

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

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Extended abstract

## **1 Introduction**

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

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.

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 the invention of a capacitor with the highest capacitance known at that time. This capacitor was called supercapacitor. Nowadays supercapacitors are characterized 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. However, the specific area of these carbon-based materials is limited and thus, the capacitance and the charge storage ability is also limited. 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 a 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.

## **1.1 Charge2Change**

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.

## 2 Methodology

### 2.1 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 new electrodes test with different current applied,
- c) NiCo-NiCo and NiCo-C used electrodes test with different current applied,
- d) Capacitance fade of used and new NiCo-NiCo electrodes and NiCo-C electrodes.

All the performed experiments were based on charge/discharge cycling, using different combinations of electrodes and parameters applied. Charge/discharge cycles demonstrate the ability of the system to store and deliver energy, or power, with respect to time, depending on the applied current.

### 2.2 Electrode quality test

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

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;

### 2.3 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 (both area and mass of electrodes were constant), 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.

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. 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.

### 2.4 Capacitance fade test

The capacitance fade 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,

### 2.5 Calculations

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

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

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

where:

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

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

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

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

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

where:

$I$  is discharge current, A

$t$  is the discharge time, sec,

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

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

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

where:

$\Delta V$  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 Results

Charge/discharge curves from the Test1 are shown on Fig.1, Fig.2 and Fig.3. One can notice that the NiCo-NiCo cell shows longer charge/discharge times compared to NiCo-C for all the currents applied. The charge time is almost two times higher when 10mA current was applied and decreases with increasing applied current, reaching a value 20% higher for 40mA.

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.4. 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 to NiCo-C in the lowest potential window 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).

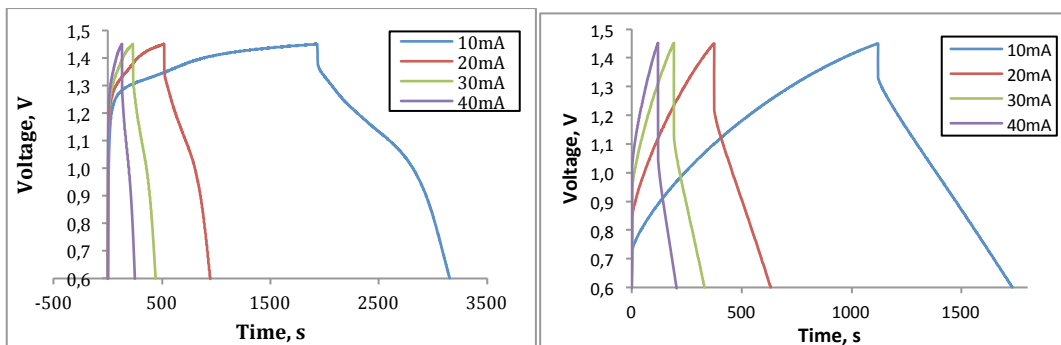


Fig. 1 Charge/discharge curves for NiCo-NiCo Test1 Fig. 2 Charge/discharge curves for NiCo-C Test1

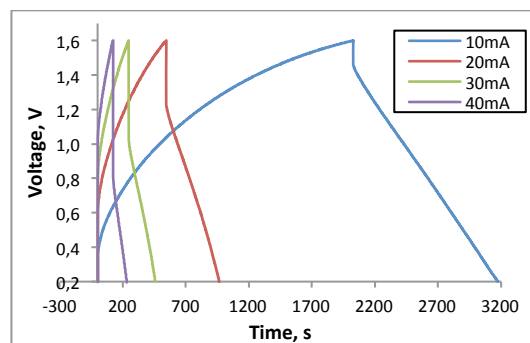


Fig. 3 Charge/discharge curves for NiCo-C in higher potential window.

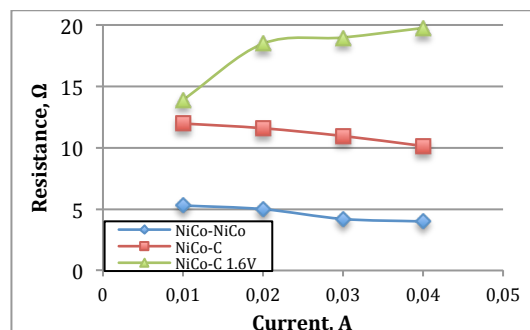


Fig. 4 Evolution of resistance with respect to applied current Test1.

Charge/discharge curves obtained in the second test (Test2) are shown in Fig.5, Fig.6 and Fig.7. 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.8 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).

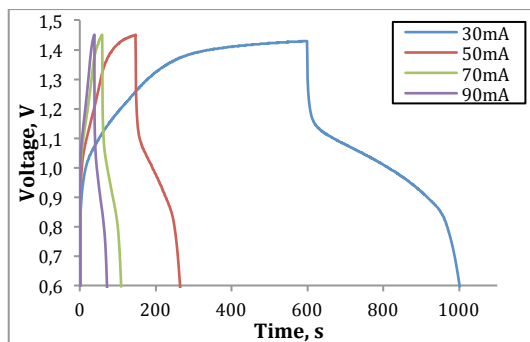


Fig. 5 Charge/discharge curves for NiCo-NiCo Test2.

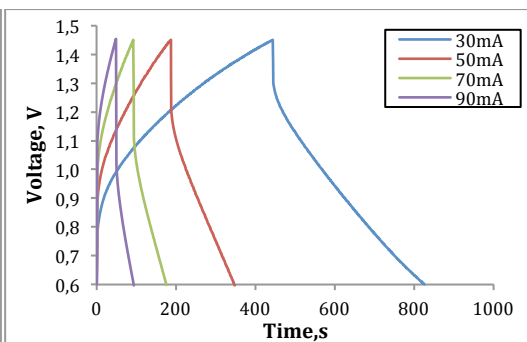


Fig. 6 Charge/discharge curves for NiCo-C Test2.

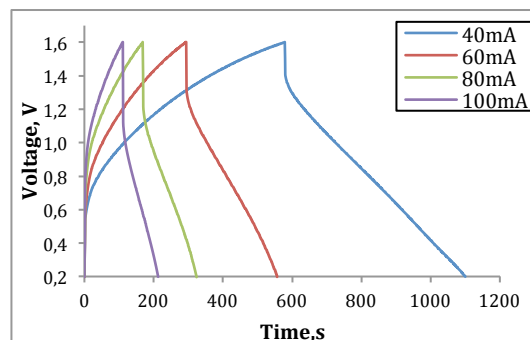


Fig. 7 Charge/discharge curves for NiCo-C in higher potential window Test2.

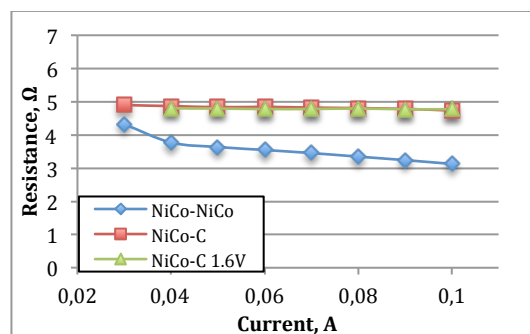


Fig. 8 Evolution of resistance with respect to applied current Test2.

Tab.1, Tab.2 and Tab.3 show results of maximum specific energy and power for Test1 and Test2. One can notice that results obtained in Test2 are much better comparing to Test1. This was a

result of new electrodes usage and reduction of the distance between electrodes. Behaviour of NiCo-NiCo electrodes with respect to applied current is similar in both tests. With increasing current specific power increases and specific energy decreases. Highest values of specific power and energy in Test2 were around 40 W/kg and 5 Wh/kg. Different behaviour was noticed for NiCo-C electrodes in Test1. For NiCo-C electrodes specific power was increasing with increasing current applied and specific energy was decreasing. For NiCo-C in higher potential window with increasing current both specific power and energy were decreasing. As it was said before this was a result of very high ohmic drop. In second test (Test2) for both NiCo-C setups the behaviour was similar. With increasing current applied specific power values stayed almost constant reaching maximum of around 47 W/kg and 57 W/kg. Specific energy values were decreasing with increasing current applied for both setups. Maximum specific energy obtained for NiCo-C and NiCo-C in higher potential window were 8 Wh/kg and 11 Wh/kg. Fig.9 and Fig.10 gather all results of maximum specific energy and power from Test1 and Test2 in form of Ragone plot.

Tab. 1 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       | 23,61                | 4,98                   | -                    | -                      |
| 0,02       | 25,03                | 3,48                   | -                    | -                      |
| 0,03       | 29,80                | 2,54                   | 28,88                | 4,92                   |
| 0,04       | 31,29                | 1,93                   | 33,15                | 3,91                   |
| 0,05       | -                    | -                      | 34,38                | 2,39                   |
| 0,06       | -                    | -                      | 35,25                | 1,69                   |
| 0,07       | -                    | -                      | 36,20                | 1,40                   |
| 0,08       | -                    | -                      | 37,36                | 1,28                   |
| 0,09       | -                    | -                      | 38,57                | 1,18                   |
| 0,1        | -                    | -                      | 39,98                | 1,19                   |

Tab. 2 Results for 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       | 19,55                | 4,69                   | -                    | -                      |
| 0,02       | 20,23                | 3,94                   | -                    | -                      |
| 0,03       | 21,40                | 3,20                   | 46,28                | 8,47                   |
| 0,04       | 23,12                | 2,58                   | 46,52                | 6,85                   |
| 0,05       | -                    | -                      | 46,86                | 5,93                   |
| 0,06       | -                    | -                      | 46,76                | 5,02                   |
| 0,07       | -                    | -                      | 46,97                | 4,25                   |
| 0,08       | -                    | -                      | 47,12                | 3,56                   |
| 0,09       | -                    | -                      | 47,36                | 2,53                   |



|     |   |   |       |      |
|-----|---|---|-------|------|
| 0,1 | - | - | 47,84 | 2,37 |
|-----|---|---|-------|------|

Tab. 3 results for maximum specific energy and power for NiCo-C in higher potential window.

| 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       | 20,55                | 6,51                   | -                    | -                      |
| 0,02       | 15,44                | 4,88                   | -                    | -                      |
| 0,03       | 15,04                | 3,59                   | -                    | -                      |
| 0,04       | 14,45                | 2,45                   | 57,53                | 11,40                  |
| 0,05       | -                    | -                      | 57,53                | 9,86                   |
| 0,06       | -                    | -                      | 57,73                | 8,61                   |
| 0,07       | -                    | -                      | 57,70                | 7,59                   |
| 0,08       | -                    | -                      | 57,53                | 6,75                   |
| 0,09       | -                    | -                      | 57,79                | 6,11                   |
| 0,1        | -                    | -                      | 57,77                | 5,53                   |

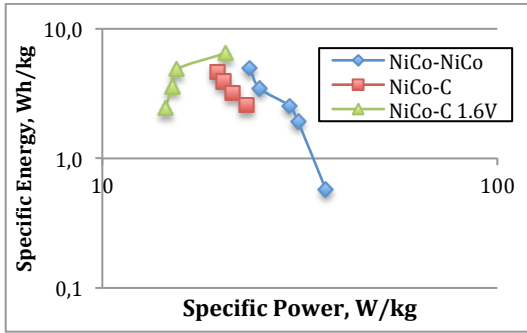


Fig. 9 Ragone plot Test1.

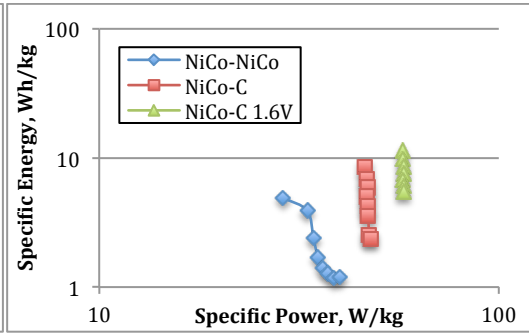
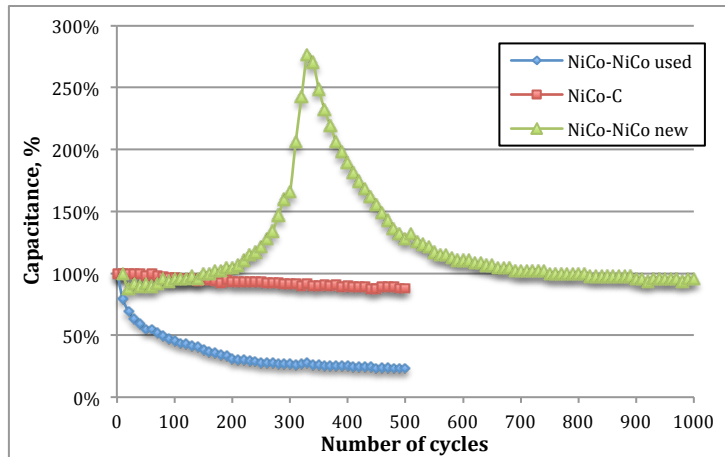


Fig. 10 Ragone plot Test2.

Fig.11 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.12. 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 [4] and has also been observed in various works ongoing.

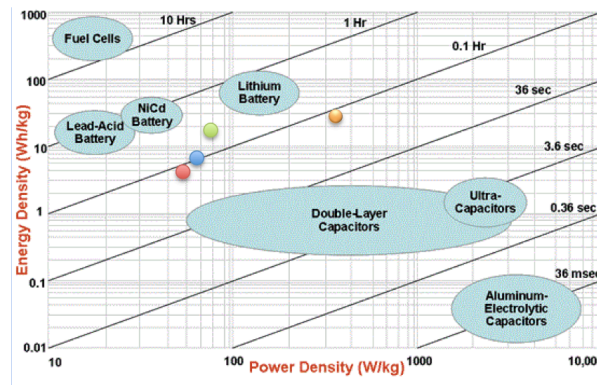


**Fig. 11 Capacitance fade test results.**

Additionally Fig.12 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. 12 Ragone plot with obtained results compared to other technologies.**

## 4 Summary

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 s 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.

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