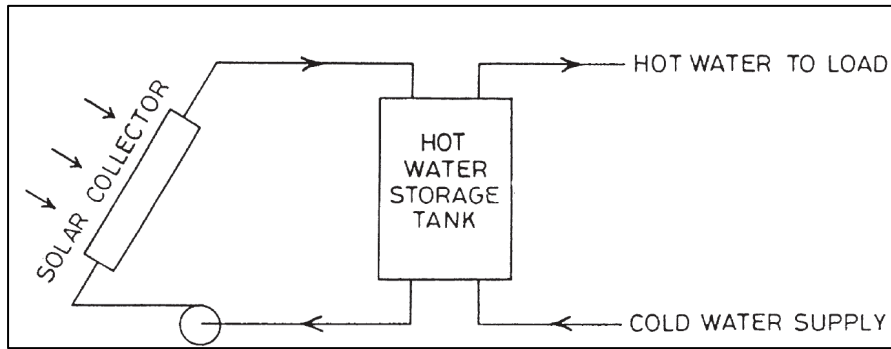


Fig.6 Small scale hot water storage [10].

As previously mentioned latent heat energy storage uses phase change phenomena. While the temperature is increasing, the chemical bonds in the phase change material break and the material changes its phase from solid to liquid. One of the most important advantages of latent heat storage is the possibility to store large amounts of heat using only small temperature differences [11].

Materials that are often used in those processes can be classified into three groups: salt hydrates that are mainly inorganic compounds and water that have high latent heat storage density; parafins that store absorbents and non-parafins that store energy through physical and chemical reactions. Fig.7 shows the schematic view of a molten salt power tower.

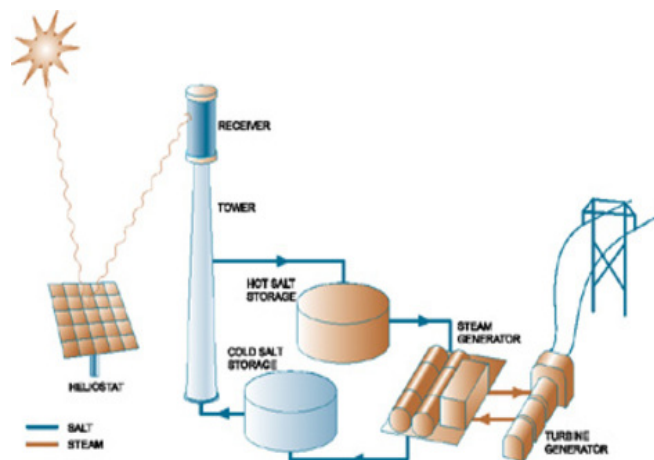


Fig.7 Schematic molten salt power tower [12].

The working principle of the solar power plant schematically depicted in Fig.7 is similar to a conventional one, with the difference that there is no fuel being combusted. The energy needed for steam production is taken from the solar radiation collected by the large number of mirrors concentrating it on the receiver. Salt is the working fluid used to receive the radiation. The absorbed heat is stored in a tank and further used to produce steam. Latent heat storage in this case expands the possibility of energy production even when the sun is not shining due to the significant amount of heat gathered in the tanks.

### 1.1.2.2 Electrochemical energy storage

Electrochemical energy storage is another branch of chemical energy storage that converts chemical energy into electrical energy. It includes batteries, capacitors, supercapacitors and fuel cells.

Batteries can be in general divided into two main groups: primary (non-rechargeable) and secondary (rechargeable). The main difference between these two groups is not the electrochemistry itself, but the composition, morphology and structure of the active electrode material allowing (or not) the charging process. Most used primary batteries nowadays are composed of zinc as anode material and manganese dioxide as the cathode and use potassium hydroxide as electrolyte. Another example are the primary lithium batteries that present high energy density compared to the alkaline Zn-MnO<sub>2</sub> batteries. Although a primary battery can be recharged, the process has very poor yield and can be repeated only a few times, with significant damage of the electrodes and high risk of short circuit. Therefore, commonly the design of primary batteries allows converting chemical energy into electrical energy just once.

Secondary batteries due to the properties of the electrode material can be recharged and, depending on the type of rechargeable battery, used multiple times from tens up to thousands of times. The most popular secondary batteries nowadays are the lithium-ion ones, which in addition to good recharge ability also display high energy density and good power density.

A battery, whether it is of first or second generation, is composed of two electrodes, working as cathode and as anode that are in contact with an ion conducting electrolyte. Typically the anode and the cathode are separated by a thin electrolyte permeable membrane that prevents from short circuit of the electrodes. The system also includes wiring and is confined into a casing. When discharging the battery, the electrons flow from anode (the electrode where the oxidation takes place and electrons are generated) to the cathode (where the reduction reaction takes place and electrons are consumed). Simultaneously the ionic species generated at the electrodes (typically cations) flow through the electrolyte. When the battery is charged both the current and ionic flows are reversed. Fig.8 shows a schematic diagram of battery under charge and discharge.

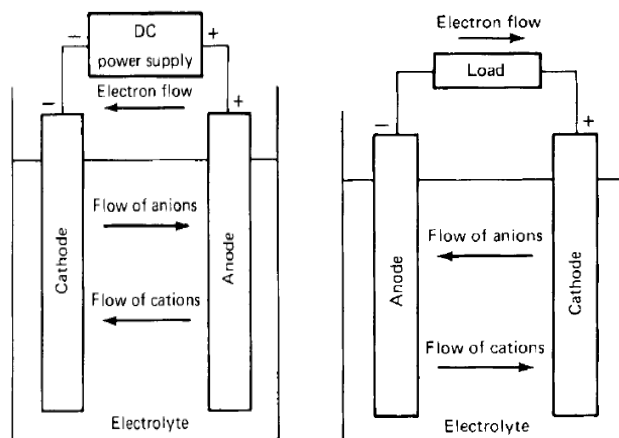


Fig.8 Schematic of battery charging (left) and discharging (right) [13].

As stated above, one of the most promising and often used rechargeable batteries nowadays are lithium-ion batteries. Lithium, because of its lightness, very good reactive properties and high electrochemical potential can provide high power (50-340 W/kg) and energy (100-265 Wh/kg) densities. Recent lithium-ion batteries use lithium metal oxide as a cathode active material, carbon (mainly graphite) as an anode and a Li ion-conducting organic solvent (usually based on lithium salt) as the electrolyte [14]. The schematic working principle of lithium-ion battery is shown on Fig.9.

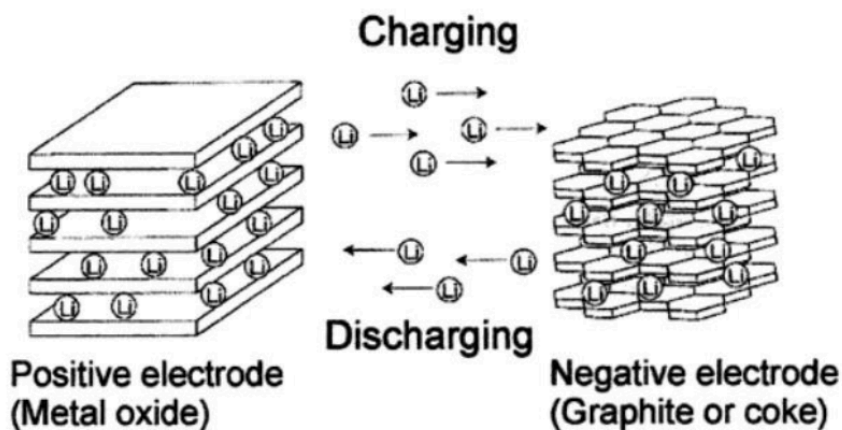
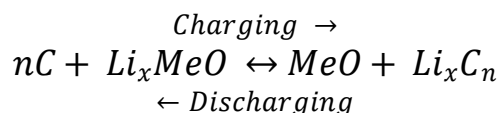


Fig.9 Schematic working principle of lithium-ion battery [14].

The scheme is similar to the one shown previously on Fig.8. While the battery is being charged, the positive electrode is oxidized and behaves as an electron donor. Simultaneously, lithium ions are extracted from the Li-Metal oxide material, leaving behind a Li-deficient metal oxide and move towards the negative electrode and are intercalated in the layered structure of the anode (graphite or Silicon). Li-ion batteries based on intercalation materials, involve intercalation processes that occur without changing the electrodes structure and composition. Lithium ions are only stored in the layered structure of the host material without any chemical reaction. Typically the process is accompanied by significant volume changes. When the battery discharges the process is reversed. In this situation the Li ions are extracted from the negative graphite electrode and inserted into the host cathode (Li-deficient metal oxide) material. The process is accompanied by a flux of electrons and can be repeated for several times. Lithium-ion battery life cycle varies between 400-1200 cycles [15]. The simplified cell reaction is shown below [14]. Some Li ion-batteries may also use conversion cathodes and in that case there is a chemical reaction with significant compositional and structural changes.



Capacitors are divided into three groups that cover: electrostatic, electrolytic capacitors and electrochemical supercapacitors. The working principle of electrostatic and electrolytic capacitors is quite similar. They are constructed from a pair of conductors (the electrodes) separated by

a dielectric with the difference that in electrostatic capacitor the dielectric can be air, mica or a polymer film [16]. In the electrolytic capacitors there is an electrolytic dielectric in direct contact with the capacitor plates. When voltage is applied to the capacitor, electrical energy is converted into electrostatic charge and stored on the capacitor's plates. When electrical energy is needed the process is reversed. Compared to electrostatic capacitors, the electrolytic ones can store up to 10 times more energy [17]. Fig.10 shows the schematic representation of electrostatic and electrolytic capacitor. The capacitors are used in a large array of electronic applications, are very reliable and can be charged/discharged several thousands of times. Typically they have very low energy density, but a high power rate and can be charged discharge for several thousands of times.

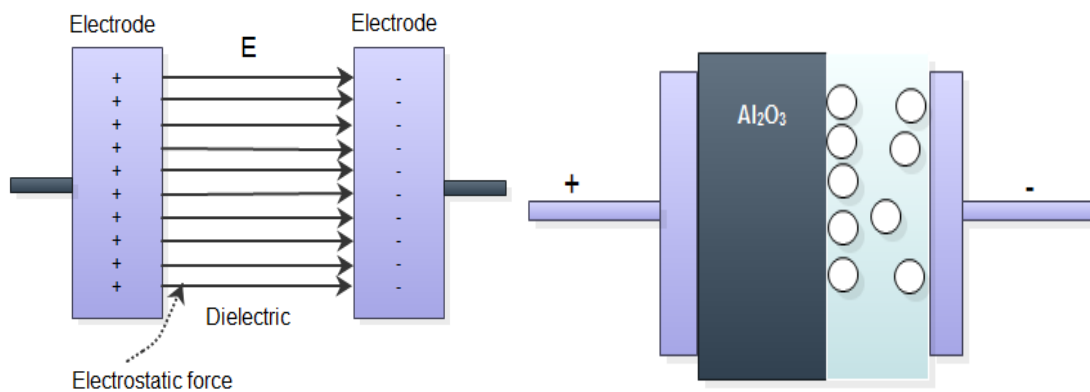
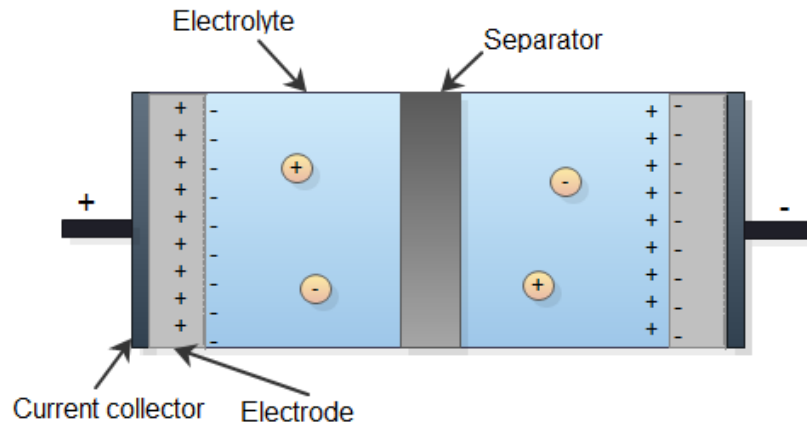


Fig 10 Electrostatic (left) and electrolytic (right) capacitor [18].

Electrochemical capacitors, often called supercapacitors or ultracapacitors, have much higher energy density compared to electrostatic or electrolytic capacitors due to the high surface area of the porous electrode structure and use of electrolyte solutions [16]. There are two classes of supercapacitors depending on the energy storage mechanism:

- double-layer capacitors based on non-faradaic charging mechanism: they store energy via the electrochemical double layer, i.e using mainly an electrostatic process.
- redox capacitors sometimes called pseudocapacitors that are based on faradaic reactions.

Electrochemical double-layer capacitors make use of electrodes composed of carbon materials of very high specific area that can reach up to 2500 m<sup>2</sup>/g [19]. The materials in general present low cost and availability. A schematic view of an electrical double-layer supercapacitor is shown in Fig.11.



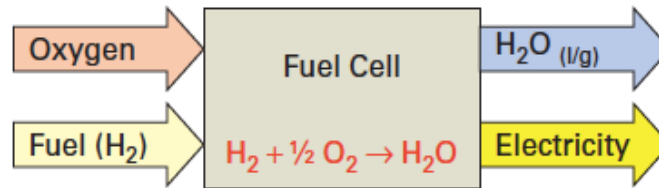
*Fig.11 Model of electrical double-layer supercapacitor [18].*

Energy storage in the double-layer supercapacitor takes place as is as follows: during charging the current collector transports electric current. Electric charges are accumulated on the surface of the electrodes and ions of opposite charge accumulate on the porous structure of the carbon-based materials on the electrolyte side (solid/electrolyte interface) [20]. Since the thickness of the electrochemical double layer is very small (just a few nanometers) compared to electrostatic and electrolytic capacitors, the capacitance (which is inverse to the thickness) is very high. Just like batteries, supercapacitors can use solid, organic or aqueous electrolyte. The nature of the electrolyte depends mainly on the final application of the specific supercapacitor because it determines its voltage. The major limitation of EDL supercapacitors is the modest charge storage capacity. As mentioned, ions accumulate at the material surface, but the surface area is limited, especially because the material is applied as a paste made by mixing the active carbon material with binders and other additives that affect both porosity and conductivity. The consequence is that the energy density is low, typically 5-10 times below a lead acid battery.

Redox capacitors, also called pseudocapacitors, work on faradaic processes and involve oxidation-reduction reactions and transfer of electrons between the two electrodes and intercalation of ions from the electrolyte. The charge/discharge processes can be longer due to the kinetics of the reactions taking place. Nevertheless, the charge/discharge times (some minutes) are much lower compared to batteries. Simultaneously with the Faradaic processes there is formation of the electrochemical double layer that occurs at the surface of active material exposed to the electrolyte. Typically about 2/3 of the charge stored comes from the redox reactions, while up to 1/3 can be the contribution of the EDL. The maximum theoretical specific capacity depends on the chemical composition and morphology of the electrode material but may attain few thousands of F/g, i.e. one order of magnitude above a pure EDL supercapacitor. Thus, it has been shown that the additional faradaic processes, occurring in the electrode can result in a significant increase of the specific capacitance. This requires selecting the proper active materials and opens a large number of possibilities in what concerns metallic oxides and hydroxides, especially the ones possessing multiple valence states. Examples are manganese, ruthenium, nickel, cobalt and vanadium oxides. Another advantage is that metallic oxides can be used in aqueous electrolytes, which are much friendlier compared to the organic ones, typically used in the commercial carbon

based supercapacitors. Limitations include limited voltage windows because of the water stability and capacity fade due to irreversible redox processes.

Fuel cells have similar working mechanism as batteries with the difference that fuel cell electrodes are only providing surface for the reaction and reacting substances are supplied from the outside. In general fuel cells use hydrogen, as a fuel, that reacts with oxygen (usually from the air). Reaction of oxygen and hydrogen results in production of electricity and water and is shown schematically on Fig.12.



*Fig.12 Fuel cell working principal [9].*

Hydrogen oxidation occurs at the anode and reduction of oxygen occurs at the cathode. Fuel cells have different power from few watts up to hundred kilowatts and can be classified according to the application:

- automotive (20-130 kW),
- stationary (100-250 kW),
- residential (2-10 kW),
- back-up power (1-5 kW),
- portable-power (<100W),

Due to problems with limited oil and gas supply, as well as the increase in energy demand fuel cell technologies are developing and attracting a lot of interest. Unfortunately because of not well-developed hydrogen infrastructure worldwide and problems with hydrogen storage this development has been slowed down.

## 2 Application and maturity of different energy storage technologies.

Depending on the type of energy storage, the applications are countless and range from small applications like mobile phones or mp3 players, through electric vehicles, up to big industrial applications. Some technologies like Pumped Storage Hydropower are well known and commercially used but on the other hand there are many technologies that are in the Research and Development or demonstration phase. Fig.13 shows some energy storage technologies for thermal and electricity storage on a development path with respect to capital requirement and technology risk.

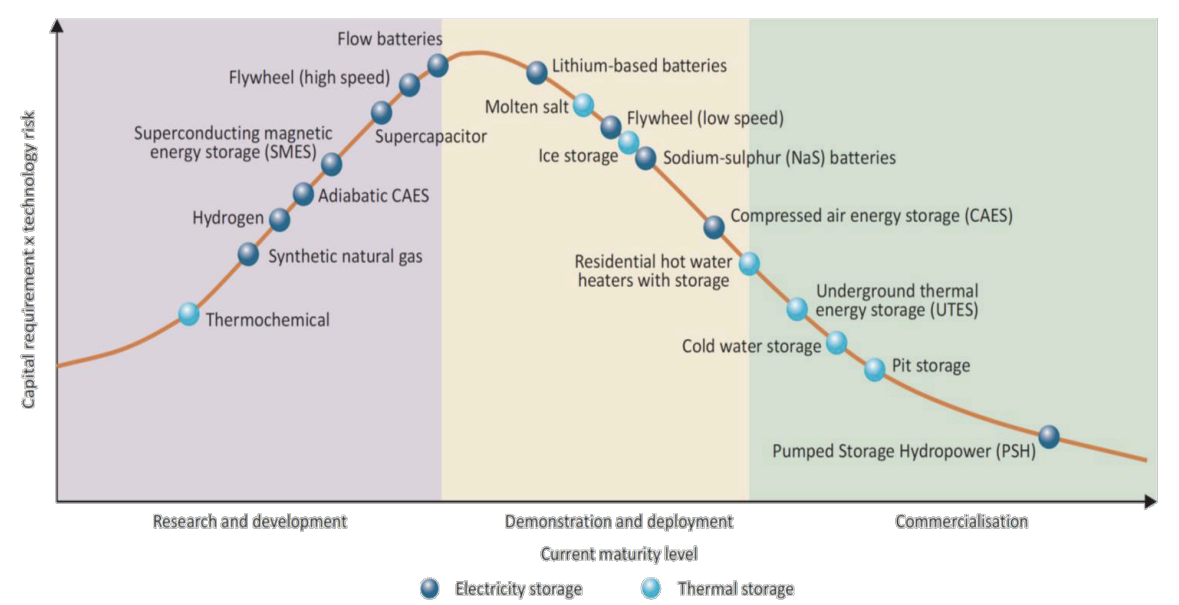


Fig.13 Development path of energy storage technologies with respect to capital and risk [21].

This roadmap shows energy storage technologies depending on the output: electricity or thermal. Nowadays storage of electricity and thermal energy is spread on different levels of development. In this figure, at the extremes of the development path it is possible to find thermochemical energy storage (on the left) and Pumped Storage Hydropower (on the right). Compared to electricity storage, thermal storage in most of the cases requires less capital requirement and is less risky and additionally is more developed. The capital requirement and technology risk increases almost linearly in the R&D part with technologies like synthetic natural gas, supercapacitors, high speed flywheels reaching its maximum at flow batteries. Lithium-based batteries are now in the second phase, that is demonstration and deployment, with the highest cost and technology risk. From that moment all the capital costs and risk is decreasing for more developed technologies.

As mentioned before energy storage can be used for different purposes. Fig.13 shows how mature are some technologies and what are the cost and risk needed to develop them. Fig.14 on the other hand, shows how the different technologies are used, depending on the required system power and the discharge time of that power.

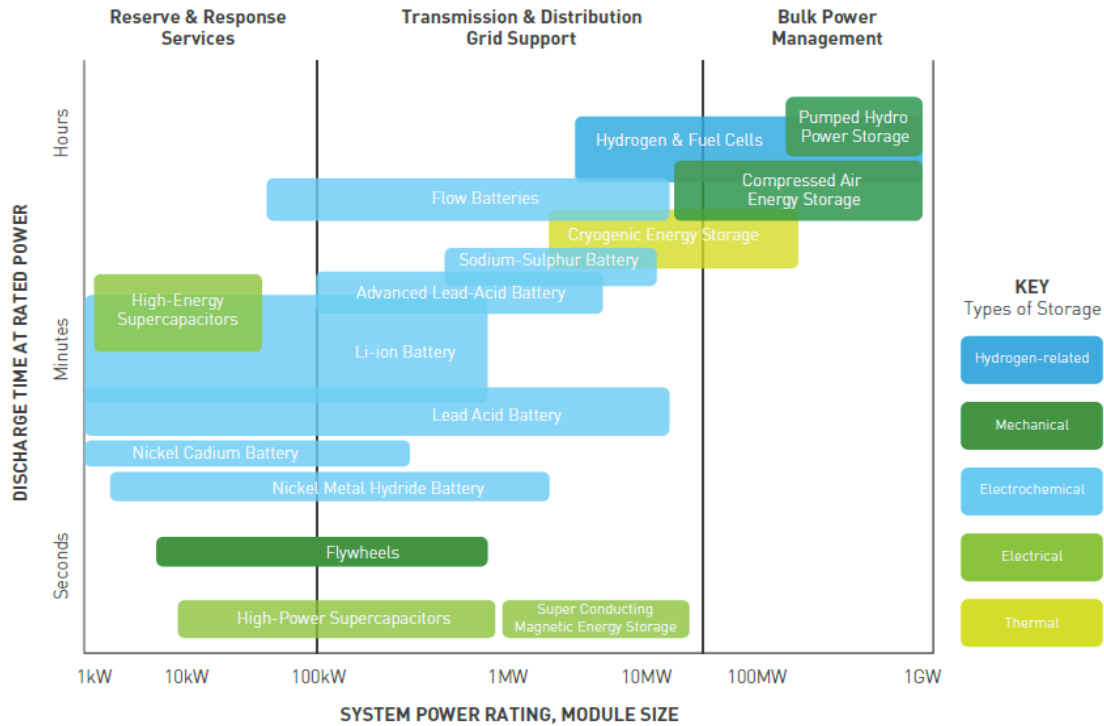


Fig.14 Application of Energy Storage technologies [22].

Graph showed on Fig.14 shows how different technologies are applied depending on the system requirements. Three different requirements can be distinguished: Reserve & Response Services, Transmission & Distribution Grid Support and Bulk Power Management. Energy storage technologies are divided into five main types: Hydrogen-related, Mechanical, Electrochemical, Electrical and Thermal. All technologies are compared with respect to system power rating, module size and discharge time are rated power. It is possible to notice that for Bulk Power Management, mainly Mechanical, Thermal and Hydrogen-related technologies are used. They are characterised by high system power rating and long discharge time. Depending on the system-required response almost all technologies can be used for Transmission & Distribution Grid Support. If fast response is needed, High-Power Supercapacitors and Super Conducting Magnetic Energy Storage can be used. If longer discharge time is required, electrochemical energy storage devices like batteries can be used. From the electrochemical technologies shown on the Fig.14 Nickel Metal Hydrate batteries have the lowest discharge time and Flow Batteries have the longest response time. On the other hand Nickel Metal Batteries can be used also if the required system power is low.

Application of technologies and its maturity is very important but usually the most relevant issue is if the application of the technology to a particular system is feasible. Fig.15 shows what are the costs of different energy storage technologies in \$/kWh with respect to response time.



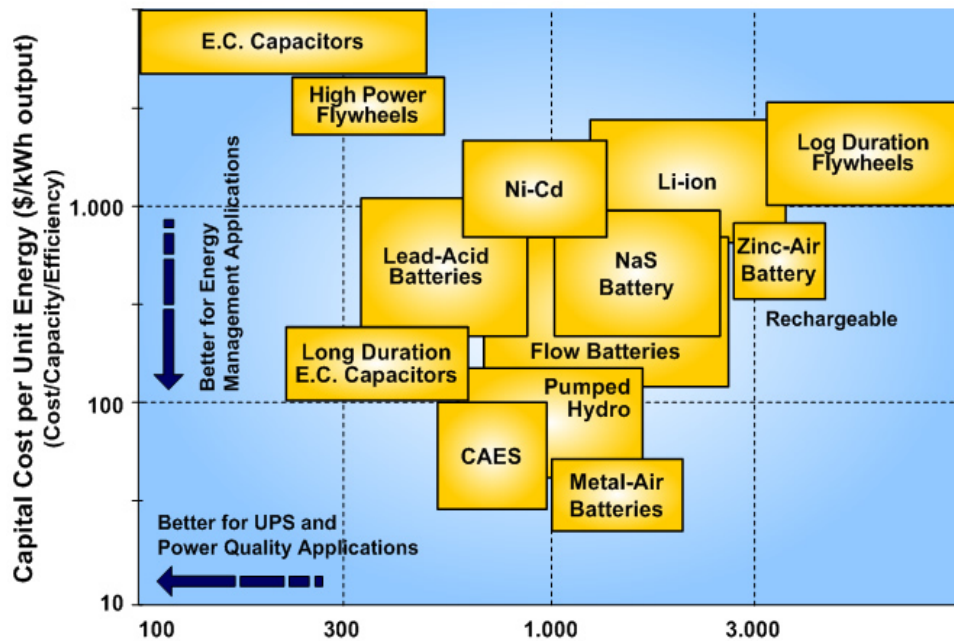


Fig.15 Cost of different Energy Storage technologies with respect to response [23].

It can be noticed from the Fig.15 that when there is a need of fast system response of the particular technology, the higher are the capital costs of technology due to high reliability need of the system. Highest costs and fastest response time are associated with electrochemical capacitors and high power flywheels. Those technologies are important for UPS and Power Quality Applications. On the other hand, lower capital cost is preferred for Energy Management Applications. Most of the technologies presented in the Fig.15 are gathered in the middle of the cost versus response time graph and this is important because those technologies represent different areas of energy storage and can have various applications.

As it was said previously the consumable electronic devices market has increased significantly through last years. Tab.1 shows the quantity of primary and secondary batteries sold for consumable electronics, the total market value and main drivers form 10 years starting from 2009. All values are presented in billions of dollars. In 2009 single use batteries were sold for around 17 billions dollars and rechargeable ones for around 19 billions dollars that gave a total value of around 36 billions dollars. Each year the increase in the battery market value was noticed. It is expected that in 2019 the market value of primary batteries will increase more than twice and for rechargeable batteries it will increase almost three times compared to the base year. From the main market drivers that should be mentioned are: laptops, mobile phones, e-books, watches or calculators.

Tab. 1 Battery market. [24]

	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019
Single use	16.8	17	18.8	19.9	21	22.3	24.3	26.6	29.6	33.7	38.7
Rechargeable	19.4	20.2	23.2	25.3	27.7	30.3	33.1	36.3	40.3	48.1	54.9
Total market value, billion \$	36.2	37.2	42	45.2	48.7	52.6	57.6	62.9	69.9	81.8	93.6

Supercapacitors on the other hand do not have such a big market nowadays comparing to batteries but looking at Tab.2 one can see that the increase in the total market value comparing to the base year 2009 is expected to be more than 100 times.

Tab. 2 Supercapacitors market [24].

	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019
Total market value, billion \$	0.009	0.1	0.18	0.3	0.44	0.59	0.74	0.89	1.04	1.19	1.34

The pathway of electrochemical energy storage is shown on Fig.16. It can be seen that there will be significant increase in the market value compared to base year 2005. This will be mostly due to the increased use of lithium-ion batteries both in portable devices and also Electric Vehicles. Increase in fuel cells use and supercapacitors is also expected. That will be a result of increased development of those technologies. The decrease in lead-acid, Ni-MH and NiCd batteries usage is expected and that would be mostly caused by the need to discard the use of lead-acid batteries due to their negative environmental impact.

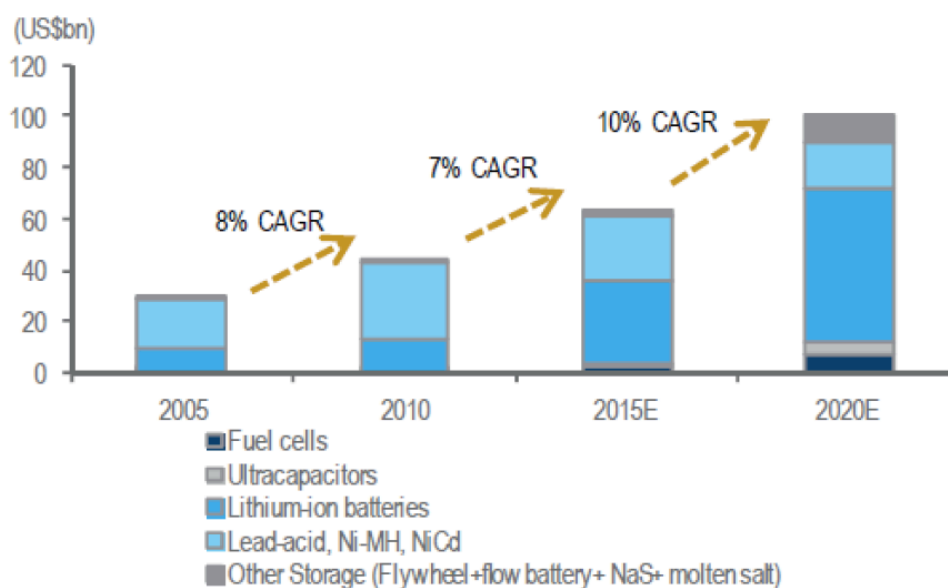


Fig.16 Future pathway of electrochemical energy storage [24].

### 3 Electrochemical Energy Storage

#### 3.1 Batteries and supercapacitors

Looking at Ragone plot depicted in Fig.17 we can see that fuel cells present the highest energy density (200-900 Wh/kg) and aluminium-electrolytic capacitors the highest power density (1500-7000 W/kg). It is possible to notice that with higher energy density the discharge time is also higher. Comparing batteries, it can be seen that lithium batteries have the highest energy and power densities of all. For lithium batteries the energy density and power density can be more than 10 times higher compared to lead acid batteries. Double-layer capacitors and ultracapacitors are tightening the gap between batteries and normal capacitors. Double-layer capacitors have very high range of power densities from 50 W/kg to 3000 W/kg, but are characterised by low energy density around 1 Wh/kg. Ultracapacitors operate only in the high power density area with similar energy density parameters.

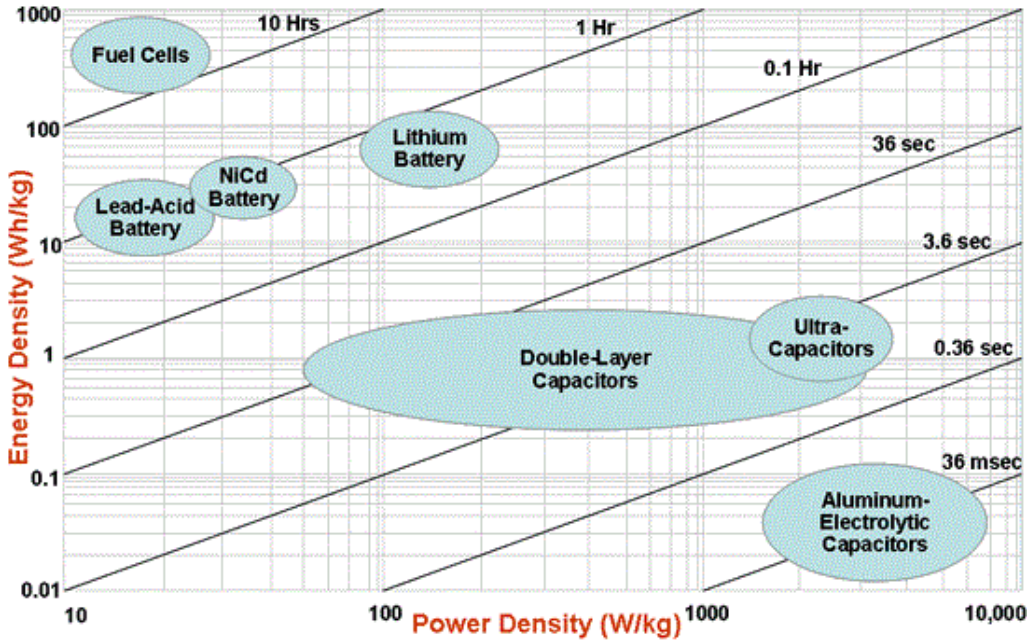


Fig.17 Ragone plot for different Energy Storage technologies [25].

Tab.3 shows the comparison of different parameters between batteries, supercapacitors and electrostatic capacitors. It can be noticed that electrostatic capacitors have the fastest charging and discharging time with efficiency close to 100%. Than on the second place there are supercapacitors with charge/discharge time between 1-30 seconds and efficiencies close to 100%. Batteries have worst performance in charge/discharge time and efficiency. When comparing the amount of energy stored per kilogram it is possible to notice that batteries can store 1000 times more energy than electrostatic capacitors and almost 100 times more when compared to supercapacitors. For the power density, those ratios are reversed. Electrostatic capacitors can store more than 10000 W/kg, which is ten times more if we compare with supercapacitors and almost two

hundred times more than batteries. Electrostatic capacitors have the highest cycle life and batteries have the lowest cycle life of all.

Tab.3 Comparison of chosen parameters [26].

Parameter	Electrostatic capacitor	Supercapacitor	Batteries
Charging time	$10^{-6} - 10^{-3}$ sec	1 – 30 sec	0.3 – 3 h
Discharge time	$10^{-6} - 10^{-3}$ sec	1 – 30 sec	1 – 3 h
Energy Density, Wh/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	0.9 – 0.95	0.7 – 0.85

From the analysis of Tab.3 it is possible to conclude that batteries have the worst performance in terms of power density, cycle life and efficiency, but higher energy density compared to supercapacitors. Depending on the requisites of the application batteries or supercapacitors can be used. In many applications, the combination of both allows at better performance and at answering the specific requirements. Fig.18 shows how suitable are those technologies for different applications.

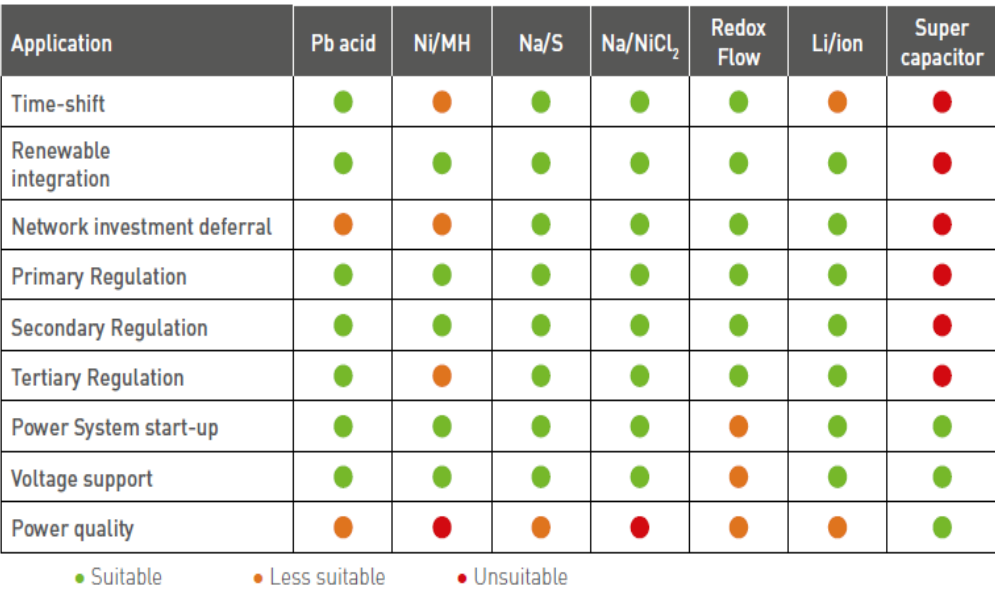


Fig.18 Electrochemical Energy Storage technologies application [27].

It can be seen from the Fig.18 that battery technologies are suitable for almost all applications that are mentioned and supercapacitors are used only in Power System start-up, Voltage Support and Power Quality. In the last one mentioned one can see that supercapacitors are most suitable if power quality is important.

Summarizing all the information about batteries and supercapacitors we can distinguish advantages and disadvantages of those technologies:

Advantages of batteries:

- high energy densities,
- high discharge time,
- most of batteries use aqueous electrolyte,
- can be used for various energy storage applications

Disadvantages of batteries:

- low cycling ability,
- low charging time
- lead acid batteries are harmful for environment,
- high cost
- low power densities

Advantages of supercapacitors [28]:

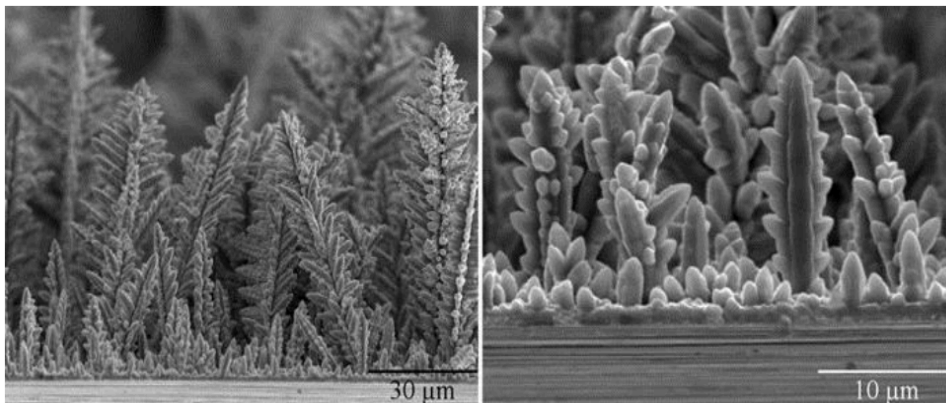
- high power densities,
- wide working temperature range,
- unlimited cycling life,
- fast charge time,
- low cost,
- very high efficiencies,
- can be used to provide peak power and backup power,

Disadvantages of supercapacitors:

- use of organic electrolyte,
- low energy densities,
- high self discharge.

## 4 Charge 2 Change

Charge2Change (C2C) is a spin off company founded by IST researchers and holds a patent for the fabrication of electrodes for Faradic supercapacitors. The company succeeded to develop a series of prototypes at lab scale, using small electrodes (few  $\text{cm}^2$ ), and is now launching the pilot scale phase. For this purpose the company outsourced the scale up and production of electrodes with  $50\text{cm}^2$  area, using the technology developed. The main goal is to produce a hybrid device for electrochemical energy storage, between a battery and a supercapacitor. This hybrid is composed of a carbon based electrode (supercapacitor type electrode), which stores charge using the electrochemical double-layer and a metallic oxide/hydroxide electrode (battery type electrode) that stores energy via redox processes. One of the electrodes used for the assembling of the hybrid device is based on transition metal oxides/hydroxides of Ni-Co coatings with a 3D dendritic structure and were manufactured directly on thin stainless steel current collectors, in a one single and fast step with the need of introducing binders and foreign additives. Stainless steel was chosen because it is cheap, mechanically stable and corrosion resistant material, being very attractive for electrodes fabrication. Ni-Co electrodes were produced through a very simple, low cost and environmental friendly process called electrodeposition. Fig.19 shows a cross-section of the Ni-Co structures, working as active material, formed directly on the stainless steel collector.



*Fig. 19 Cross-section of Ni-Co structures [29].*

One can see that formation of dendrite structures increases the specific area of the active material significantly. Moreover, these materials can operate in aqueous (including neutral) electrolytes without any environmental impact and decrease of performance, thus replacing actual organic compounds and binders typically used in EDL supercapacitors. The most important advantages of the technology developed by C2C are:

- one step, simpler and faster fabrication process of electrodes,
- no need of binders or other foreign additives,
- high adhesion, via chemical bonding, to the bare collector
- flexibility in adapting to any required electrode shape,
- environmentally friendly compounds and electrolytes,
- cheap technology,

- higher specific capacitance.

Fig.20 shows Ragone plot in which the prototype developed by C2C at laboratory scale (using 1 cm<sup>2</sup> electrodes) is compared with different technologies.

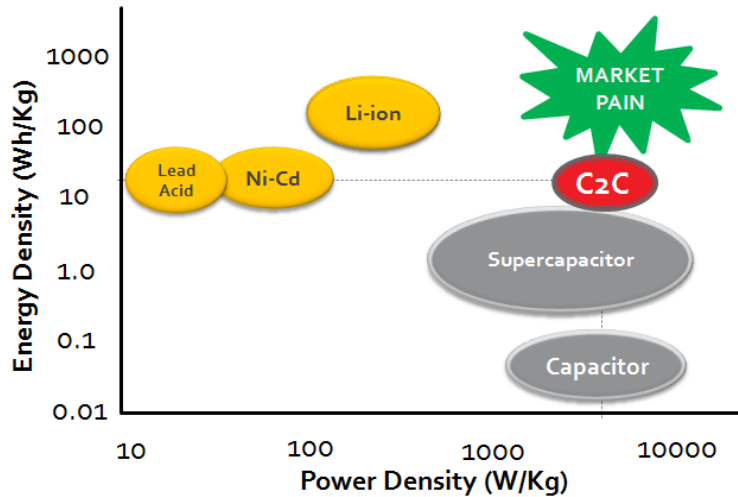


Fig. 20 Ragone plot for C2C comparison.

One can notice that the C2C prototype has higher energy density compared to conventional supercapacitors used nowadays, similar to lead-acid or nickel-cadmium batteries. It also shows much higher power density when compared to batteries and similar values compared to supercapacitors or capacitors. This data was obtained using small-scale electrodes. Tab.4 shows comparison of C2C with recently available technologies.

Tab. 4 Comparison of C2C with other technologies.

Component	Supplier	Energy Density, Wh/kg
Supercapacitor	CapXX, Maxwell, ACT	0.5-30
Lead Acid battery	Exide	30-40
C2C hybrid	Charge2Change	30-50
Lithium ion battery	Matsushita	160

The next step of the C2C technology is the scale up of the electrodes area for 50 times. After that it is necessary to evaluate the performance of these electrodes. The final step is the project and testing of a prototype in an electrical vehicle - forklift. C2C envisages to test two different types of devices: a Faradaic supercapacitor using two identical electrodes made of the Ni-Co high surface area dendritic coatings and a hybrid (or asymmetric) device using one carbon electrode (the anode) and the same Ni-Co dendritic coating as cathode. The first objective is to build the respective lines in the Ragone plot for these two combinations using the larger electrodes that were produced for C2C. Fig.21 shows schematic view of NiCo-NiCo and NiCo-C electrodes and additionally Fig.22 shows schematic view of NiCo-C prototype.

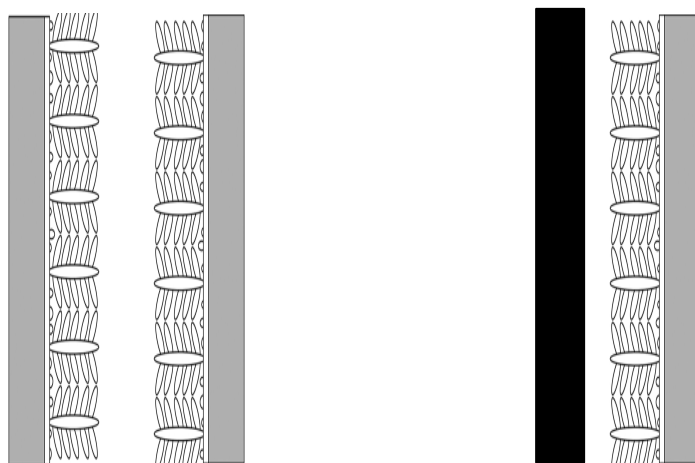


Fig. 21 Schematic NiCo-NiCo (left) and NiCo-C (right) setup.

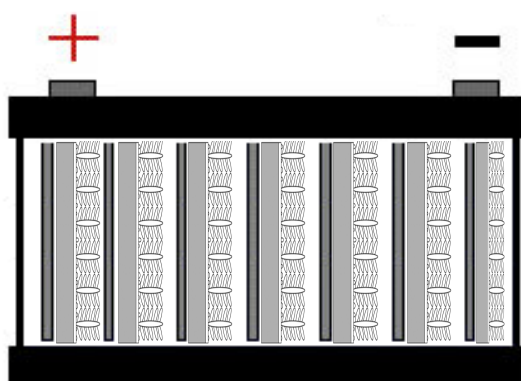


Fig. 22 Schematic view of NiCo-C prototype.

#### 4.1 Aim of the thesis

The main objective of the thesis is to design and test a new energy storage device, an hybrid between a battery and supercapacitor, to evaluate its performance and to compare it with currently available electrochemical devices, namely lead acid batteries and electrochemical double layer supercapacitors. Work included:

- preparation of the testing setup
- testing of electrodes quality,
- determination of energy and power densities
- construction of respective Ragone plot for different setups to compare with recently available technologies,
- perform capacitance fading test of different setups to check the behaviour of electrodes



## 5 Methodology

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### 5.1 Description of the experiment

The experimental work was divided into four tasks:

- a) Development of the electrode quality test to check NiCo electrodes performance and reliability,
- b) NiCo-NiCo and NiCo-C used electrodes test with different current applied
- c) NiCo-NiCo and NiCo-C new electrodes test with different current applied,
- d) Capacitance fade of used and new NiCo-NiCo electrodes and NiCo-C electrodes.

Term “used” was given for electrodes that were already tested, handled and have lost some active material. “New” electrodes were as received electrodes that have not been tested. All the performed experiments were based on charge/discharge cycling, using different combinations of electrodes and parameters applied. Charge/discharge cycle demonstrate the ability of the system to store and deliver energy, or power, with respect to time, depending on the applied current. Fig.23 shows an example of the charge/discharge curves typical of an assembly of two identical NiCo-NiCo electrodes. The figure shows that the first cycle is longer than the next succeeding it. This is probably caused due to activation (oxidation) of the active material with dendrite structures. It is also worth stressing out that most of the process of storing and delivering of the energy takes place in a specific potential range.

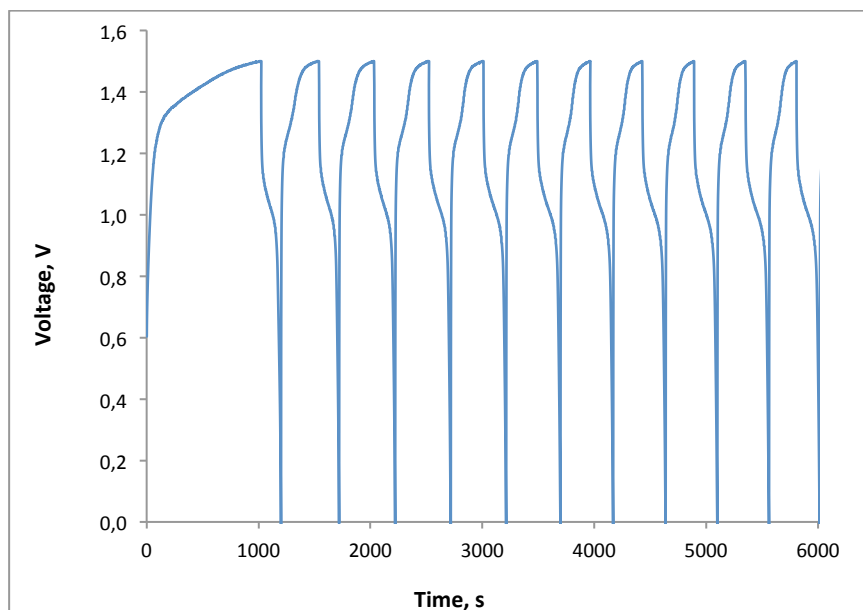


Fig. 23 Example of charge/discharge curves of two identical NiCo-NiCo plates under an applied current of 0,04 A.

### 5.1.1 Electrode quality test

Electrode quality test was performed using a *VoltaLab PGZ 100* potentiostat with integrated *VoltaLab* software that is shown in Fig.24. Tests were conducted by holding the electrodes inside a container, specifically prepared for the test of cells made of these electrodes (Fig.24 and Fig.25). The electrolyte used in all tests was KOH 1 molar. All tests were conducted at room temperature.

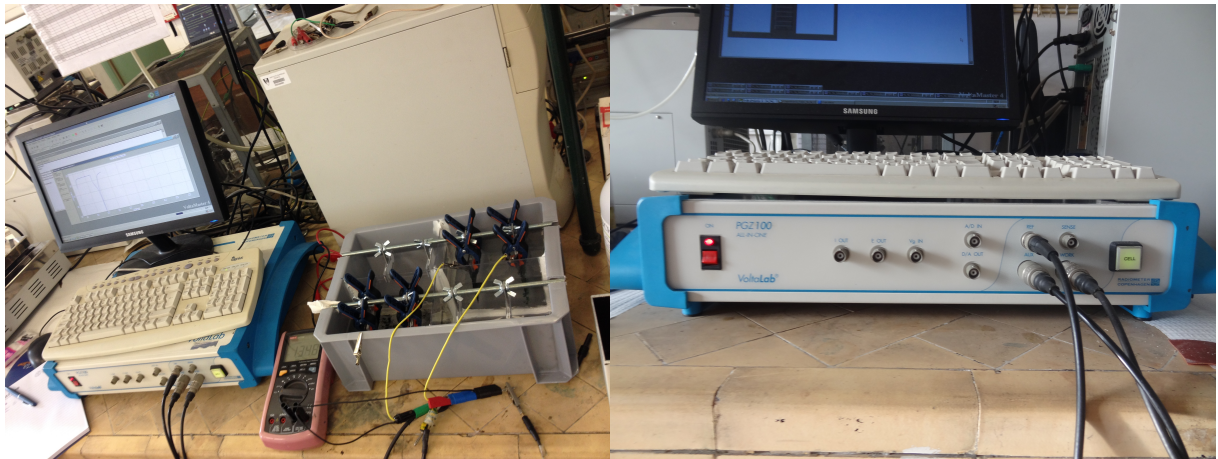


Fig. 24 Test-bench and *VoltaLab PGZ 100* potentiostat.

Testing procedure of the electrodes was as follows:

- a) As received (new) Nickel Cobalt (NiCo) electrodes were placed in the container, wired and connected to the *VoltaLab PGZ 100* (Fig.25),
- b) testing parameters were set in Voltalab software (Fig.26),
  - applied charge/discharge current: 40mA,
  - charge/discharge maximum time: 300 sec,
  - measurement period: 1 s,
  - minimum potential: 0 mV,
  - maximum potential: 1500 mV
  - number of cycles: 5,
- c) electrodes were accepted as good ones if the previously set limits were achieved in a time frame close to 5 min; if the cycle took more than this time or less than 4 minutes electrodes were rejected;
- d) This procedure was repeated for successive pairs of electrodes;

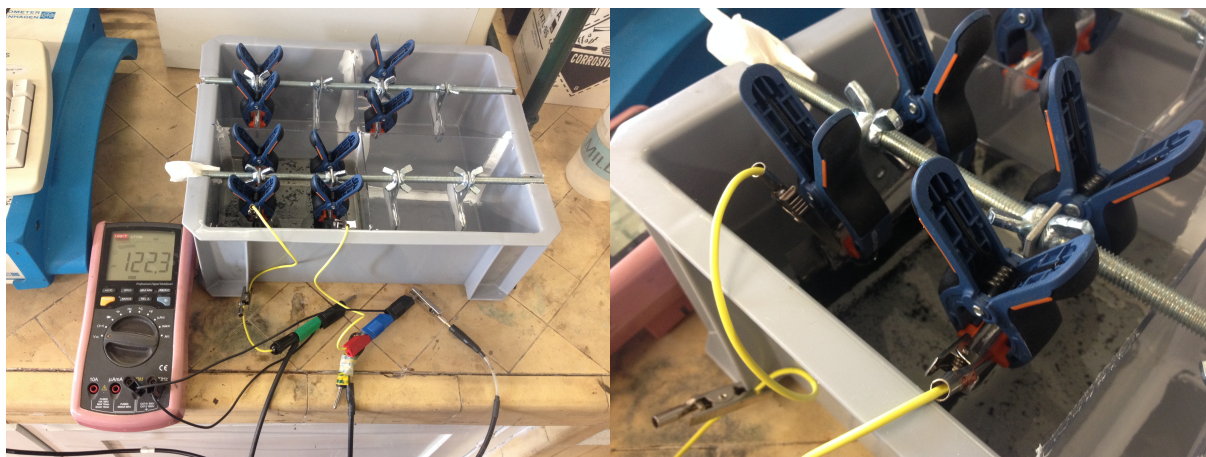


Fig. 25 Experimental set-up.

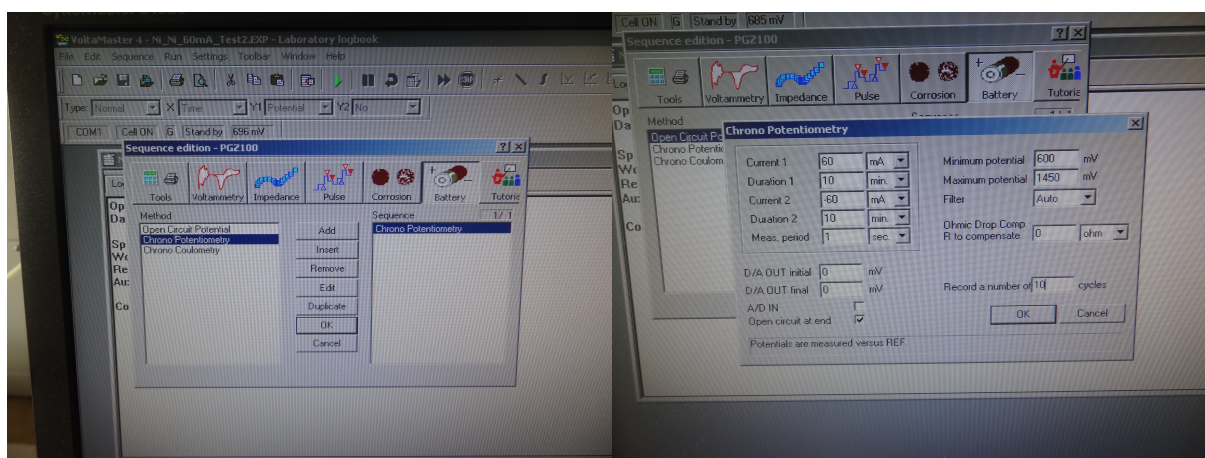


Fig. 26 VoltaLab software set-up.

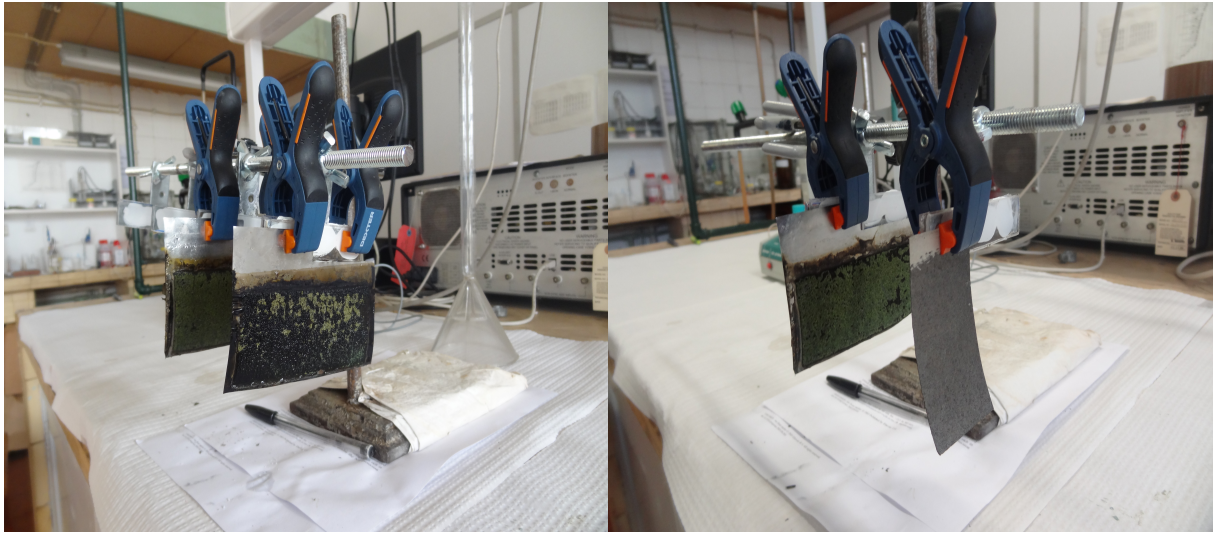
### 5.1.2 NiCo-NiCo and NiCo-C electrode test

After the electrode quality test, one pair of NiCo-NiCo electrodes was chosen to prepare the electrochemical cell. One NiCo electrode was used as positive electrode and a Carbon commercial nanofoam sheet was selected as negative electrode; together they were used to prepare the hybrid cell. Charge/discharge curves were carried out for both cells using different applied current densities. The NiCo-C electrodes were tested in the same potential window of the NiCo-NiCo and also tested in a larger potential window. The experimental parameters used can be summarised as follows:

- applied charge/discharge currents: 10mA, 20mA, 30mA and 40mA,
- charge/discharge maximum time: 300 sec,
- measurement period: 1 s,
- minimum potential for NiCo-NiCo and NiCo-C: 600 mV,
- maximum potential for NiCo-NiCo and NiCo-C: 1450 mV,
- minimum potential for NiCo-C in higher potential window: 200 mV,
- maximum potential for NiCo-C in higher potential window: 1600 mV,

- number of cycles: 5

Fig. 27 shows the NiCo-NiCo and the NiCo-C set-ups for Test1.



*Fig. 27 NiCo-NiCo (left) and NiCo-Carbon (right) tested plates.*

In the first task, a high voltage drop was noticed for NiCo-C electrodes as well as a significant active material loss from the NiCo electrode. To minimise this problem, a pair of new electrodes was assembled together, but much closer and using a paper-based separator. The cell was tested using the same protocol as for the previous NiCo-NiCo, NiCo-C and NiCo-C electrodes, in a higher potential window. Fig.28 shows the assembly of the electrodes and separator and Fig.29, and Fig.30 show the setup for Test 2. It is worth mentioning that to avoid excessive destruction of active material electrodes, the cellulosic separator and electrodes were wetted with KOH solution before assembly.



*Fig. 28 Assembly of NiCo-NiCo plates (left) and already assembled NiCo-NiCo and NiCo-C plates.*



*Fig. 29 NiCo-NiCo Test2 set-up.*



*Fig. 30 NiCo-C Test2 set-up.*

The testing procedure in Test2 was similar to Test1 but the experiment was carried out with higher various applied currents: 30mA, 40mA, 50mA, 60mA, 70mA, 80mA, 90mA and 100mA.

### 5.1.3 Capacitance fade.

The capacitance fade or capacitance retention is important to assess the stability and the cycling ability of the electrodes. The test was carried out for used NiCo-NiCo electrodes, new NiCo-NiCo electrodes and NiCo-C electrodes. The experimental protocol was similar to the previously applied tests but the number of cycles was increased:

- for used NiCo-NiCo electrodes and NiCo-C electrodes: 500 cycles,
- for new NiCo-NiCo electrodes: 1000 cycles,

Fig.31 shows an example of a set of plots obtained through the experiment.

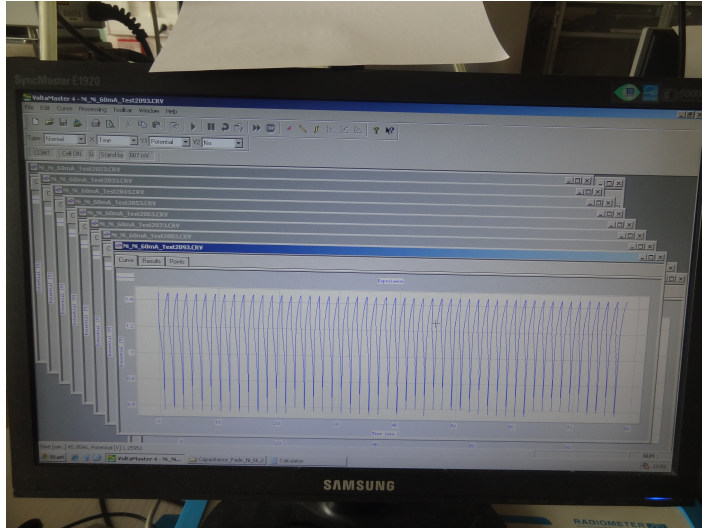


Fig. 31 Charge/discharge curves of capacitance fade experiment in VoltLab software.

## 5.2 Calculations

To obtain the Ragone plot, the average and maximum specific energy and the specific power were calculated from obtained data and additionally cell efficiencies were calculated.

1) Average Specific Energy, Wh/kg is given by – eq. 1:

$$E = \frac{C \times \Delta U^2}{2 \times 3600 \times m} \quad (1)$$

where:

$\Delta U$  in Volts (V) is the change in potential calculated from a protocol proposed in literature [30] and  $U$  is the maximum voltage – eq (2):

$$\Delta U = (0,9 \times U)^2 - (0,7 \times U)^2 \quad (2)$$

Fig.32 shows a schematic measurement profile. Where  $\Delta U_3$  and  $\Delta U_4$  are the values of ohmic drop needed to determine respectively Equivalent Distributed Resistance (EDR) and Equivalent Series Resistance (ESR). ESR that is often called pulse resistance corresponds to all resistive components of the supercapacitor whereas EDR includes ESR values and additionally takes into account charge redistribution process in the electrode pore matrix. It can be seen that most of the energy is delivered in the range of 0,9 and 0,7 V within the total potential window applied.

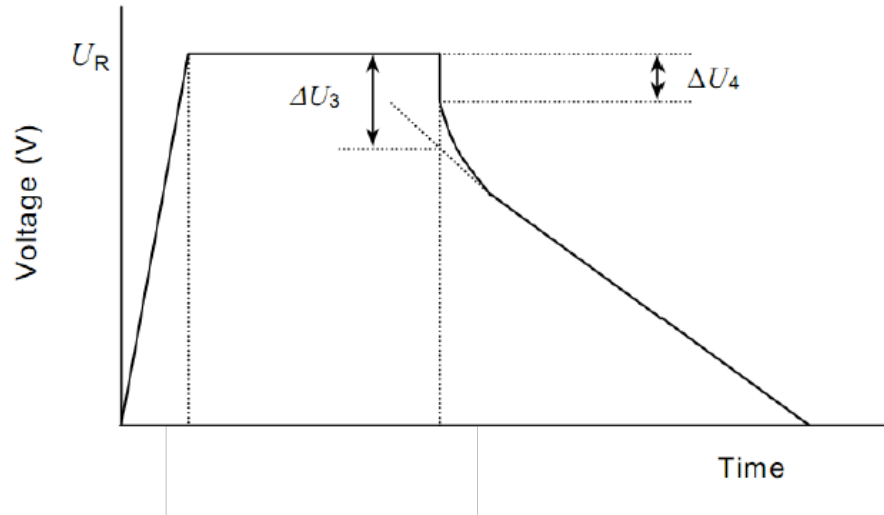


Fig. 32 Illustrative charge/discharge curve illustrating the ohmic drop and the potential window to extract the capacitance.

Additionally the  $\Delta U$  value was compared to the discharge curve (Fig.33) obtained in one of the tests and it seems that applied method is enough accurate.

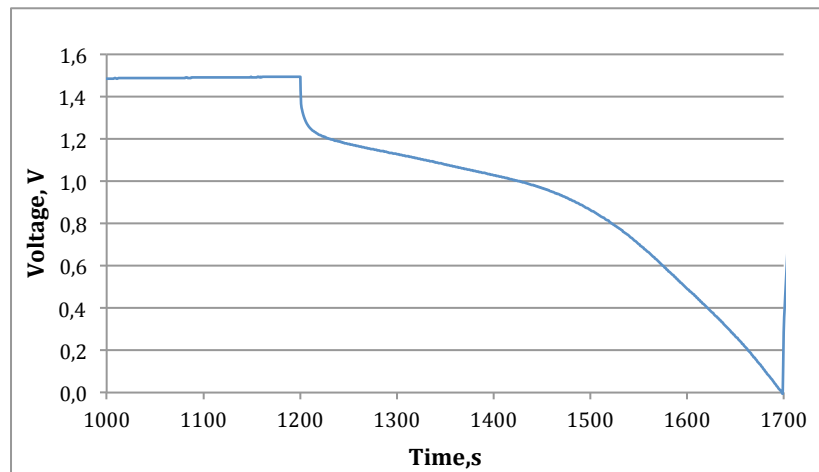


Fig. 33 Example of a discharge curve for the NiCo-NiCo electrodes.

Additionally in eq (1)  $m$  is mass of the active material on NiCo electrodes and mass of carbon electrode kg, (NiCo-NiCo=0,0042kg and NiCo-C=0,002318kg),

$C$  is the capacitance, F, and was calculated from the following –eq. 3:

$$C = \frac{I \times t}{\Delta U} \quad (3)$$

where:

$I$  is discharge current, A

$t$  is the discharge time, sec,

$\Delta U$  is the change in potential, V, calculated as previous.

2) Average Specific Power, W/kg- eq. 4:

$$P = \frac{\Delta U^2}{4 \times R} \quad (4)$$

where:

$\Delta U$  is the change in potential, V, calculated as previous,

$R$  is the resistance,  $\Omega$ , and was calculated as follow- eq. 5:

$$R = \frac{V_{drop}}{I} \quad (5)$$

where:

$V_{drop}$  is the voltage drop, V, value was taken from obtained results as the difference in maximum potential value and value of first discharge step,

$I$  is the discharge current, A,

Maximum Specific Energy and Power were calculated in the same way as Average Specific Energy and Power with one difference:  $\Delta V$  was changed into  $V_{max}$  that for NiCo-NiCo and NiCo-C were 1.45 V and for NiCo-C in higher potential window was equal 1.60 V.

3) Efficiency

$$\eta = \frac{t_{discharge}}{t_{charge}} \quad (6)$$

where:

$t_{discharge}$  and  $t_{charge}$  were respectively discharge and charge times.



## 6 Results

### 6.1 Electrode Test1 and Test2

Charge/discharge curves from the Test1 are shown on Fig.34, Fig.35 and Fig.36. One can notice that the NiCo-NiCo cell shows longer charge/discharge times compared to NiCo-C for all the currents applied. The obtained charge time is almost two times higher when 10mA current was applied compared to asymmetric cells and decreases with increasing applied current.

The test with NiCo-C revealed a larger ohmic drop compared to the cell with the two identical NiCo-NiCo electrodes. Normally higher voltage drop does not affect the discharge time, but in this case because the ohmic drop was quite high, it affected the potential windows where more energy is stored. Comparing the NiCo-NiCo plots with the NiCo-C ones obtained in a higher potential window, it is possible to observe similar results, even in the higher potential window was applied. This is also consequence of the high potential drop that contributed to the overall resistance of the cell. Resistances obtained in Test1 are shown on Fig.35. On Fig.37 one can see that for NiCo-NiCo the resistance values are the lowest and do not change much when different currents were applied. For NiCo-C, in higher potential window, the obtained resistances were higher compared to NiCo-NiCo and were varying significantly when the applied current increased. It is also worth mentioning the charge/discharge curve for NiCo-NiCo is more battery type (a curve) and for NiCo-C is more supercapacitor type (a sloped line).

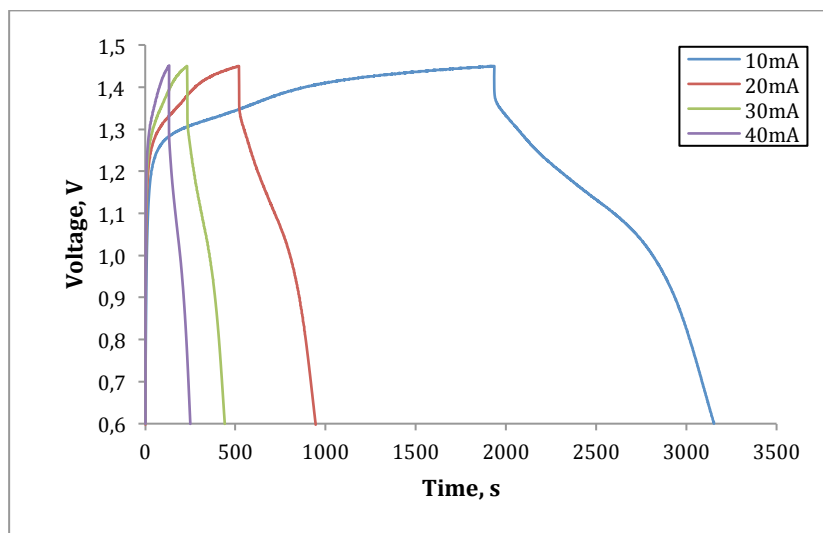


Fig. 34 Charge/Discharge curves for NiCo-NiCo Test1.

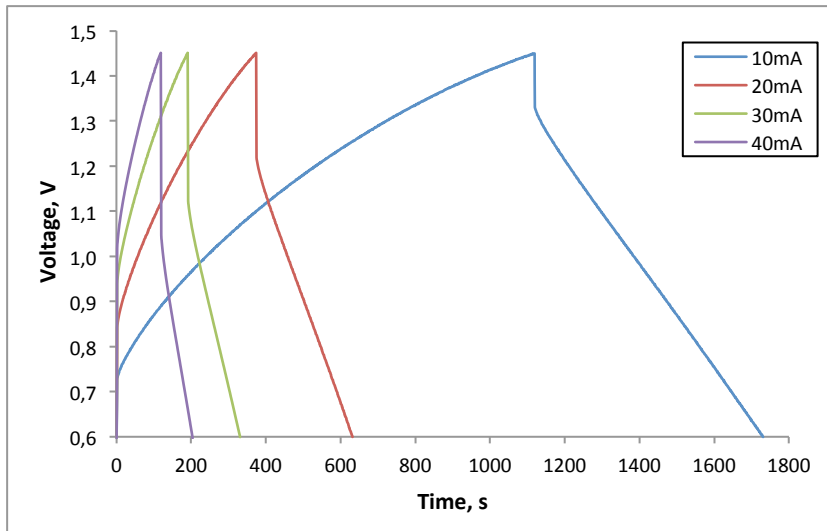


Fig. 35 Charge/Discharge curves for NiCo-C Test1.

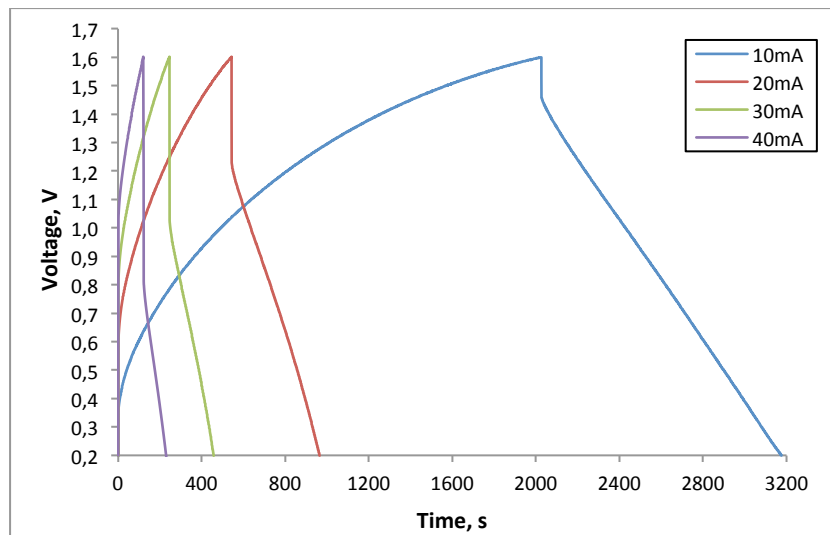


Fig. 36 Charge/Discharge curves for NiCo-C in higher potential window Test1.

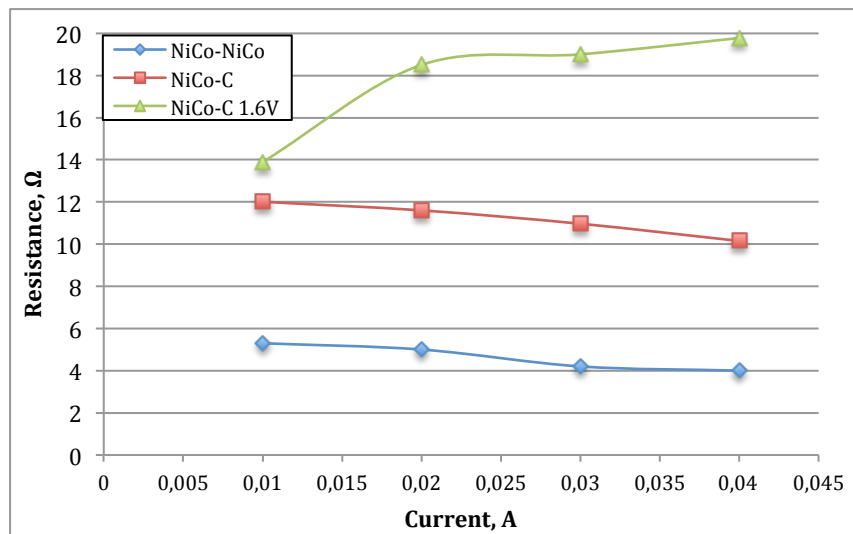


Fig. 37 Evolution of resistance with respect to the applied current in Test1.

Charge/discharge curves obtained in the second test (Test2) are shown in Fig.38, Fig.39 and Fig.40. One can notice that the NiCo-NiCo cell shows higher charge/discharge time for the lowest applied current compared to NiCo-C but when the applied current was higher, the charge/discharge time for NiCo-C was higher compared to NiCo-NiCo.

The highest values of charge/discharge times were obtained for NiCo-C in higher potential window. This was expected because in Test2 the voltage drop was more reduced compared to Test1. Fig.39 show the resistances obtained for Test2. The lowest resistances were obtained for NiCo-NiCo cell and were decreasing slightly with the increase of the applied current. For the NiCo-C cells the resistance values were higher compared to NiCo-NiCo and the values were independent of the applied current and the resistance values were constant. Additionally it can be seen that the charge/discharge curve for NiCo-NiCo is more battery type (a curve) and for NiCo-C is more supercapacitor type (a sloped line).

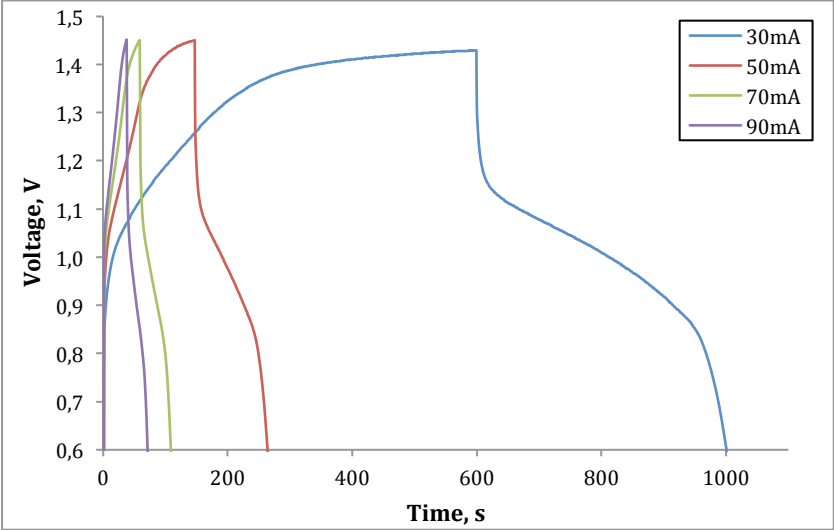


Fig. 38 Charge/Discharge curves for NiCo-NiCo Test2.

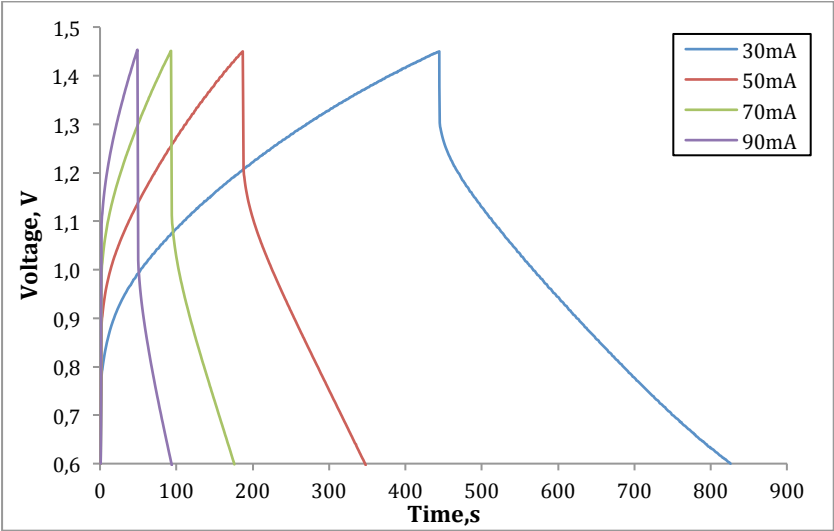


Fig. 39 Charge/Discharge curves for NiCo-C Test2.

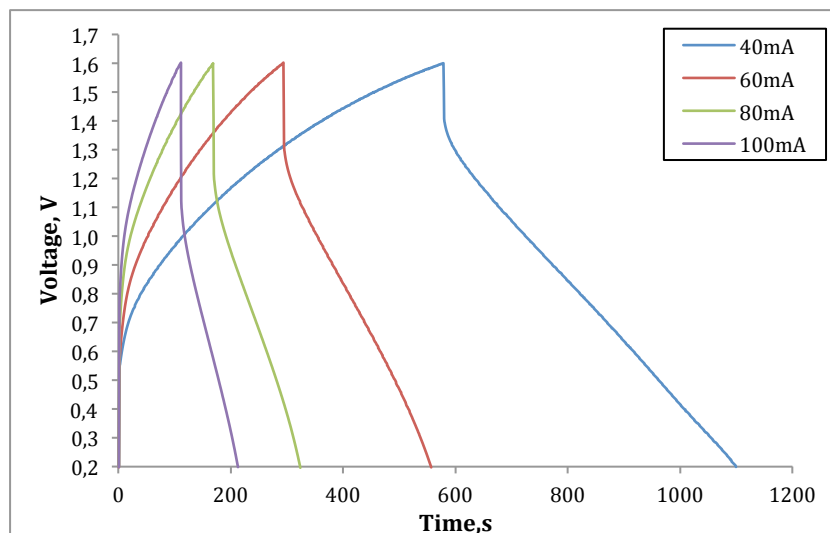


Fig. 40 Charge/Discharge curves for NiCo-C 1.6V Test2.

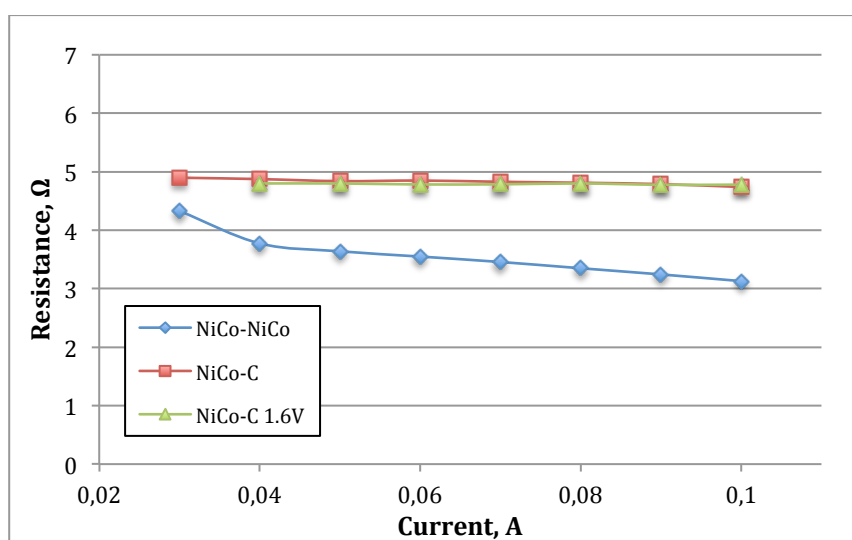


Fig. 41 Evolution of resistance with respect to the applied current in Test2.

Tab.5, Tab.6 and Tab.7 show the results obtained for average specific energy and power for Tests1 and Test2.

Tab. 5 Results of average Specific Energy and Power for NiCo-NiCo.

Current, A	Test1 NiCo-NiCo		Test2 NiCo-NiCo	
	Specific power, W/kg	Specific Energy, Wh/kg	Specific power, W/kg	Specific Energy, Wh/kg
0.01	0.235	0.342	-	-
0.02	0.249	0.239	-	-
0.03	0.296	0.175	0.287	0.338
0.04	0.311	0.133	0.329	0.269
0.05	-	-	0.341	0.164
0.06	-	-	0.350	0.116
0.07	-	-	0.360	0.096
0.08	-	-	0.371	0.088
0.09	-	-	0.383	0.081
0.1	-	-	0.397	0.082

The results show that the average specific power obtained for NiCo-NiCo plates in both tests is similar due to the similar voltage drop values obtained. Nevertheless it can be also seen that specific energy values obtained in Test2 are much higher compared to Test1. Lower values obtained for Test1 are probably due to the higher amount of active material on the electrode. This material was partially lost during the experiment in Test1. For both tests the increase in current resulted in an increase of the specific power by around 30% compared to lowest and highest currents applied; the specific energy decreases 2.5 times in Test1 and almost 4 times in Test2.

Tab. 6 Results of average Specific Energy and Power for NiCo-C.

Current, A	Test1 NiCo-C		Test2 NiCo-C	
	Specific power, W/kg	Specific Energy, Wh/kg	Specific power, W/kg	Specific Energy, Wh/kg
0.01	0.194	0.322	-	-
0.02	0.201	0.271	-	-
0.03	0.212	0.220	0.460	0.582
0.04	0.230	0.177	0.462	0.471
0.05	-	-	0.465	0.407
0.06	-	-	0.464	0.345
0.07	-	-	0.466	0.292
0.08	-	-	0.468	0.244
0.09	-	-	0.470	0.174
0.1	-	-	0.475	0.163

Comparing results from Test1 and Test2 for NiCo-C electrodes reveal that specific power values obtained in the second test are much higher compared to the first test. The specific power values obtained in Test2 are more than 2 times higher compared to Test1. This was caused by the lower voltage drop that resulted in lower resistance values. Specific energy values obtained in Test2 are almost 3 times higher compared to Test1. For both tests the increase in current did not cause increase in specific power comparing to lowest and highest currents applied. Nevertheless the current increase caused a decrease in the specific energy by factor 2 in Test1 and a factor 3.5 in Test2.

Tab. 7 Results of average Specific Energy and Power for NiCo-C 1.6V.

Current, A	Test1 NiCo-C 1.6V		Test2 NiCo-C 1.6V	
	Specific power, W/kg	Specific Energy, Wh/kg	Specific power, W/kg	Specific Energy, Wh/kg
0.01	1.234	0.997	-	-
0.02	0.927	0.746	-	-
0.03	0.903	0.549	-	-
0.04	0.867	0.375	3.453	1.745
0.05	-		3.453	1.510
0.06	-		3.465	1.319
0.07	-		3.463	1.163
0.08	-		3.453	1.034
0.09	-		3.469	0.936
0.1	-		3.467	0.847

Comparing results from Test1 and Test2 for NiCo-C electrodes in a larger potential window shows that the specific power values obtained in the second test are much higher than in first test. Specific power obtained in Test2 is more than 4 times higher compared to Test1. This behaviour is similar to the NiCo-C cell and is caused by the resistance of the cell.

Specific energy values obtained in Test2 are almost 4.5 times higher compared to Test1. In Test1 the increase in current induced a decrease in the specific power by around 30% comparing to lowest and highest current applied and a decrease in specific energy almost 3 times. For Test2 the increase of current did not affect the change of specific power but affected the specific power that decreased by a factor 2.

Tab.8, Tab.9 and Tab.10 show the results of Maximum Specific Energy and Power for Test.1 and Test.2. On can notice that the behaviour of the results is the same when compared to the average results with the difference that maximum values obtained are higher than average. The highest value of specific power (57,77 W/kg) and energy (11,4 Wh/kg) were obtained for NiCo-C electrodes in the highest potential window in Test2.

Tab. 8 Results of maximum Specific Energy and Power for NiCo-NiCo.

Current, A	Test1 NiCo-NiCo		Test2 NiCo-NiCo	
	Specific power, W/kg	Specific Energy, Wh/kg	Specific power, W/kg	Specific Energy, Wh/kg
0.01	23.613	4.981	-	-
0.02	25.030	3.476	-	-
0.03	29.797	2.540	28.881	4.928
0.04	31.287	1.930	33.155	3.918
0.05	-	-	34.383	2.395
0.06	-	-	35.253	1.694
0.07	-	-	36.203	1.404
0.08	-	-	37.365	1.287
0.09	-	-	38.573	1.183
0.1	-	-	39.987	1.192

Tab. 9 Results of maximum Specific Energy and Power for NiCo-C.

Current, A	Test1 NiCo-C		Test2 NiCo-C	
	Specific power, W/kg	Specific Energy, Wh/kg	Specific power, W/kg	Specific Energy, Wh/kg
0.01	19.552	4.685	-	-
0.02	20.227	3.941	-	-
0.03	21.395	3.197	46.281	8.478
0.04	23.116	2.576	46.521	6.856
0.05	-	-	46.864	5.939
0.06	-	-	46.765	5.023
0.07	-	-	46.973	4.253
0.08	-	-	47.121	3.562
0.09	-	-	47.365	2.536
0.1	-	-	47.848	2.377

Tab. 10 Results of maximum Specific Energy and power for NiCo-C 1.6V.

Current, A	Test1 NiCo-C 1.6V		Test2 NiCo-C 1.6V	
	Specific power, W/kg	Specific Energy, Wh/kg	Specific power, W/kg	Specific Energy, Wh/kg
0.01	20.553	6.513	-	-
0.02	15.442	4.875	-	-
0.03	15.036	3.588	-	-
0.04	14.447	2.449	57.533	11.401
0.05	-	-	57.533	9.863
0.06	-	-	57.735	8.615
0.07	-	-	57.705	7.599
0.08	-	-	57.538	6.752
0.09	-	-	57.794	6.112
0.1	-	-	57.770	5.535

Tab.11, Tab.12 and Tab.13 show the charge/discharge times and cell efficiency obtained in Test.1 and Test.2. One can see that in all cases the charge/discharge times were higher in Test2. This can be explained based on the fact that the use of new electrodes, which did not loss active material, results in more charge storage capacity. Comparing the efficiencies it can be seen that the efficiencies for NiCo-NiCo were higher in Test1 probably due to NiCo material activation that was not fully achieved when the new material was tested. In fact, these redox active materials need to be electrochemically activated before they reach the maximum efficiency. For NiCo-C electrodes higher efficiencies were obtained in Test2 an effect that is also connected with voltage drop. The efficiency values were stable with current change for NiCo-C, but for NiCo-NiCo plates the efficiency increases with the current.



Tab. 11 Charge/discharge times and efficiency of NiCo-NiCo Test1 and Test2.

Current, A	Test.1 NiCo-NiCo			Test2. NiCo-NiCo		
	Charge, s	Discharge, s	Efficiency	Charge, s	Discharge, s	Efficiency
0.01	1432	1218	0.85	-	-	-
0.02	488	425	0.87	-	-	-
0.03	231	207	0.90	680	401	0.59
0.04	129	118	0.91	341	239	0.70
0.05	-	-	-	146	117	0.80
0.06	-	-	-	83	69	0.83
0.07	-	-	-	58	49	0.84
0.08	-	-	-	45	39	0.87
0.09	-	-	-	36	32	0.89
0.1	-	-	-	33	29	0.88

Tab. 12. Charge/discharge times and efficiency of NiCo-C Test1 and Test2.

Current, A	Test.1 NiCo-C			Test.2 NiCo-C		
	Charge, s	Discharge, s	Efficiency	Charge, s	Discharge, s	Efficiency
0.01	940	611	0.65	-	-	-
0.02	372	257	0.69	-	-	-
0.03	189	139	0.74	443	381	0.86
0.04	117	84	0.72	277	231	0.83
0.05	-	-	-	186	160	0.86
0.06	-	-	-	129	113	0.88
0.07	-	-	-	92	82	0.89
0.08	-	-	-	66	60	0.91
0.09	-	-	-	48	38	0.79
0.1	-	-	-	36	32	0.89

Tab. 13 Charge/discharge times and efficiency for NiCo-C in higher potential window for Test1 and Test2.

Current, A	Test.1 NiCo-C 1.6V			Test.2 NiCo-C 1.6V		
	0.01	2024	1149	0.57	-	-
0.02	541	430	0.79	-	-	-
0.03	244	211	0.86	-	-	-
0.04	220	108	0.49	583	520	0.89
0.05	-	-	-	395	360	0.91
0.06	-	-	-	292	262	0.90
0.07	-	-	-	216	198	0.92
0.08	-	-	-	168	154	0.92
0.09	-	-	-	131	124	0.95
0.1	-	-	-	109	101	0.93

Fig.42 and Fig.43 show the Ragone plots obtained from Test1 and Test2. These Ragone plots are the summary of previously commented results.

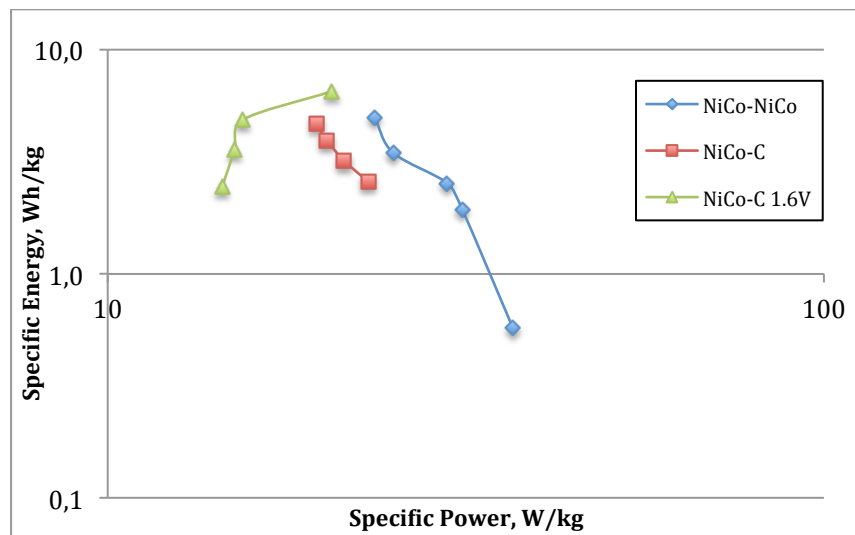


Fig. 42 Ragone plot Test1.

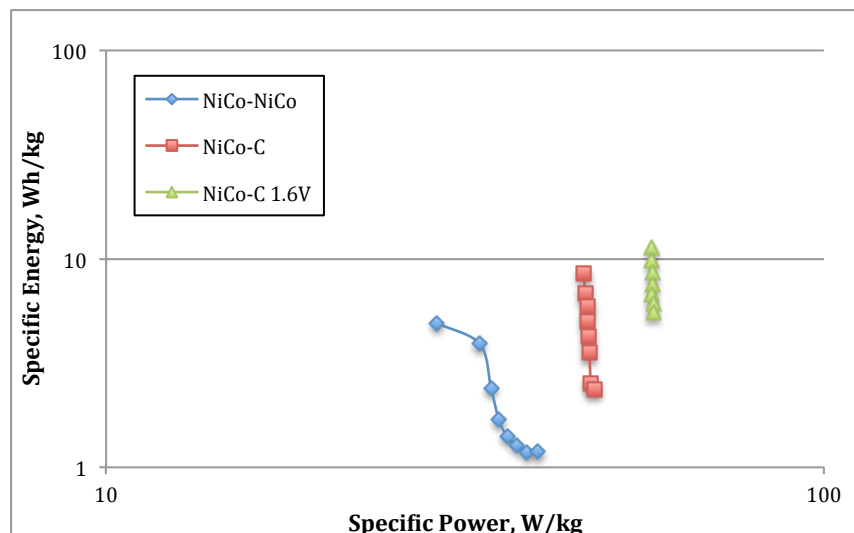


Fig. 43 Ragone plot Test2.

## 6.2 Capacitance fade experiment.

Fig.44 shows the results for the capacitance fade experiment. One can see that for used NiCo-NiCo electrodes there was a significant fade of capacitance after 500 cycles, almost 70%. For NiCo-Carbon electrodes the capacitance fade was in the range of 10% that is a very satisfactory result for energy storage applications.

The most interesting plot was obtained for new NiCo-NiCo electrodes. It can be seen that there is a significant increase, over 277%, of capacitance up to around the 350<sup>th</sup> cycle. After 1000 cycles the capacitance fade was in the range of 3-5%. Additionally after obtaining these results new values of specific power and energy for the maximum capacity were calculated at the maximum of the peak, it means after around 330 cycles. The values of specific power are ten times higher and specific energy value was almost 20 times higher compared to results obtained from Test2. The value of specific power obtained was equal 352,5 W/kg and specific energy was almost 32 Wh/kg. Plotted value and comparison to results from Test2 is shown on Fig.45. These results clearly demonstrate that the NiCo-NiCo electrodes need to be electrochemically activated to reach the maximum energy density. This is in agreement with literature [31] and has also been observed in various works ongoing.

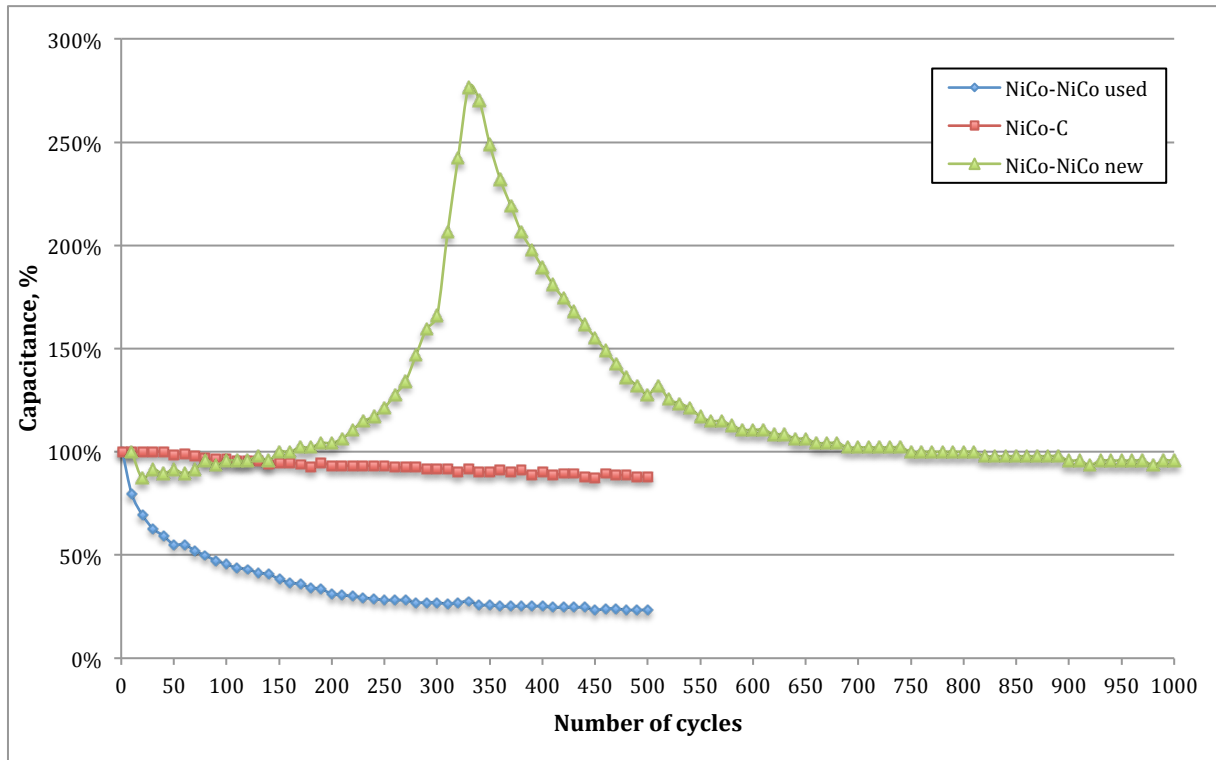


Fig. 44 Capacitance fade results.

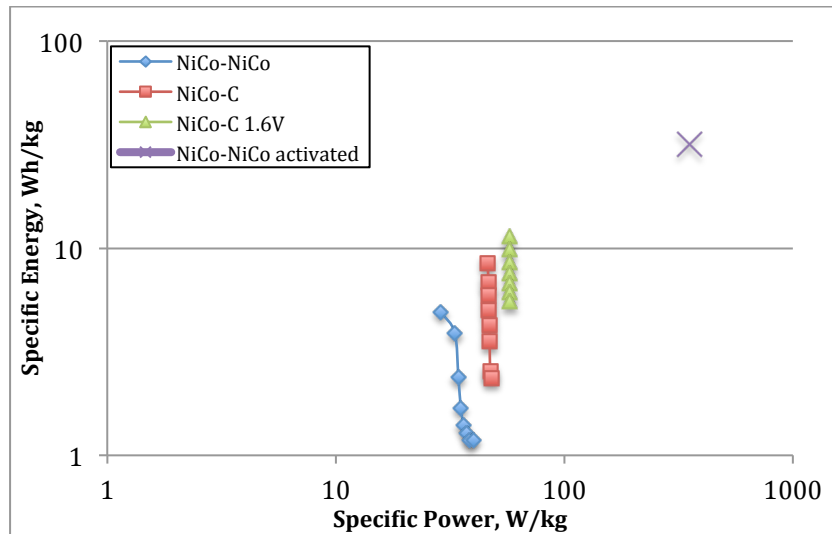


Fig. 45 Ragone plot with calculated value after capacitance fade test.

## 7 Summary

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Summarizing all the experimental work and results obtained it can be concluded that:

- 1) Methodology assumed for the quality test experiments did not give an accurate answer. The results obtained for electrodes were not reliable. Additionally significant amount of active material was lost while the experiments were carried out. It is worth to stress out that while testing the active material, electrochemical activation was not taken into consideration and many electrodes were rejected due to that mostly because of not the results were not fully reproducible. A different methodology needs to be developed in order to check the quality of electrodes. In that case it should be considered whether to check each electrode individually, or alternatively couple of them from the produced batch due to fragility of the electrodes. This would not affect the performance of further used electrodes because electrodes used in quality test should not be used to assemble the hybrid cell. Activation of the active material should also be taken into consideration. To do that the number of cycles should be increased. Additionally the applied current for quality test can be higher to reduce the time needed for the test.
- 2) The procedure applied for the experiments carried out in Test1 with already used electrodes was similar to quality test experiments and showed that the distance between NiCo-C electrodes increased the resistance that affected specific energy and power by decreasing the discharge time and increasing the voltage drop. Nevertheless the distance between NiCo-NiCo did not affect the resistance significantly. Similarly to the quality test significant amount of active material was lost.
- 3) Test2 showed that the cell assembly of electrodes and separator was a good solution in order to test electrodes performance. It decreased the resistance between electrodes and also prevented material loss. The best results obtained for NiCo-NiCo (40 W/kg and 5 Wh/kg) NiCo-C (around 45 W/kg and 8 Wh/kg) NiCo-C in higher potential window (around 57 W/kg 11 Wh/kg) were quite satisfactory comparing to other available supercapacitors technologies. To prevent the excessive material lost in the future it is worth to take into consideration testing electrodes horizontally than vertically as it was done in all experiments.
- 4) Capacitance fading test was carried out for used and new NiCo-NiCo and for NiCo-C electrodes. It showed significant capacitance fade for used NiCo-NiCo electrodes. Nevertheless the decrease in capacitance was not significant for NiCo-C electrodes but the most interesting was the result for NiCo-NiCo electrodes. It showed that activation of material occurred after around 300 cycles and increased the capacitance more than 2.5 times. Obtained values for power and energy density were equal 352 W/kg and 32 Wh/kg, respectively, and were relatively high when placed on Ragone plots and compared to other

technologies. This result places this device between the range of lead acid batteries and close to lithium-ion batteries, with the advantage that the device can be charged and discharge at least up to 1000 cycles with very little capacitance fade and charged with very high efficiency (around 90%). These results are very promising for future developments of the C2C prototypes. Fig.46 shows maximum obtained values in Test2 and additionally calculated value for highest capacitance compared to other technologies.

Placed dots corresponds respectively:

- red- NiCo-NiCo
- blue- NiCo-C
- green- NiCo-C higher potential window
- orange- NiCo-NiCo activated

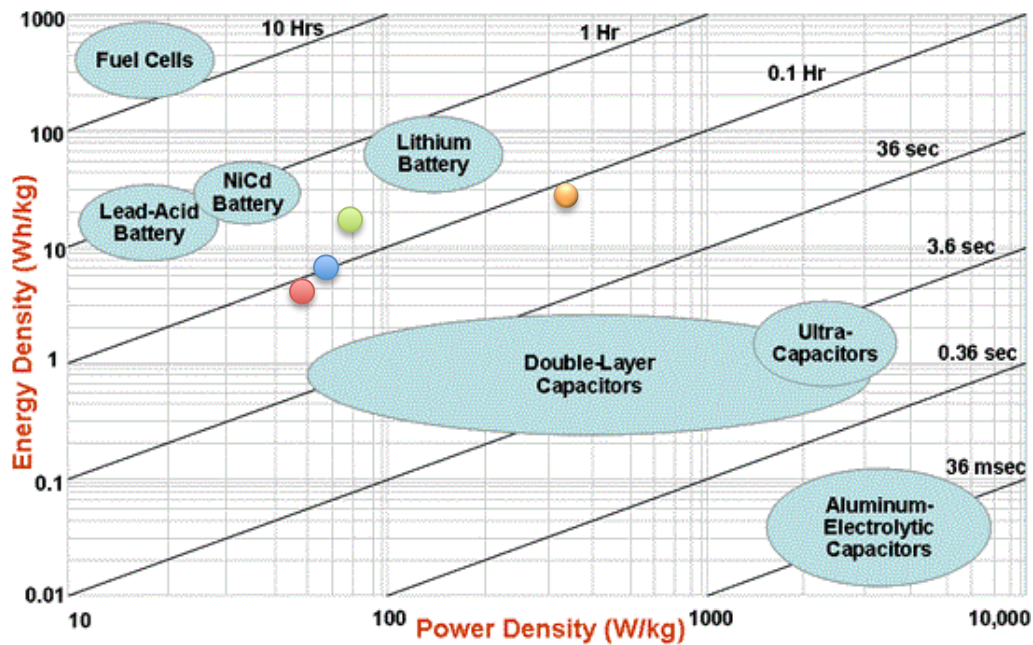


Fig. 46 Ragone plot with obtained results compared to other technologies.

## **8 Suggestions for future work**

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All the carried out experiments and results obtained can help in the future to:

- develop and improve a quality check of electrodes,
- understand the behaviour of the material activation,
- assemble and test under load of a prototype with multiple electrodes connected in series,
- assemble and test under load of a prototype with multiple electrodes connected in parallel,

## References

- [1] <https://www.iea.org/> [accessed on December 2015]
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