K-BUS Project: Scientific Aspects

This document intends to provide an overview of the scientific technological concepts behind the K-BUS Project. This project proposes a system of public mobility alternative to those using fossil fuels and is protected by a patent - created by and property of Sequoia Automation - recently granted by the main competent authorities in the world [1], [2], [3] (United States Patent and Trademark Office, European Patent Organization and the Canadian Intellectual Property Office).

This solution, considered technically and economically credible and having a low environmental impact, is based on energy storage devices with a very long service life (potentially superior to that of the vehicles employed) and on their particularly rapid recharge ability (accomplished in a matter of seconds). This paper will therefore try to provide a logical path to the technical characteristics of these two components, which are the heart of the system.

After a brief and general contextualization, the paper will move on to address the various technological aspects related to the project. It will subsequently present an overview on the accumulation of energy, illustrating the products available on the market today, with their advantages and disadvantages, thus defining what technology is more functional towards the implementation of the suggested project. It will focus on the present features and future potential of this energy storage system, both in technical and economic terms. It will also briefly address the topic of electric mobility, thus presenting the second key component of the K-BUS, which is the system of rapid charging of the batteries. Lastly, the most innovative and technological aspects of this system will be analyzed, not neglecting to mention the economic assessments that, as of now, demonstrate the competitiveness of the project.

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A modern society cannot ignore the availability of low cost energy sources, and today it is clear that the environmental and social impacts of the use of fossil fuels is becoming increasingly unsustainable. The development of new and efficient technologies for the production of energy from renewable sources is therefore an urgent necessity. In this context, a recent report from the U.S. Department of Energy [4] stated the need for new energy storage technologies, which are essential to overcome the discontinuity of two of the most important of these sources - the sun and the wind - to limit the fluctuations on the power grid (always present, regardless of the energy source employed) and to provide energy for future portable devices, as well as those new-generation electric vehicles inevitably destined to replace the inefficient and polluting thermal motor vehicles; all uses the requirements of which are not met by the storage devices available on the market today.

In today's technological horizon, energy storage devices functional for these purposes can be grouped into three families: batteries, electrochemical capacitors and hybrids between the first two (Figure 1). The class of electrochemical capacitors, for the type of use examined here, is limited to the so-called supercapacitors or ultracapacitors. Concerning batteries, only rechargeable batteries (secondary batteries) can be used, since all the applications under consideration include continuous charge and discharge cycles. Lastly, hybrid devices, also known as supercabatteries, which are the combination of a supercapacitor and a battery, and are easily classifiable in the descriptions that will be given for the types of accumulators individually taken into consideration.

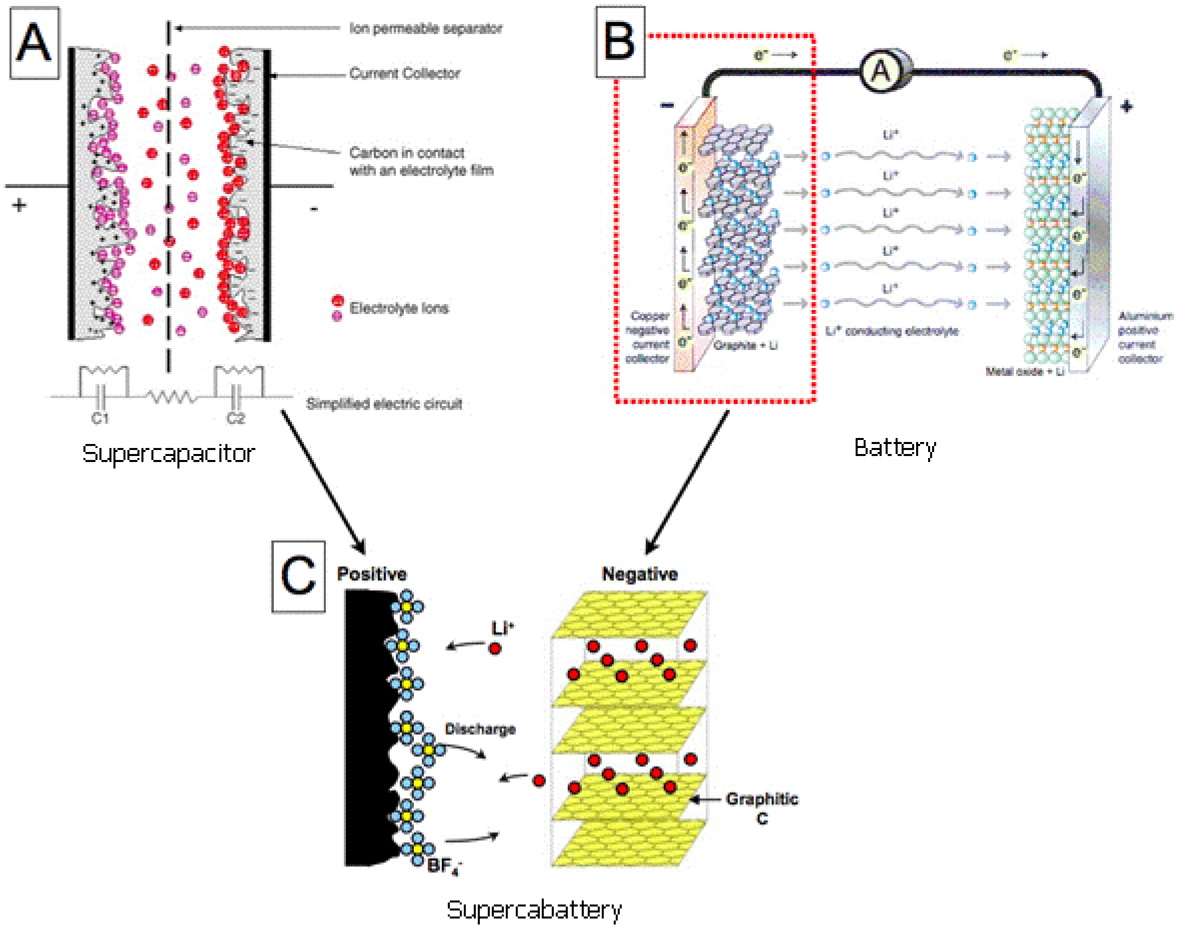


Figure 1: Scheme of the described energy storage devices: A) supercapacitor, B) battery and C) hybrid between the two (supercabattery) [5], [6].

All described types of accumulators have a substantially similar structure, consisting of two electrodes immersed in an electrolyte solution and separated by an insulating membrane, the purpose of which is to avoid electrical contact between the plates while allowing an ionic-type conduction (Figure 1).

As to the physical principles on which the accumulation of energy is based, the batteries are characterized by a series of oxidation-reduction Faradic reactions, which determine the generation of electric charges [7]. Said charges produce the actually usable electric power by passing from one plate to the other of the battery thanks to the different electric potential that is generated, which remains relatively constant until it almost runs out of reagents. The main advantage of this type of reaction is in the high energy density that can be electrochemically stored. But it is the same chemical nature which also causes the main disadvantages because, during the repeated charge and discharge phases, the active material of the electrodes is degraded, leading to a progressive loss of performance which makes the device unusable in a rather short time, and because the oxide-Faradic reductions involve relatively slow reaction times, which also limit the power density delivered by the device.

Supercapacitors, instead, store energy by accumulating an electrostatic charge in the electrodes, as in traditional capacitors. In their family, there are two main types: the **EDLC** (*Electric Double-Layer Capacitors*) and **pseudo-capacitors**.

The **EDLC** capacitors are the most common, and already on the market since the 70s. Their capacity derives from the density of the electrostatic charge accumulated in the interface surface of the electrodes, in function of the applied electrical potential. [7] Thus, in the charging and discharging process, they do not undergo chemical reactions or changes in the volume, and the cycle is thus perfectly reversible, resulting in high efficiency and a high speed response. The most significant advantages of supercapacitors arise from these characteristics [8]: an extremely long service life and high power density, which not only ensures high power output during their active cycle, but also an extremely rapid charging time (a few seconds), combined with a very elevated efficiency.

As for their structure, their electrodes are currently made up of a carbonaceous material with a very porous honeycomb structure [9] which provides a good electrical conductivity, a large specific surface area and thus large space for the accumulation of the electrostatic charges. This active material is generally pressed - and stabilized by means of a binder - on a sheet of aluminum, which acts simultaneously as an electrical collector and as a mechanical support to the carbon powder (Figure 2).

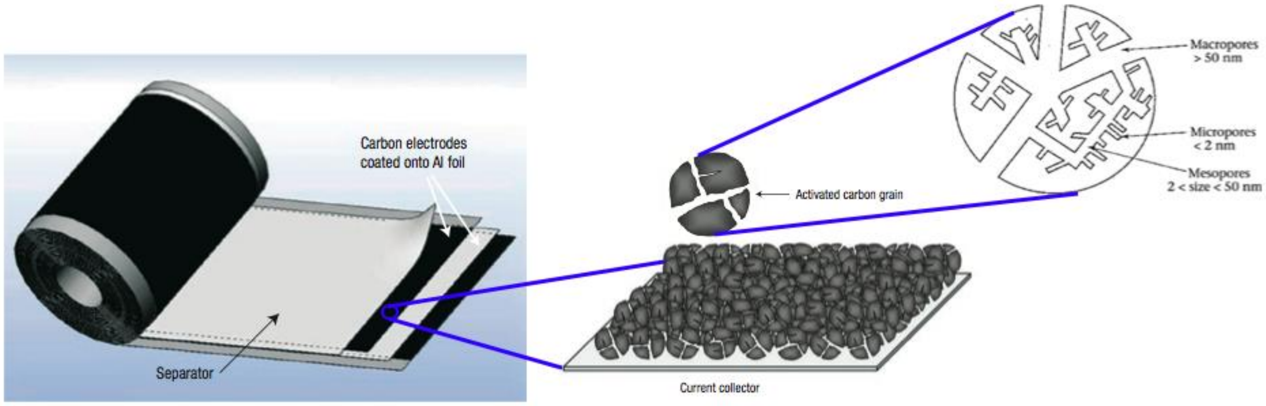


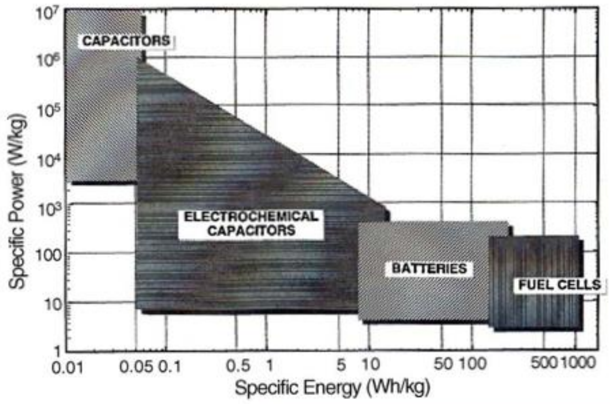
Figure 2: Building structure of a typical EDLC supercapacitor [9], [10].

As for **pseudo-capacitors** [8], although they possess interesting features that place them in-between batteries and supercapacitors, they are still far from being commonly present on the market, due to a few technological issues that need to be solved - similar to the technical inconveniences shown by batteries - which mainly arise from the storage system through pseudo-Faradic reactions. Furthermore, there are economic problems that hinder their utilization, since both the raw materials and the synthesis processes employed are still too expensive to be able to compete in the supercapacitors' market.

When generally comparing the characteristics of supercapacitors and commercial batteries [5], [11], it is evident how the former possess a power density of almost two orders of magnitude higher than that of the latter, resulting in greater efficiency and considerably lower recharge times - in addition to the possibility of obtaining an efficient energy harvesting - and a considerably higher useful life: a few million cycles, against a few thousand at best (Figure 3).

On the other hand batteries, as already observed, have an energy density of at least ten times and an initial cost for accumulated Wh of about one-tenth (though the cost per amount of

stored energy, when calculated on the respective life cycles of the devices, still plays in favor of the long-living supercapacitors - for further details, see the appendix).
Other aspects, not directly related to the accumulation of energy, but equally important, are ***reliability*** and ***maintenance***. Both elements operate in favor of the supercapacitors, which require virtually no maintenance, are less prone to risks from overheating and, unlike batteries, are indifferent to "deep discharge" (can be discharged completely without any damage).



Category	Batteries	Ultracapacitors
Operating temperature range	-20 to 40°C	-40 to 65°C
Maintenance period	Annual	None
Replacement period	2 to 4 years	>10 years
Cycling capability	10 to 50 k	>1 million

Characteristic	State of the Art Lithium Ion Battery	Electrochemical Capacitor
*Charge time	~3-5 minutes	~1 second
*Discharge Time	~3-5 minutes	~1 second
Cycle life	<5,000 @ 1C rate	>500,000
Specific Energy (Wh/kg)	70-100	5
Specific power (kW/kg)	**0.5 -1	5-10
Cycle efficiency (%)	<50% to >90%	<75 to >95%
Cost/Wh	$1-2/Wh	$10-20/Wh
Cost/kW	$75-150/kW	$25-50/kW

Figure 3: Ragone Graph and comparative tables of the general characteristics of supercapacitors and batteries [5], [10], [12].
*** Time required to charge/discharge the actually usable total energy accumulated in the device,**
**** Power of a battery usable for short periods in partial discharge with a 90% efficiency.**

Moreover, thanks to the type of electrolyte used and the physical process of energy accumulation, the supercapacitors are capable of operating at a wider temperature range (-40/+65 °C, Figure 3) and are much more efficient, especially at low temperatures [13]. The electrostatic accumulation, when compared to the charge via Faradic reactions, typical of batteries, in fact makes them less sensitive to operating conditions, thus granting them a greater degree of safety.

It is evident, however, how these two families of devices, in view of their existing characteristics, still have complementary properties. Which explains the reasons why one strives to integrate them in many applications. The development of **AEDLC** (*Asymmetric Electrical Double-Layer Capacitor*), is based on the same reasoning. These are also known as supercabatteries or hybrid supercapacitors, in which one framework is composed by a supercapacitor electrode and the other by a pre-doped electrode with lithium-ions, thus similar to a battery electrode [6], [10]. The intention, pursued by technicians and producers of these devices, which are already on the market, is to mediate the properties of the two types of accumulators; however they have not, as of yet, actually managed to solve the inherent limitations, while complicating the constructive architecture of the devices themselves.

Despite this attempt to bridge the gap between the two technologies is arousing interest among a few new companies in the sector, many experts agree that the most profitable road to follow is that of the pure supercapacitor. An analysis, this, dictated by several parallel factors in virtue of which, in recent years, the growth trend of the top of the range performance of supercapacitors has been higher than that of the similar batteries. If this trend persists, it could even predict that, within 15-20 years, supercapacitors will be able to compete with batteries also with regards to the density of the stored energy.

Although the possible theoretical improvements still give ample room for performance growth to both technologies, if on looks at the real trend obtained from marketed products, at the relative "youth" of the research on supercapacitors, and at the same theoretical potential limits, a marked improvement in features seems more likely to occur in supercapacitors, rather than in batteries. Based, in fact, on graphene as the active material (Figure 4), supercapacitors could theoretically achieve in the medium to long term an energy density six times higher than that of lithium-ion batteries, while maintaining a clear superiority in number of life cycles, reliability and power density [14].

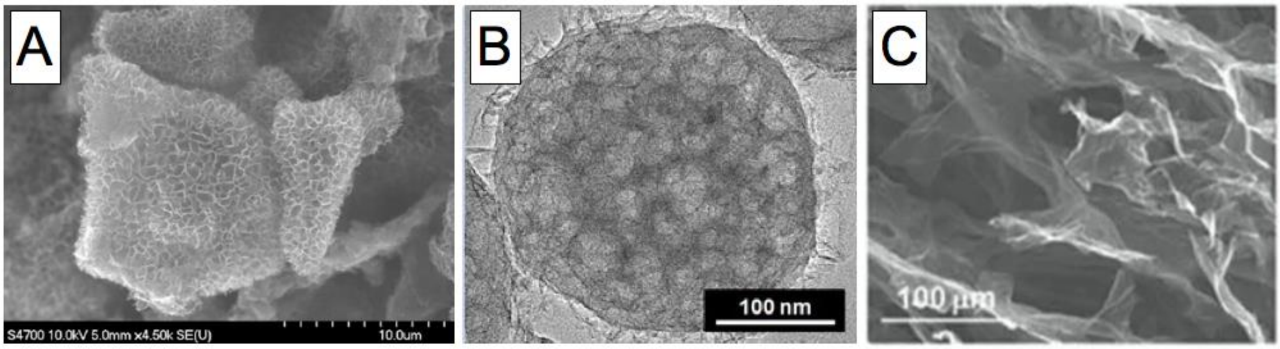


Figure 4 : Examples of nanostructured graphene for applications in supercapacitors : A) 3D honeycomb structure [15], B) CVD nanoballs [16], C) air gel sponge [17].

In the short term, a joint study of Varco - a company participating in the K-BUS Project - and the University of Trento, has shown that, even using materials already on the market, there is still some room for improvement. In particular, by exploiting active materials already on the market, one can evaluate to significantly reduce the weight of the aluminum collectors (which are an inert mass in the supercapacitor) and reduce the internal complexity of the device. Then, by replacing the membrane separation of the electrodes (usually, a sheet of cellulose) with a permeable coating, it might further lower the electric internal resistances and facilitate the manufacturing process. Another interesting area of research is on electrolytes. The guiding ideas, to replace the solvents widely used today, are two: **a)** to expand the usable voltage window, in order to increase the stored energy, **b)** to use liquids which are harmless both to human health and to the environment and are not flammable, which offer various possible promising solutions [18], [19]. Not to be overlooked, finally, is the research on packaging because, given the current weight of supercapacitors, new materials and new technologies could reduce it by an appreciable extent, without compromising their high safety standards for the end user.

The margins to create new opportunities are therefore very wide, even with regards to consolidated concepts and materials. This has been further confirmed by a recent interview to Earl Wiggins, VP of Operations at Maxwell Technologies, leading industry in the field of supercapacitors [20], which states that even Maxwell Technologies is operating in this sense in the short period, in order to increase the performance of its supercapacitors, while reducing production costs.

It is therefore clear why supercapacitors have been the first choice for the K-BUS and how they may be at the base of the zero-emission mobility ideas studied by Sequoia Automation. In fact, thanks to the high number of cycles of charge and discharge, of several orders of magnitude higher than that of batteries, they can both largely amortize the higher costs of the initial investment, and, in the long run, result in being much cheaper than batteries, which in the course of the life of a public electric vehicle require to be replaced many times (cf. the economic data presented below).

The supercapacitor is also a good choice for the future; both because the potential for performance growth is high, and because the market is reacting well to this type of new technology and is ready to invest heavily in research and finance plants with increasing production volumes. In fact, despite the commercial value of the sector is still marginal when compared to that of secondary batteries, the market for supercapacitors is growing by 30% per year (trend unchanged despite the crisis) and it seems the number of producers is expected to triple over the next ten years [21]. It is also interesting to note that the market, in the same time frame, will reach an eleven billion dollars revenue and that, maintaining the current employment, about a quarter of the production will be absorbed by Europe [13].

Unfortunately, however, to further emphasize the lack of attention of the old continent for a number of strategic sectors, we can note that less than 7% of producers are European and we are not seeing any signs of improvement. This means a net loss of capital, as well as opportunities, in an important technological sector such as the energetic field.

In general, however, the number of applications in which the supercapacitors are employed is already considerable. The normal trend is to support or even replace them with secondary batteries, but the scenery is constantly changing, and it can happen that the supercapacitors themselves often suggest new applications and products.

As aforementioned, in those cases in which the weight of the stored energy is not a problem, the supercapacitor offers an excellent performance when working at low temperatures, when it is subject to many cycles of charge and discharge or when upload and/or download speeds are crucial. Examples of applications in which supercapacitors are already widely used are: emergency opening systems in buses, UPS systems, KERS and Stop-Start technology in cars (especially hybrids) and the partial replacement of batteries in trucks (to give them more starting torque, especially in cold climates) [13], [20], [22]. They are also used in energy intermittence protection systems in wind or solar power generation plants, in the energy recovery apparatus of overhead cranes and hoists and, recently, also in mobile devices (powerful flashes and wi-fi), that require a higher power than that supplied by batteries.

The complete list would be too long and too difficult to up keep because the market for supercapacitors is so dynamic that it registers new applications with great frequency. Currently, however, the automotive sector appears to be the most suitable for their employment. As correctly speculated by Sequoia Automation, in fact, many companies are focusing on vehicles equipped with supercapacitors, of which the wide spectrum of applications varies from limited uses, such as the aforementioned KERS systems and Start-Stop technology, to a wide range of uses, such as battery support systems to provide extra power torque or more uphill power to preserve the batteries in electric or hybrid vehicles.

Figure 5: Subway CSR Zhuzhou Electric Locomotive with supercapacitors to power the electric motors.

It is possible to quote several examples. The greatest, in economic terms, is a $ 318 million tender, won by Meidensha/Sojitz, to provide 2 MW of supercapacitors to the South Island Metro Line of Hong Kong. This installation should reduce by 10% the consumption along the 7.1 km, five-station route. [21] In Paris, BatScap will provide tens of thousands of supercapacitors to install on Bluecars (electric cars) as an aid to traditional batteries. The first fuel cell cars, and other vehicles using super-capacitors to power and maintain traction, will be in production as early as 2015. In 2014, China will begin the initial testing of trams and electric trains, in which a hybrid system of traction, equipped with supercapacitors, will allow the employment of the vehicle even in an emergency situation and to furthermore eliminate, for aesthetic reasons, the aerial power lines in sites of particular value or at intersections. Bombardier, a well-known manufacturer of buses with low environmental impact, seems to be considering the use of supercapacitors for energy recovery during braking and Riversimple intends to use them in assisting the fuel cells that power its vehicles [22].

Even more radical solutions, in which energy is accumulated only by supercapacitors, are for now used only on city buses. It should be emphasized how the transition from hybrid systems without supercapacitors to other mixed battery/supercapacitors systems, and then to systems with only supercapacitors, has taken place at an amazing speed. Yet another proof of the unexpected technological opportunities that this type of batteries can offer. MAN and CSR Zhuzhou Electric Locomotive [23] supply examples of "fully electric" vehicles using only supercapacitors. The latter is testing the prototype of a light metro - therefore on rails - in which a "plug", located under the floor of the train, can connect supercapacitors, fitted on the roof, to a "grip" on the ground (Figure 5). The refills take place during the stops, require only 30 seconds each, and provide 2 km of autonomy, thanks to the recovery of braking energy. The producer expects its distribution in 2014, with a potential market of about one hundred small and medium cities in China and, of course the foreign market.

Therefore, although the idea of powering an electric road vehicle just through the use of supercapacitors may seem extreme, the concept still attracts the attention of various manufacturers throughout the world.

The main problem of this type of accumulators - lower energy capacity in equal weight with respect to secondary batteries - has been overcome by Sequoia Automation with a quick-charge system which recharges the supercapacitors in a few seconds during the stops of the vehicle, the mobility of which is only slightly modified, while passenger transport and loading/unloading times remain virtually unchanged.

During the recharging phase, contact between the ground super-capacitors and those on-board the vehicle is assured by a system structured in two parts: **a) under the chassis of the vehicle**, through an electromechanical arm that holds a conductive plate, equipped with a thick cluster of metal pins; **b) on the road surface**, through a "carpet" of metallic hexagons, each one electrically isolated from the others, but each one connected to the electrical and electronic charging system, and made from a material that ensures long-lasting resistance to deterioration, which do not pose limits or constitute danger to the mobility of vehicles or pedestrians. The arm can drop or rise in a few moments and can adapt to any change in the vehicle's balance in order for the plate to optimally descend and settle on the "carpet" and maintain a stable electrical contact during the entire charging phase.

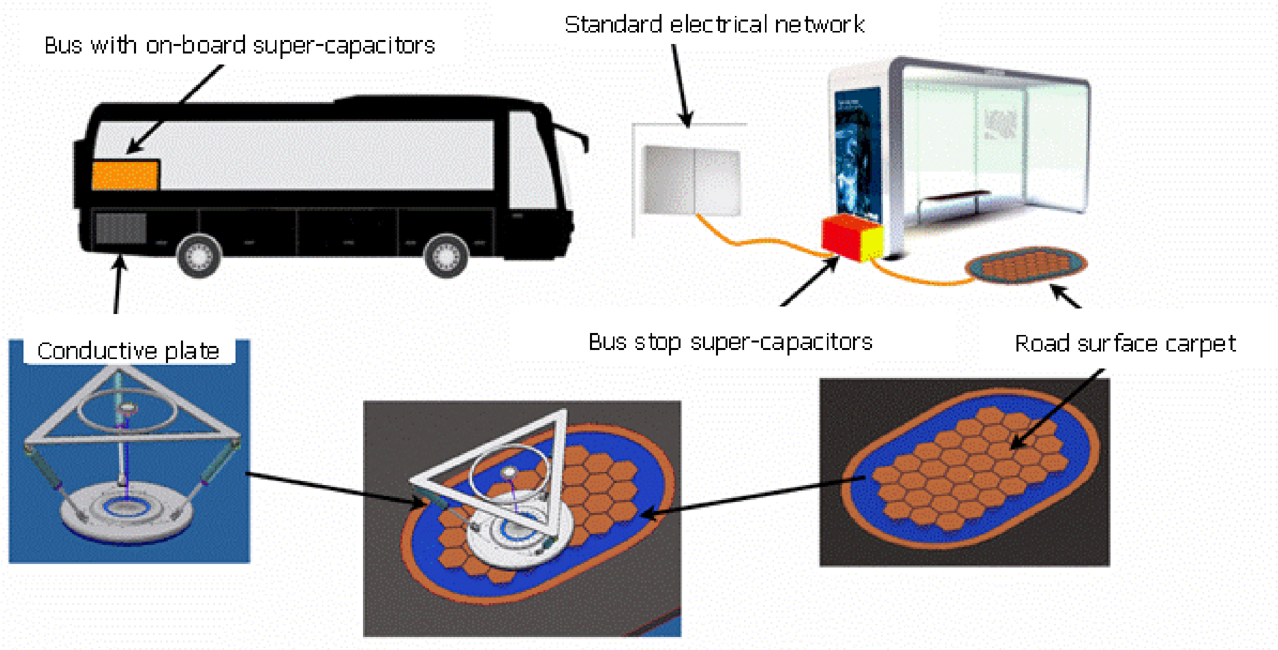


Figure 6: K- BUS Fast-Charging System Operating Diagram

Plate and carpet therefore ensure the electrical connection between the supercapacitors installed on the vehicle and others placed on the ground, allowing to recharge the former in a very short time. The power flow is very high indeed - hence a recharge time similar to that required for normal passenger loading and unloading - but is risk free for people or things thanks to the architecture planned for the coupling of plate and carpet, and to the electronic assistance. The dimensions of the carpet, in addition, facilitate the placement of the charging device, since they allow margins of error of tens of centimeters, which is much greater than those that are required, for example, by inductive charging systems.

One of the key points of the system is the set of supercapacitors to the ground, "energy reservoirs" that can supply, within seconds, quantities of power unthinkable for the normal electrical networks from which they draw energy during the much longer time that elapses between the passage of one bus and the next. This avoids having to lay expensive and complex cabling.

Another key-feature is that, for safety purposes, the charging phase is compliant with the following procedure: **a)** a Wi-Fi signal allows the vehicle's electronic system to perceive the approach to a charging point and starts the descent of the supply arm; **b)** the plate, which is also equipped with a brush to clean the carpet from any possible debris, is pressed against the carpet to ensure an optimal electrical contact; **c)** a few of the pins on the plate are distributed on concentric circumferences: the inner ones are the positive pole, while the outer ones, "protective", are the ground; **d)** contact between each pin and the hexagonal metal of the carpet is verified by an electronic device capable of identifying the socket and bus code number, the exact position of the vehicle with respect to the carpet, the number of pins in touch with every single hexagon and the absence of “bridges” or conductive contact interruptions due to external causes; **e)** only after verifying that there are no obstacles to a safe energy transfer the electronic system supplies power *only* to the hexagons in contact with the positive pole pins, and the charging phase takes place (Figure 7).

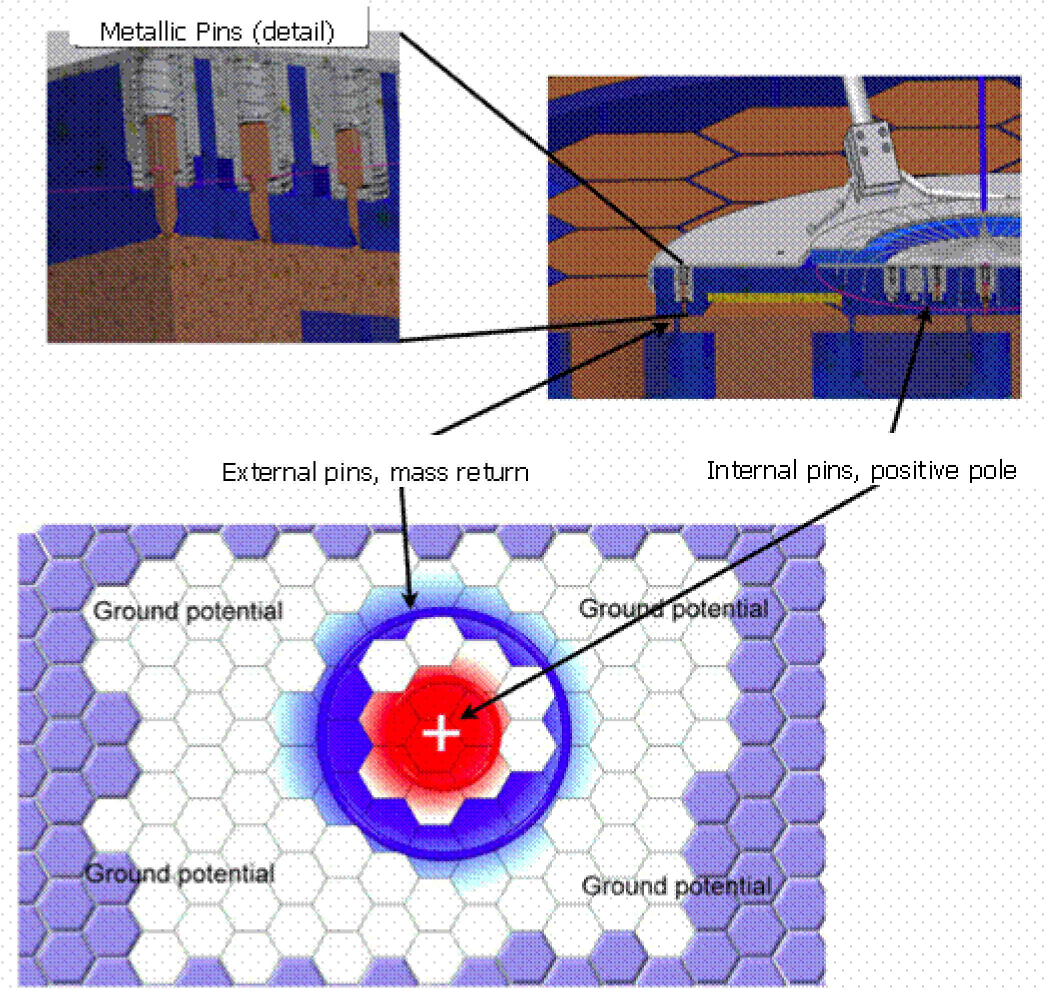


Figure 7: Construction details of the conductive plate in the vehicle and its power supply.

In case an unforeseen event should hinder the recharge of the K-BUS at a certain station, each vehicle is equipped with a limited sized electrochemical battery with a capacity that allows the vehicle to safely cover twice the maximum distance between two stations.

This zero-emissions solution therefore allows to have a limited battery weight on board the vehicle, without limiting the range of action, thus decreasing the operating costs (Figure 8). It furthermore makes the vehicle perfectly functional in urban traffic, without having the restrictions other means have, such as on-rails vehicles, and with the flexibility of use offered by road vehicles.

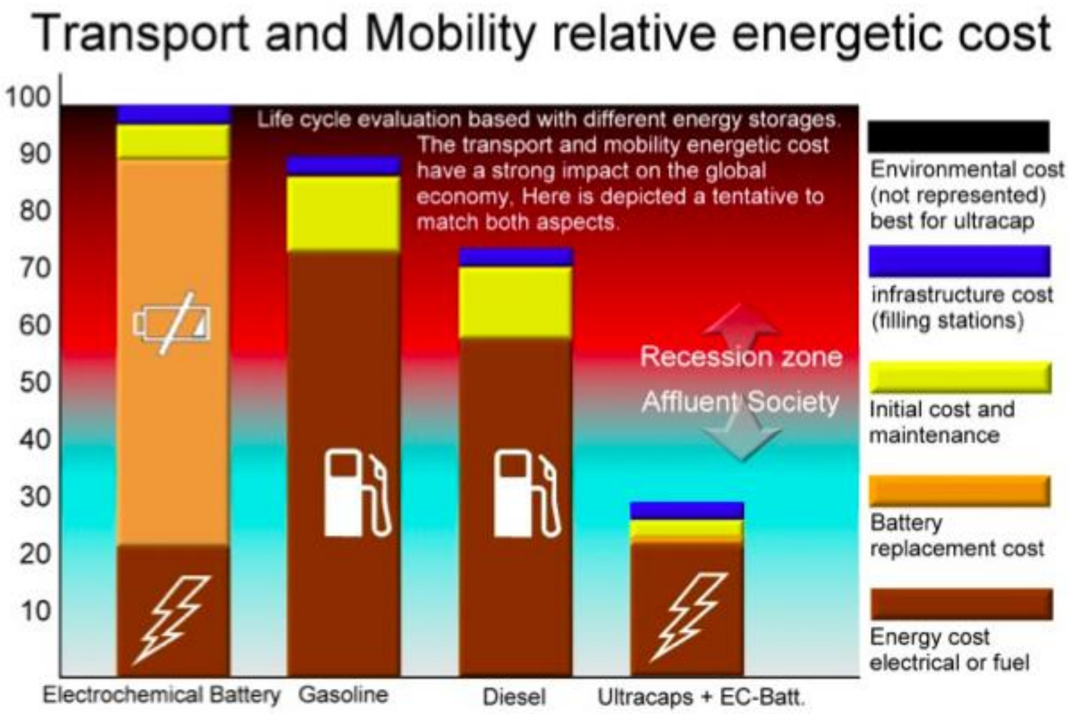


Figure 8: Comparison of operating costs between various alternative power systems for urban buses.

The charging stations would also have limited initial investment and management costs, when compared, for example, to a system of overhead power lines, which also involves a remarkably unpleasing aesthetic impact.

In addition, in order to limit the overall energy use on routes with marked differences in altitude, the K-BUS project determines that the vehicles, while proceeding downhill, recharge their supercapacitors through recovery during braking. The supercapacitors then supply energy to the ground supercapacitors through the same charging system and this energy is then channeled to the uphill stations to provide low-cost supply to the next vehicle.

A practical example of income statement was based on a comparison of data between the GTT Star 1 current urban electric bus line in Turin with those of a hypothetical similar line, equipped with K-BUS vehicles. The current system is served by electric battery-powered buses, which cover a distance of nearly 12 km and that undergo partial recharges at the terminal stations and a total recharge during night.
The resulting data showed that if the current system were replaced with one built according to the innovative Sequoia Automation K-BUS protocol, the initial investment costs would amount to little over half the sum which had been spent at the time the current system was implemented. Moreover, the revenue account at 12 years (including maintenance and material substitution costs) would amount to less than half of what the current system requires, due to the frequent replacement of batteries that it entails.

In a similar way, in the context of urban public transport, an electric K-BUS vehicle, even with an operational autonomy limited to a few kilometers, could replace an internal combustion engine vehicle thanks to the quick charge system patented by Sequoia Automation. This system, in fact, does not in any way limit the operations of the vehicle or be detrimental to the public, but rather would provide a big advantage in terms of environmental pollution and, in the medium term, even in economic terms.

It is obvious to think that its application could be extended to other areas of the same type, i.e. services for which a number of vehicles perform fixed routes and fixed points, such as garbage collection, the collection and delivery of mail, company or airport logistics. Nor can one rule out, in theory, the possibility that multiple services, independent of each other, recharge their electric vehicles' supercapacitor through a single network of appropriately distributed K-BUS type "carpets".

The powering of the K-BUS through the use of photovoltaic modules has also been theorized; these modules, installed on the roofs of adequately exposed bus stop charging platforms, could supply their "tanks". Given the amount of energy that needs to be produced and transferred, and the type of power involved, in most cases this type of recharge system would be supplementary to the electrical supply provided by the electric network. It would however be the ideal solution for extra-urban stations with a limited daily vehicle passage, especially if there were no possibility to easily charge the K-BUS vehicles through the normal electrical supply network (Figure 9).

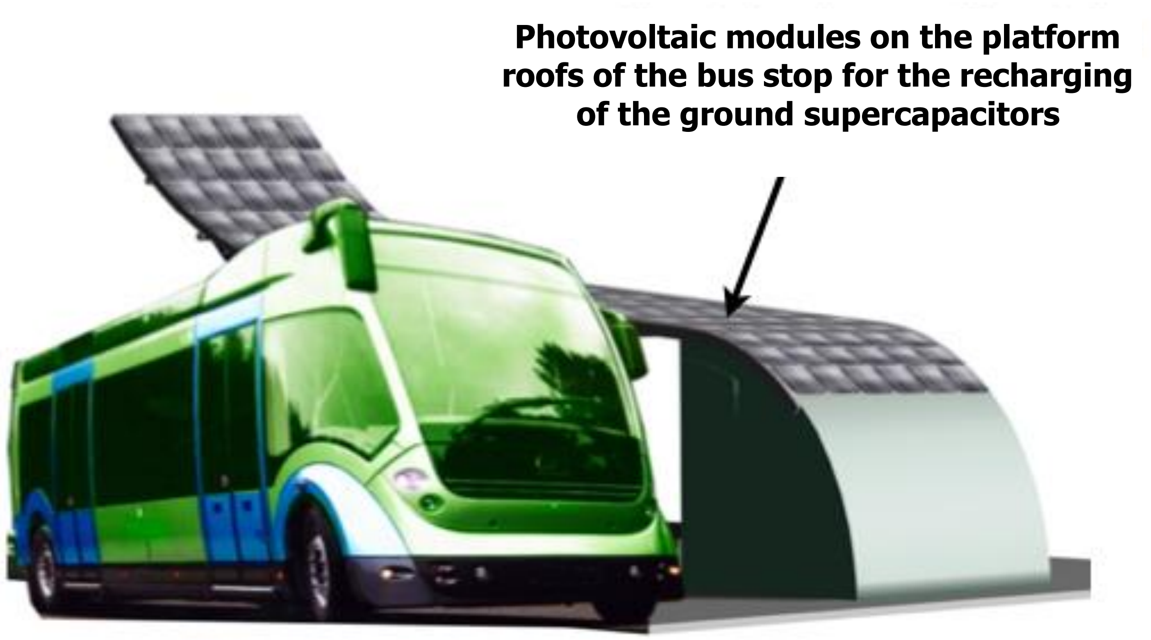


Figure 9 : Bus stop powered by solar panels (photovoltaic system).

The technical and scientific experience gained by Sequoia Automation in the fields examined in this document has allowed us to address and potentially solve one of the most vexing problems related to modern urban roads. The K-BUS is in fact a zero-emissions system, with a competitive cost with respect to those powered directly from fossil fuels (while not considering possible incentives for electric vehicles), with technical solutions that ensure an efficient and versatile transport and that, in addition, while not affecting the existing vehicular traffic, maintains the practicality of the public service. In short, a concrete solution for the mobility of the future.

Appendix:
References on the Physical Processes Typical of Supercapacitors and their Properties

A traditional electrostatic capacitor is composed of two metal plates separated by an electrically insulating material, called dielectric. Applying a voltage on the two plates between the two poles of the capacitor, an accumulation of charges of opposite sign is generated at the interface between metal and dielectric. The amount of accumulated charge, Q, as a function of voltage, V, is defined as the capacity, C, according to the equation:

$$C = \frac{Q}{V} \quad (1)$$

In turn, the energy accumulated between the capacitor plates is:

$$E = \frac{1}{2} * C * V^2 \quad (2)$$

where E is the electrostatic energy accumulated and C and V are the capacity and the voltage applied.
The maximum applicable voltage, beyond which an electric discharge between the plates is generated, depends on the thickness and the so-called dielectric strength of the insulating material.
If one were interested in more easily comparable data, one considers the capacity per unit volume, namely the density of capacity, C_v:

$$C_v = {}^{C}/_{v} \quad (3)$$

where v is the volume of the condenser. Similarly, the energy density, E_v:

$$E_v = {}^{E}/_{v} \quad (4)$$

The same considerations illustrated above apply to an **EDLC** (*Electrical Double-Layer Capacitor*), but, thanks to the properties of some materials, some of its specific characteristics can greatly increase, including and in particular the energy density.

In general it is true that :

$$C = \frac{\varepsilon_0 * \varepsilon_r * A}{d} \quad (5)$$

where ε_0 is the constant dielectric in a vacuum, ε_r is the relative dielectric of the insulating material, A is the area of the plate and d is the distance between the plates (or, in general, the thickness of the dielectric).

In the particular case of the electrochemical capacitor, the attempt is to try to increase the capacity (and therefore the energy contained) by increasing the area and decreasing the thickness of the dielectric. When analyzing in detail the structure of this type of capacitor, it can immediately be observed that a dielectric comparable to the conventional capacitor no longer exists. In fact, an electrolyte, located between the plates allows a flow of electrical charges, unlike in the previous case. Although it may seem a contradiction to replace an electrical insulator with a conductive liquid, this does in fact significantly reduce the thickness of the dielectric. The latter is reduced to only one layer of solvent molecules that separates the charges dissolved in the electrolyte from the plate of the capacitor (Figure 10). This thin layer is called “solvation shell” of the ions of the electrolyte and form a more or less stable shell of solvent molecules that balances the charge of the ions. The average thickness is in the order of angstroms (10-10 m) and, observing the formula (5), it can be understood how, with such a small *d* value, the capacity can arrive to such elevated values .

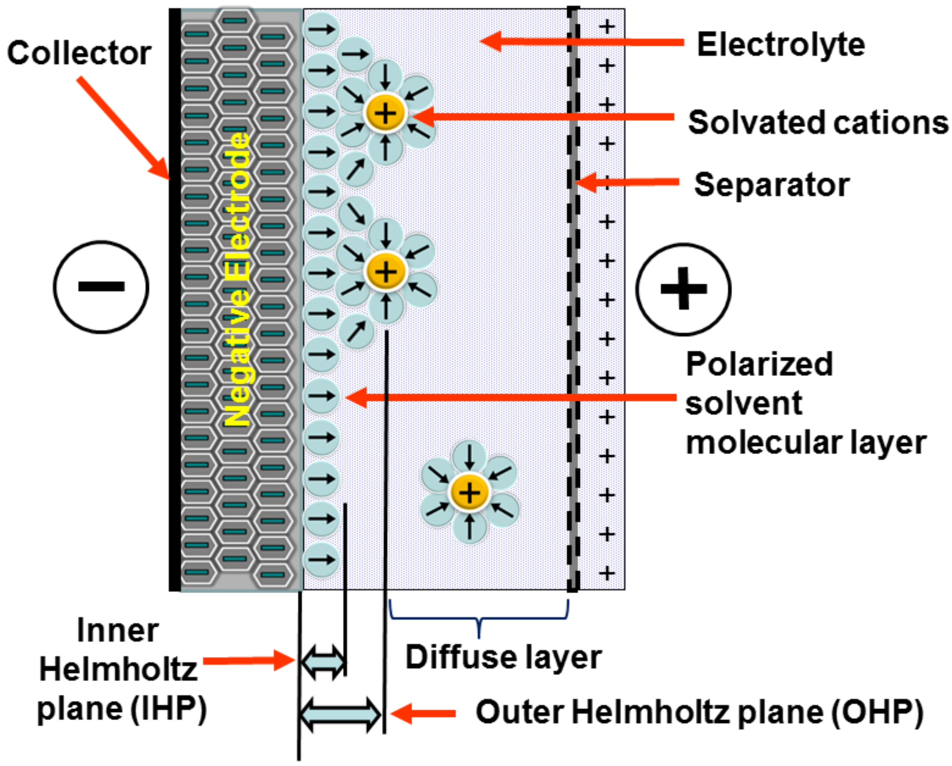


Figure 10: Simplified diagram of a double layer of electrode negative ions and positive ions solvated in the liquid electrolyte, separated from each other through a layer of polarized molecules of solvent (salvation shell).

Since the charge accumulated on each electrode is counterbalanced by the ionic charges dissolved in the electrolyte, one can also deduce how, in fact, a supercapacitor is composed by two capacitors in series, each consisting of one of the electrodes, whose charge is balanced by a sort of “counter-electrode” created by the electrolyte.
This diagram can also explain the reason for which, in order to avoid electrical conduction by contact between the plates, it is necessary to interpose a membrane that, while electrically isolating the two poles, allows the flow of the electrolyte. It moreover clarifies the foundation of the physical processes according to which, by applying an electrical potential to the electrodes, the charges accumulated therein generate a flow of ions from the electrolyte to balance the net charge that has been generated (Figure 11). These processes then are inverted in the discharge phase.

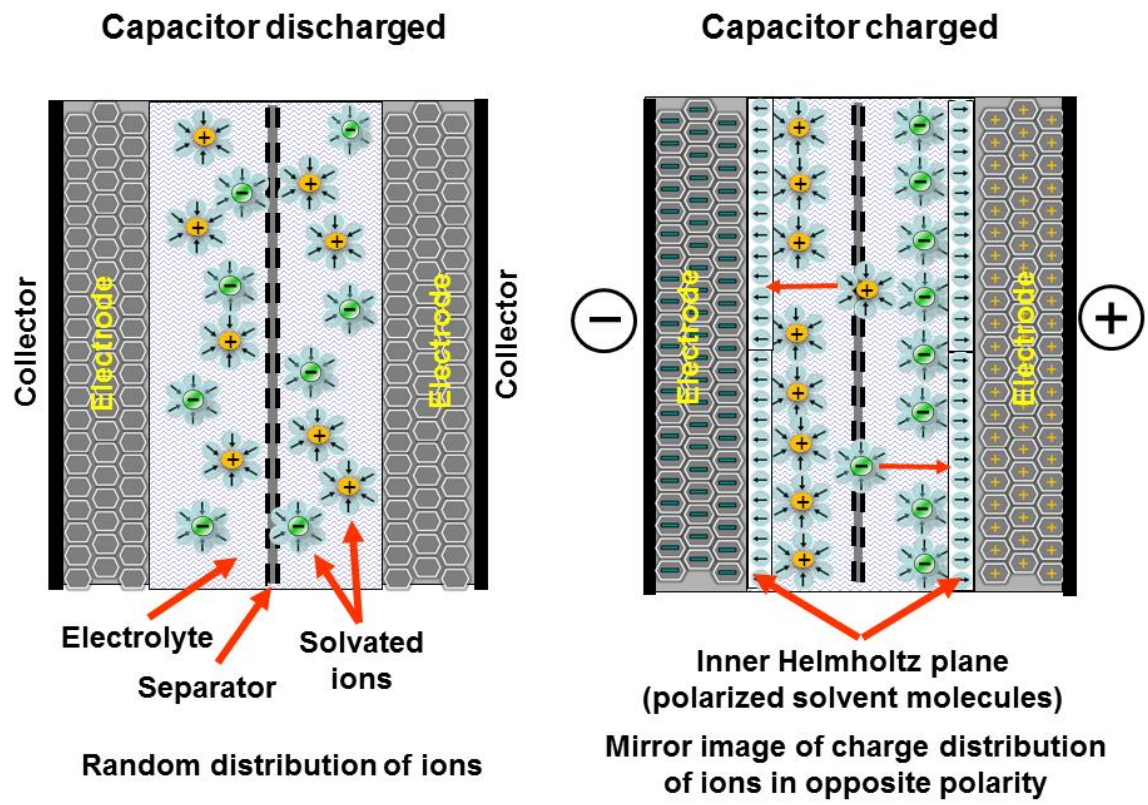


Figure 11: Behavior pattern of charged particles in a supercapacitor "at rest" (left) and during the charging phase (right).

The other parameter that is used to maximize the capacity is the increase of the specific surface area of the electrodes, therefore providing large areas, at equal volume, where the accumulation of electrostatic charge is allowed. Considering the capacity of the electrolyte (solvent and dissolved ions) to penetrate deep into pores of nanometer size, it is possible to build an electrode with a high specific surface area, so that it is able to provide large capacity density. To do this carbonaceous materials are typically used (since they are good conductors) with specific areas of hundreds of square meters per gram of substance (even more than 2000 m2 / g).
Presently, the most used material is activated carbon derived from the controlled combustion of coconut shells, activated by steam or, to obtain even better performance, by chemical baths, such as solutions of potassium hydroxide or phosphoric acid.
To improve the characteristics of supercapacitors, other types of active carbons have recently been developed, of vegetable, mineral or synthetic origin. But, as previously mentioned, the future of supercapacitors seems linked to a series of innovative materials, which have begun to be developed only in the last few years. Among these, carbonaceous-based air gel, porous carbons derived from carbides, carbon nanotubes and, in particular, graphene, which seems to offer higher performance prospects in supercapacitors, than those currently offered by existing batteries.

Obviously, there are also the already mentioned materials with pseudo-capacitive properties, based on metal oxides or conductive polymers. However, given the low presence of these active materials in the supercapacitors business, we prefer to defer to specific texts for more details on the physical processes underlying the pseudo-Faradic reactions that characterize

them [24]. Here it is enough to note that, despite their good theoretical characteristics, they still have too many problems of technological and economic nature to solve before considering their employment in widely used devices.
Regardless of the nature of the active materials, very often they are in powder form and it is therefore necessary to use aluminum foil as a mechanical support in order to have a really usable electrode. It also is used as an electrical collector because the conductivity of carbon is such that it can be used only for electrodes with a thickness inferior to a few tens of microns. Otherwise, the resistance that it causes are too high for practical uses and require, in fact, a metal support for the electrode. Polymer-based binders are employed to stabilize the carbonaceous powders, which help form a compact and stable mass and increase the adhesion of dust to the metal collector. They are generally inert polymers, such as carboxymethylcellulose or polyvinyl fluoride, and ultra-high molecular weight polyethylene, but especially polytetrafluoroethylene. They must, however, be used with caution. If employed in excessive quantity, they will bring about an increase of the electrical resistance (they are insulators) and a consequent decrease of the energy density, representing a dead weight for the accumulation of energy purpose.

Another essential part of the super capacitor, as noted above, is the separator between the plates: a porous membrane which must electrically isolate the electrodes, but also allow the flow of ionic charges in the electrolyte. A stream that must be hindered as little as possible to minimize the electrical resistances of the internal supercapacitor - which occurs with an adequate porosity - but preventing physical contact between opposing plates. The separator must also be chemically inert, so that it won't degrade over time, and it is for this reason that, in the case of organic electrolytes, wide use is made of cellulose fibers or non woven polypropylene fabric, while in the case of aqueous electrolytes fiber glass is often used.

Although the importance of the active materials is often highlighted, another component that plays a crucial role in the supercapacitor is the electrolyte, upon which many of its final characteristics depend. Both the products already on the market and those being tested essentially use three types of electrolyte: an aqueous one, one with an inorganic solvent, and one based on an ionic liquid. The first is a solution of water with a dissolved salt or a very soluble acid, such as potassium hydroxide or sulfuric acid, which offer an excellent ionic conductivity. Its chemical nature gives this type of electrolyte a good wettability of the electrode and a high relative permittivity, which allow to obtain high density capacities. At equal electrode conditions, it is possible to obtain even double values when compared to an electrolyte in an organic solvent. Its other strengths are its high electrical conductivity - up to one order of magnitude higher than that of organic electrolytes - and a low chemical risk, both in flammability and in toxicity. Nevertheless, the most widely used electrolytes, in commercial products, are organic-based for the greater accumulation of energy they allow, when compared to those with an aqueous base. Because even if, as already mentioned, in equal conditions an aqueous electrolyte capacitor gives a higher density of capacity, it can bear only voltages not greater than about 1 V. Beyond this threshold, it begins to degrade for the electrochemical reactions that primer when interfaced with the active material, with the result that part of the supplied energy is used to destroy the device.
Organic electrolytes, on the other hand, are able to withstand voltages up to 2.7-2.8 V before incurring in the same problem. And since the amount of accumulated energy, as is apparent from equation (2) above, is function of the square of the maximum voltage applicable, it is clear why, despite the organic electrolytes under equal conditions confer the capacitor an inferior capacity, they can grant it better performances in terms of energy density.

In the balance between strengths and weaknesses of the various electrolytes one must also consider the lower electrical conductivity of the organic ones that, in fact, involves a reduction of the power density, P_v. It should be noted that if:

$$P_v = \frac{V^2}{4 * R_i * v} \quad (6)$$

with R_i Internal Resistance of the device (also known as **ESR**, *Equivalent Series Resistance*), increasing the resistance of the electrolyte, the overall resistance R_i will also increase. In the comparison between aqueous and organic electrolytes, however, the reduction in power is minimal and acceptable, given the gains in terms of stored energy. Furthermore, the fact of using an organic solvent allows the device to be able to work up to about -40°C, while with a water-based solvent the limit does not go much below 0°C.
Therefore, with regards to the commercial products, the use of organic solvents is preferred and two among these, acetonitrile and propylene carbonate, are considered the best. Both have a voltage limit at 2.8 V, but the former allows the supercapacitor to operate at lower temperatures and, more generally, with lower internal resistances, while the latter has significant advantages in terms of chemical risks: i.e. a lower flammability and lower toxicity to human health and to the environment in case of accidents.

The third category of electrolytes is that of ionic liquids, which are organic-based salts with a melting temperature close to the environmental temperature, or even lower. They do not therefore require solvents and generally pose no fire hazard or risks to human health. Their most important quality, however, is the applicable voltage range, that can also exceed 5 V. This would obviously be a great advantage in terms of cumulative energy, but, due to the types of electrolytes hitherto synthesized, the electrical resistance at room temperature is still such as to prevent their marketing. The maximum voltage applicable, furthermore, depends a lot on moisture (even a few ppms of water can curtail the voltage limit), which would result in significant problems both in the construction and for the production facilities themselves.

The individual components described are generally assembled by following two different geometries. In the first, a series of electrodes and separators are folded and overlapped to form a parallelepiped block (Figure 12A). In the second, long strips of electrodes, divided by the separators, are wrapped to form a cylinder (Figure 12B). This configuration is generally preferred for its simplicity, which reduces production costs.

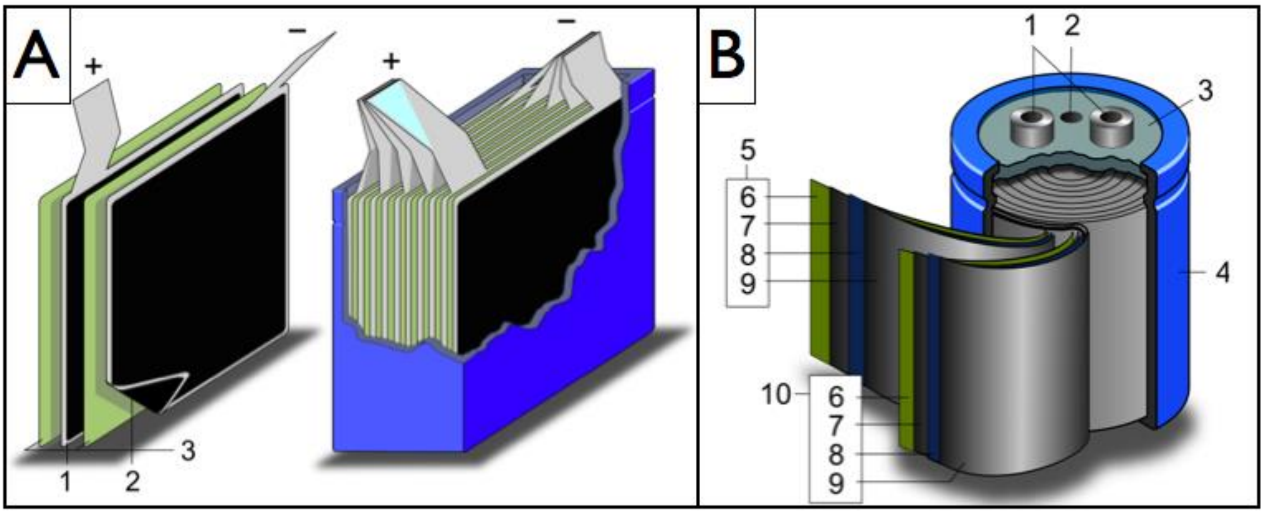


Figure 12: A) Construction scheme of a supercapacitor with overlapped electrodes: 1. Positive electrode, 2. Negative electrode, 3. Separator
B) Construction scheme of a supercapacitor with wrapped electrodes: 1. Poles, 2. Safety vent, 3. Cap, 4. Aluminum housing, 5. Positive pole winding, 6. Separator 7. Active material electrode, 8. Electric collector, 9. Active material electrode, 10. Negative pole winding

Regarding performance, the products on the market today have an energy density range between 6 and 14 Wh/dm^3 in supercapacitors of a few hundred Farads, while they can decrease to 3 or less Wh/dm^3 in small supercapacitors. Compared to the over 300 Wh/dm^3 obtainable from the lithium-ion batteries of the latest generation, this data may appear modest, but in actual fact, the power densities obtainable from these devices can be superior to 15 kW/dm^3, versus the actual limit, even for the best batteries, of less than 1 kW/dm^3. This explains the adoption of supercapacitors when high power is required to be delivered in a relatively short time.
Another point in favor of supercapacitors is their extremely long service life. They can indeed deal with hundreds of thousands of charge/discharge cycles without significantly losing in performance, and at a wide range of temperatures. Batteries, instead, do not exceed a few thousand cycles, at best, and only avoiding deep discharges. Therefore, if the application requires a very long service life and/or a very high number of cycles, the supercapacitors may be a more convenient choice than batteries since, as already mentioned, the cost for the amount of stored energy, calculated on the respective cycles of life, still plays in their favor. Considering a utilization of many years, in fact, even if the initial cost per accumulated Wh is in favor of batteries (approximately 1$/Wh versus 10$/Wh), in the long run supercapacitors tend to become economically more profitable because, while batteries require periodic maintenance and several substitutions, supercapacitors do not. As the English say, "*fit and forget*" devices.

Furthermore, on single cycles, supercapacitors offer other advantages. First of all, charging and discharging times are much shorter: a few seconds against a few minutes at best. The process itself is, generally, also more efficient in supercapacitors, which are able to maintain a high yield (over 95 %) on both reduced charge/discharge times and on a wide range of temperatures. This has opened the door to new technologies, as for instance the quick charge system devised by Sequoia Automation, but also to other very interesting systems, which are based on the unique properties of supercapacitors. Among these, for the purposes of the project here described, the recovery of energy from non-conventional sources is very important to what in English is called *energy harvesting* or *energy scavenging* - with particular reference to the recovery of braking energy. The system is conceptually simple: by using the electric motor as a generator, a braking torque is obtained which, besides slowing down the vehicle, also produces electric energy which is stored in supercapacitors. Their high efficiency and power density makes them particularly suitable for this type of use because the regenerative brake can generate electrical currents so high that, without supercapacitors, they could not be stored and would ultimately disperse into heat.

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