Chapter 5

The Future of Energy Storage Systems

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Additional information is available at the end of the chapter

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1. Introduction

During the past several years, we have witnessed a radical evolution of electronic devices. One of the major trends of this evolution has been increased portability. Laptops and smart-phone are the most common examples but also cameras or new technologies such as tablets are equal important. The request of efficient energy storage system becomes even more important if we extend it to different applications such as electrical/hybrid vehicles that require hundreds of times larger power when compared with smaller device. Unfortunately the technological improvements of batteries are slower than electronics, creating a constantly growing gap that need to be filled. For this reasons it is very important to develop an efficient energy storage system that goes beyond normal batteries. In the first part of this chapter we will give a general overview of some existing solution such as electrolytic batteries, fuel cells and microturbines. In the second part we will introduce an evolution of simple capacitors known as Supercapacitors or Ultracapacitors. This technology is very promising and it might be able to substitute, or at least improve in a considerable way current energy storage systems.

1.1. Nanotechnologies for energy related issues

Nanotechnologies (NTs) can play an important role to help to overcome to energy-related challenges and opportunities. However, what specific kinds of nanotechnologies and how can they provide such advantages? Sepeur [56] defines nanotechnologies as *"'the systematic manipulation production or alteration of structure systems materials or components in the range of atomic and molecular dimension with/into nanoscale dimensions between 1nm and 100nm"'*. In particular two subfields of NTs are interesting for energy problems: Nanofabrication and nanomaterials. By combining these two techniques we are for example able to create structures with a large surface area per unit mass, and by selective etching and deposition of different material layers we are able to fabricate very complex mechanical structures. Furthermore the use of new materials in the process allow us to create films and layers with a specific characteristic (such as conductivity, stress distribution, mechanical resistance etc). By combining nanomaterials and nanofabrication it has for example been possible to build solar cells much more efficient compared to the standard type, to build new classes of materials such

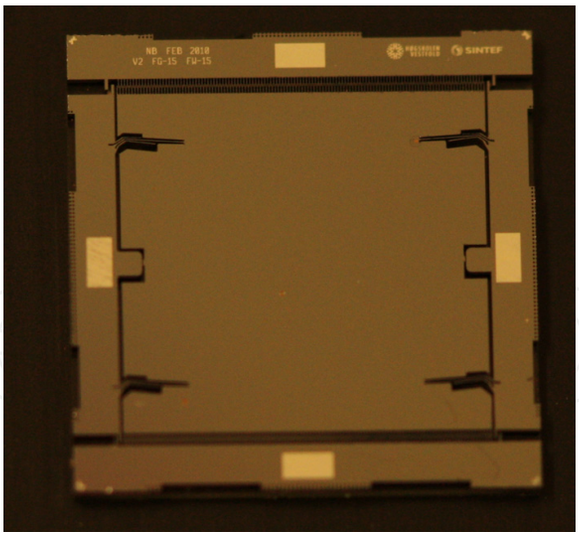

Figure 1. Example of MEMS Energy harvester device [6]

as carbon nanotubes or graphene that are revolutionizing the electronic world. Researchers have already shown that with NT it is possible to create thin film batteries Kuwata et al. [28], Ogawa et al. [44] printable on top of substrates, or creating a smart fibers that can store energy (so called *E-textiles*) Gu et al. [18], Jost et al. [25]. Furthermore, in the literature there are presented many demonstrators of energy harvesting devices that are able to "'harvest"' energy from many different physic sources (such as mechanical vibrations, temperature gradients, electro-magnetic radiations, etc) and transform it into electrical energy.

2. Current state of the art

2.1. Batteries

Nowadays electric batteries represent the most common energy storage methods for portable devices. They store the energy in a chemical way and they are able to reconvert it into electrical form. They consist of two electrodes (anode and cathode) and one electrolyte which can be either solid or liquid; In the redox reaction that powers the battery, reduction occurs at the cathode, while oxidation occurs at the anode [43]. This energy storage form has changed substantially throughout the years, even though the basic principles have been known since the invention by the Italian physicist Alessandro Volta in year 1800. The first type was consisting in a stack of zinc and copper disk separated by an acid electrolyte. Thanks also to the boost of mobile phones during the last years they have evolved to the Nickel-Cadmium (Ni-Ca) and Nickel Metal Hydrate (Ni-Mh) which dominated the market until the developments of Lithium batteries. This latter class rapidly gained market thanks to the higher specific energy (150-500 Wh/Kg versus 50-150Wh/Kg of NiMh, NiCa, See Fig.2) and are nowadays one of the most common batteries available in the market. They can further be divided into another two subclasses which are Lithium Ion (Li-Ion) batteries and Lithium Polymers (Li-Po) batteries (which basically are an evolution of the Li-Ion). The high volume of the market (around 50 billion dollar market in 2006 [39]) is expected to grow even more in the coming years, forecasted to reach around 85.76 billion dollars by 2016 with a Compounded Annual Growth rate around 7% over the next 5 years [34]. This is generating a very high volume of revenues and part of it is re-invested in battery research

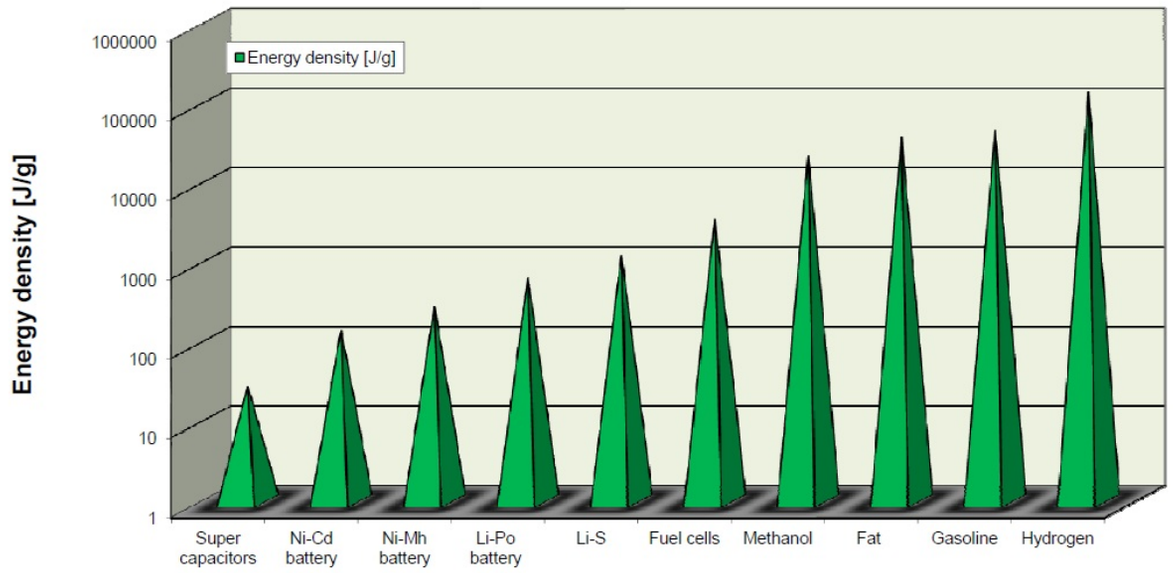

Figure 2. Energy density of different sources (adapted fromPetricca et al. [50])

which is focused to improve energy density, life time and cycling stability, without using dangerous materials that can create health hazards. Unfortunately it is difficult to find all these proprieties optimized in one material combination. One way for enhancement of the battery capacity is using nanotechnologies for increasing and structuring the surface area of the electrodes (for example by depositing nanomaterials or by growing nanostructures such as nanotubes) [43]. But despite all these efforts, the technological improvements of batteries are still much, much slower when compared with the evolutionary progress of electronics. For these reasons many researchers are trying to include smart circuitry inside the batteries for optimizing the discharge curve by optimizing the load. They call it intelligent batteries [35] and they exploit some battery-related characteristic such as charge recovery effect, for improving their lifetime.

2.2. Fuel cells

Fuel cells are one of the most developed alternatives to batteries and they are already available on the market, with many vehicles currently working on Fuel cells based engines [14]. They are electrochemical devices able to convert the chemical energy stored in the fuels into electrical energy. They mainly consist of two electrodes and a membrane which form a reaction chamber and have external stored reactants. The working principle is similar to batteries, however in this case the species at the electrodes are continuously replenished and they can be refilled, ensuring a continuous electricity supply over a long period. There are many types of fuel cells available on the market, and they mainly differ from the species used as fuel, but all of them use one element as fuel and a second element as oxidizer (commonly air) [37].

Theoretically with fuel cells we would be able to generate any power or current by changing the physical dimension of the cell and the flow rate of the fuel. However, the voltage across the single cell electrode is fixed and it is not possible to change it. In general this

voltage is very low (less than 1V for realistic operating condition [37]) and thus multiple cell stacks connected in series are needed to achieve larger potentials. Mixed series and parallel connections between different cells can also be used for increase the voltage and the maximum current supplied. Among all the fuel cell types the most promising are the Proton Exchange Membrane (PEM) and the direct Methanol fuel cells (DMFC) which can be considered a PEM special case.
A graphic representation of a PEM fuel cell is shown in Fig.3; In this case the cell use Hydrogen and Oxygen as species. The membrane present between the two electrodes allows passing only the ions while electrons are forced to "'go"' trough the electric circuit.

The chemical reaction at anode is:

$$H_2 \rightarrow 2H^+ + 2e^- \tag{1}$$

On the cathode side, the electrons will recombine with the Ions and they will react with the cathode species (Oxygen in this case) forming water through the following reaction:

$$4H^+ + O_2 + 4e^- \rightarrow 2H_2O \tag{2}$$

Since water is the only waste product of the reaction, this type of fuel cell is very environmental friendly. Unfortunately there are many problems associated with PEM that are preventing the mass market diffusion of this technology. Hydrogen does not naturally occur in nature and must be produced in factories or laboratories. Furthermore *"'hydrogen has a very high mass energy density (143000 J/g) (See Fig.2) but a very low volumetric energy density (10790 J/L), which makes it difficult to store."'* [50]

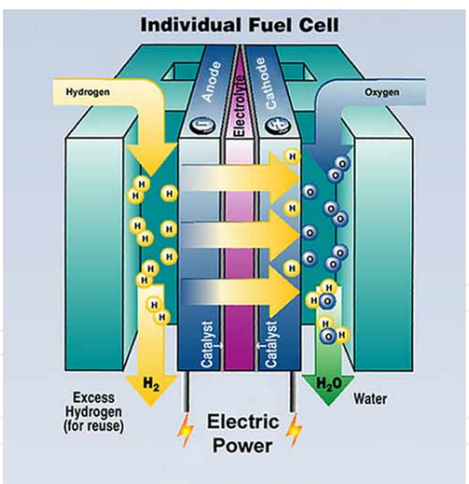

Figure 3. Fuel cell representation [unknown author]

Other problems associated with PEM are the impurity present in the hydrogen fuel, *"'such as CO, H2S, NH3, organic sulfur carbon, and carbon hydrogen compounds, and in air, such as NOx, SOx, and small organics"'*, which are brought in fuel and air feed streams into the electrodes of a PEMFC stack, causing performance degradation or membrane damages [5]. In particular they demonstrated that even small amounts of these impurity materials can poison the anode, cathode or the membrane of the cell, causing a sharp performance drop. To overcome some of these problems (especially the one associated with the hydrogen production and storage),

researcher from University of Southern California's Loker Hydrocarbon Institute developed a new type of fuel cells which use a direct oxidation of Methanol instead of Hydrogen. Unlike Hydrogen, Methanol offer also the advantage of being liquid at room temperature making storage and transportation much easier. This new class of fuel cells are called Direct Methanol Fuel Cell (DMFC) and the working principle is similar to the PEM fuel cell, but with more complicated reactions at the anode (3) and at the cathode (4) [19]:

$$CH_3OH + H_2O \rightarrow CO_2 + 6e^- + 6H^+ \tag{3}$$

$$12H^+ + 6O_2 + 12e^- \rightarrow 6H_2O \tag{4}$$

Methanol has energy volume and mass densities of 4380 Wh/l and 5600 Wh/kg, which are about 11 times higher than current Li-ion batteries ($\approx 500 Wh/l$). *"'This means that the FP/FC unit has superior energy density even with an overall conversion efficiency as low as 7%. In the case where no water recycling is employed to minimize system complexity, water has to be carried with methanol for the reforming. With a stoichiometric steam to carbon ratio of 1:1, this reduces the net energy density to 3000 Wh/l (4550 Wh/kg)"'* [57]. Unfortunately, unlike Hydrogen PEM, where we can assume that all of the polarization losses are located at the cathode, in DMFC the losses at the anode and cathode are comparable. Furthermore DMFC *"'utilizes cathode Pt sites for the direct reaction between methanol and oxygen, which generates a mixed potential that reduces cell voltage"'* [19]. Despite these problems, many companies are already present on the market offering DMFC [17, 53] or disposable methanol fuel cartridges [64].

2.3. Micro engines and micro turbines

It has been more than 150 years since the first Internal Combustion Engine (ICE) was developed and nowadays it is the most common power source for vehicles and large engine-generators. However in the last years thanks to the improvements of microtechnologies, many researchers started to design and develop micro internal combustion engines that may be used in the future as power source for small electrical devices. They consist of three main parts [45],

1. Combustion Chamber
2. Ignition
3. Moving Parts

forming a few cubic millimeters system able to generate power in mW to Watts range. However, Micro engines are not only a smaller version of the large size counterparts [58]. Some of the technical issue present at this scale are resumed in Fernandez-Pello [13], Sher et al. [58], Suzuki et al. [62], Walther & Ahn [65]. In particular the main challenge is to obtain a genuine combustion in a limited volume of the combustor [45]. Furthermore, at this scale the relative heat losses increase and may cause quenching of the reaction (fuel inside the combustion chamber that rapidly cools down, prevents it from burning) with consequent degradation of performances [13, 45, 65].Moreover, the engine speed and the gap width between the piston and the cylinder walls are two key parameters that can create issues in standard ICE (cylinder-piston engine)as reported by Sher et al. [58]. They simulated the miniaturization limits of a standard ICE with a rotation speed of 48000 rpm, a gap width of 10 um and a compression rate larger than 18 and they found a minimum size limit

between 0.3 and 0.4 cc. This limit has already been passed by [62] which has developed a microfabricated standard ICE of 5mmŒ3mmŒ1mm in dimension (0.015 cc) supplied by a mixture of Hydrogen and Oxygen, able to generate a mechanical power of 29.1mW. However, the tests of this silicon engine were performed at 3 rpm and it has shown a compression ratio around 1.4. A similar class of micro engines is based on rotary engine (Wankel design) instead of cylinder-piston design. Example of these MEMS engines can be found in [7, 29]. Interesting is the prototype developed by [7] which consisted of a 13 mm rotor diameter coupled with a dynamo meter, able to generate up to 4W of electric power (other versions of 90mW and 50W are under development). Another interesting alternative is using micro turbines. We are already used to find in the market large gas turbines for electric energy production that may generate up to several hundreds of Megawatts [51]. However, in the last years, with the advent of MNTs, many researchers started to investigate the possibility to create a small micro turbine that are able to generate few Watts, enough to supply most of today's electronic devices. The basic concept is similar to large scale turbine which consists on an upstream rotating compressor, a combustion chamber and a downstream turbine. Furthermore, since it will be used for generating electric power, there will also be an alternator coupled with the turbine. The fabrication material is mainly Silicon, thanks to the well established and controlled processing technologies available for this material. Furthermore, when compared with common nickel alloy, single crystal silicon has an *"'higher specific strength, it is quite oxidation-resistant and has thermal conductivity approaching that of copper, so it is resistant to thermal shock"'* [11]. Several authors [1, 33, 49] successfully designed micro turbines by using silicon (Si) as material. However, silicon has some limitation on high temperatures and for these reasons some other authors reported micro turbine fabricated whit other materials. In particular Peirs et al. [48] reported an example of a 36g micro turbine made of stainless steel. This 10mm diameter turbine was able to generate a maximum mechanical power of 28W with an efficiency of 18%. The turbine was then coupled to a small brushless dc motor, which was used as a three-phase generator. The total system was around 53mm long and 66g in weight, capable to generate 16W of electric power, corresponding to a total efficiency of 10.5%. A similar efficiency is also expected by another microturbine developed by Jacobson et al. [22] in which the preliminary test done so far are very encouraging. We should notice that even if the total efficiency is relative low, hydrogen and hydrocarbon fuels have a much higher energy density when compared with batteries (see fig.2), so the result is a substantial increase of the net energy density of the system.

In conclusion, is certainly possible that ICE and MEMS gas turbines may one day be very useful as compact power sources for portable electronics, equipment, and small vehicles [11].

3. Supercapacitors

As we briefly state above, batteries suffer from various limitation, such as limited life cycles, high manufacturing cost and relative low power density. Furthermore, in case of large batteries, they require also several hours for being fully charged. On the other hand, standard capacitors offer high power density, almost unlimited life cycles, and fast charge. However their energy density is currently too low for been used as primary energy storage system. Supercapacitors may combine the advantages of both battery and capacitor for creating a system that has high power density, virtual unlimited life cycles keeping at the same time acceptable energy density. In these devices, the internal leakage current (in the form of dipoles relax and/or charges re-combination) will determine how long the energy can be stored, while

ADVANTAGES	1. High Power Density 2. Virtually unlimited life cicles 3.Long shell life 4. Fast charge 5. High efficiency 6. Wide temperature operation range 7. Safety
DISADVANTAGES	1. Lower energy density 2. Higher cost 3. High self-discharging rate 4. Low cell voltage 5.Linear voltage drop

Table 1. Super capacitors: Advantages and Drawbacks

the maximum power will depend on the internal resistance (ESR) [55]. In TABLE 1 advantages and drawbacks of supercapacitors respect to batteries are listed.

Figure4 is the Ragone plot for all three technologies. As we can see, supercapacitors will be able to fill the gap between standard capacitors and batteries. It should be noticed that despite supercapacitors there will certainly have a lower energy density of batteries, which can be easily recharged from any power network in seconds or fraction of seconds.

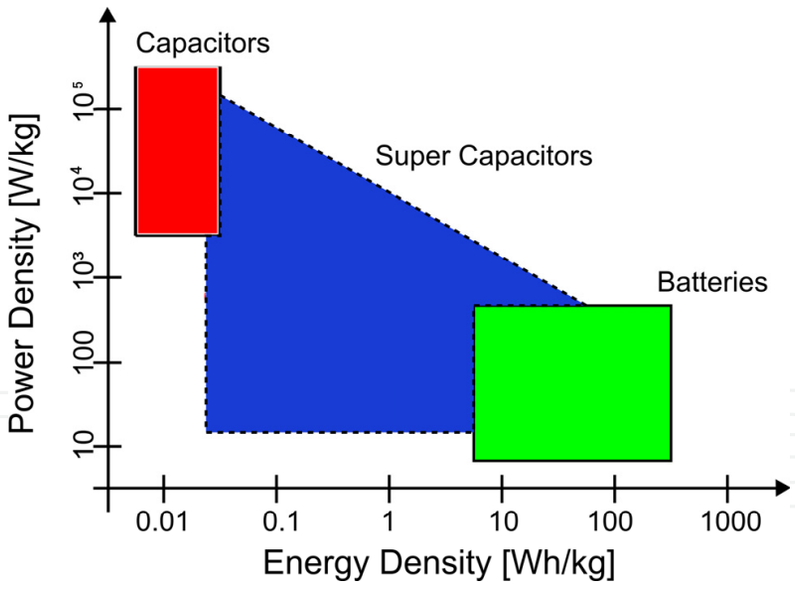

Figure 4. Ragone plot for Capacitors, Super Capacitors and Batteries; adapted from Everett [12], Halper & Ellenbogen [20], Kotz & Carlen [27]

For better understanding the working principle of supercapacitors, it is convenient to start with some basic capacitor theory. The simplest capacitor (plane capacitor) consists of a two electrodes separated by a dielectric. Calling d the distance between the two electrodes, S their overlapped area and ϵ the dielectric constant of the dielectric, the total capacitance C can be defined as:

$$C = \epsilon S/d \tag{5}$$

which corresponds a stored energy E:

$$E = \frac{CV^2}{2} \tag{6}$$

where V is the voltage between the electrodes. From equations 5 and 6 it is clear that the energy density is proportional to the overlapped area and inversely proportional to the distance between the two electrodes. Thanks to nanotechnology it is possible to drastic reduce the effective distance d and create structures with large surface, resulting of an increasing of total capacitance. Moreover, it is possible to combine special types of dielectrics and ionic conducting liquid (electrolyte) in order to store not only electrostatic energy but also electrochemical energy. Supercapacitors can be classified into double-layer capacitor (EDLC) and electrochemical pseudo capacitor (EPC). Based on the storage mechanism we can divide supercapacitors into three categories [20]:

1. Electric Double Layer Capacitors (EDLC)
2. Electrochemical pseudo capacitors (EPC)
3. Hybrid Supercapacitors

In the following sections we will give an overview of each class.

3.1. Electric double layer capacitors

These supercapacitors are called also non-Faradaic supercapacitors since they do not involve any charge transfer between electrode and electrolyte. The energy storage mechanism is thus similar to standard capacitor where the area is much larger and the distance is in the atomic range of charges [70]. EDLC consist of two electrodes, one membrane between the two electrodes which separates the electrodes and electrolyte that can be either aqueous or non-aqueous depending on EDLC [23]. The material of the electrode is very important for the final supercapacitors performances. For the supercapacitors of today's innovation, the most common material of the electrodes is activated carbons because it is cheap, has large surface area and is easy to process [27, 70]. This material is organized in small hexagonal rings organized into graphene sheets [24]. The result is a large surface area due to the porous structure composed by micropores (< 2nm wide), mesopores (2 - 50 nm), and macropores (>50 nm) [20]. The basic structure of a carbon activated EDLC is shown in Fig.5.

For the analytic model of these capacitors equation 5 can still be considered true, where ϵ is the electrolyte dielectric constant, S is the specific surface area of the electrode accessible to the electrolyte ions, and d is the Debye length [70], however *"determination of the effective dielectric constant ϵ_{eff} of the electrolyte and thickness of the double-layer formed at the interface is complex and not well understood"* [3]. Indeed we would expect that doubling the area of the active carbons would double also the capacitance. However experimental data are in contrast with the theory, since empiric measurements were showing a smaller capacitance than expected. Many scientist explained this phenomena by electrolyte ions that are too large to diffuse into smaller micropores and thus unable to support electrical double layer [20, 24, 69]. For this reason many authors have affirmed that mesopores are high desirable in EDLC electrodes since they can optimize their performances [8, 69]. However, recently [40] showed the important role of small pores in the EDCL and they affirmed that ions can

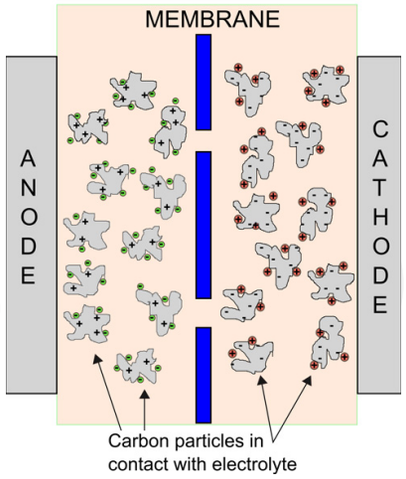

Figure 5. Graphic representation (not in scale) of active carbon EDLC, adapted from [66, 70]

penetrate dissolved in the nanopores. Furthermore it also concludes that the optimal pore size of the electrode mainly depends from the current load due to the distortion of cations and/or intercalation-like behavior [40]. This new discovery lead many scientists to re-consider roles of the micropores. The analytical models can be modified by splitting the capacitive behavior in two different parts depending on the pore size [40]. Despite of all these studies the EDLC is still not completely understood yet [59]. Active carbons super capacitors also change their capacitance respect to the electrolyte materials, aqueous electrolytes allow higher capacitances (ranging from 100 F/g to 300 F/g) than organic electrolytes (less than 150 F/g). [70].

For the carbon electrodes, one valid alternative to activated carbon is carbon nanotube (CNT), which consists of carbon atoms organized in cylindrical nanostructures and can be considered as rolled-up graphene sheets (which consist in carbons atoms organized in 2-D cells see fig.6). The roll up orientation is expressed by two indexes (n and m) and is very important in CNTs since different directions result different proprieties. The two indexes n and m are used for calculate the roll up direction as shown in figure6.

Both SingleWalled (SWNTs) and Multiple Walled (MWNTs) were investigated for EDLC electrodes. Thanks to their high conductivity and their open shape both SWNTs and MWNTs are particularly suitable for high power density capacitors. Indeed their quickly accessible surface area and their easily tunable pore size enable electrolyte ions to diffuse into the mesopores (fig.7), therefore, reduced internal resistance (ESR) and increased maximum power can be achieved [9, 20, 70].

Unfortunately the specific surface area of CNT (< 500 m^2/g) is much smaller than that of activated carbons (1,000Ű3,000 m^2/g) [32, 70], resulting in lower energy density for the capacitor (in average between $1Wh/kg$ and $10Wh/kg$)[52]. This, together with their limited availability and high cost, currently limits their usage [52].

Beside Active Carbons and Carbon Nanotubes, in literature are presented many other materials that can be used for the EDCL electrodes. Among this we should cite carbon aerogel [54], (similar to gels but where the internal liquid is replaced with gas), xerogels [15] and carbon fibers [30]. Carbon aerogel electrode material gave promising capacitive properties, despite the difficulties in preparation [70].

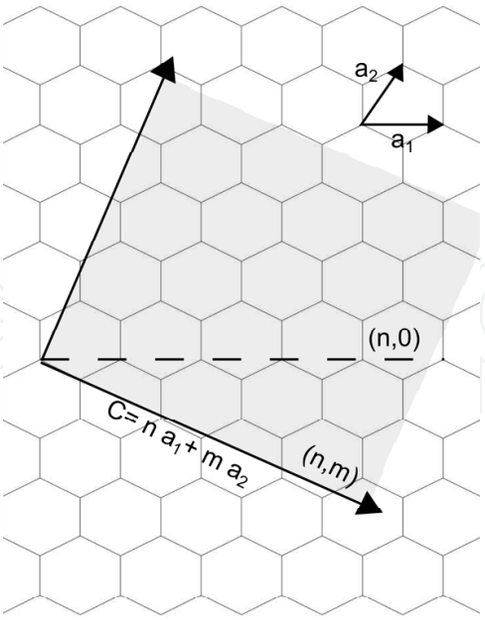

Figure 6. Carbon nanotube: orientation indexes: adapted from GNU license images

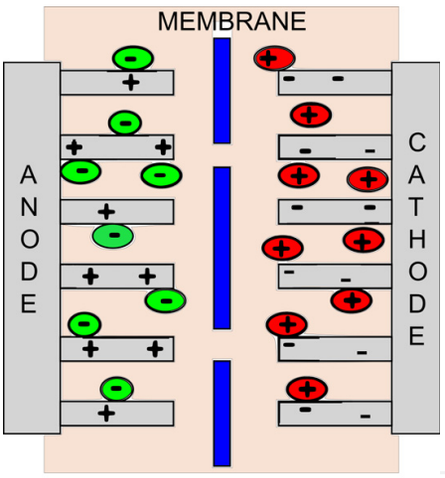

Figure 7. Graphic representation (not in scale) of carbon nanotube EDLC, adapted from [24]

3.2. Electrochemical pseudo supercapacitors

Unlike EDLC, Electrochemical pseudo supercapacitors use charge transfer between electrode and electrolyte for storing energy. This Faradic process is achieved mainly by [20, 66, 70]:

- Rapid and reversible Red-Ox reactions between the electrodes and the electrolyte
- Surface adsorption of ions from the electrolyte
- Doping and undoping of active conducting polymer material of the electrode

The first two processes belong to surface mechanism, so the capacitance will strongly depend on the surface materials of the electrodes, while the third one is more bulk-based process and

thus the capacitance will weakly depend on the surface materials of the electrodes [3]. Since these processes are more battery-like rather than capacitor-like, thus, the capacitors are named as the electrochemical pseudo supercapacitors (EPC). When compared with EDLC, EPC have smaller power density since Faradic processes are normally slower than that of non Faradic reactions. However EPCs can reach much higher capacitances [3, 59] and thus they store much higher energy density.

Currently research efforts are focused on investigating two types of materials for achieving large pseudo-capacitance: metal oxides and conductive polymers. Among all the metal oxide present in nature, Ruthenium oxide (RuO_2) has been largely investigated [26, 31, 47, 63], thanks to its intrinsic reversibility for various surface redox couples and high conductivity [70]. In particular, the research has focused to explore the chemical reactions of RuO_2 in acid electrolytes. The results have explained the pseudo capacitance of EPC as adsorption of protons at Ruthenium Oxide surface, combined with a quick and reversible electron transfer, as in 7 [59, 66]:

$$RuO_2 + xH^+ + xe^- \leftrightarrow RuO_{2-x}(OH)_x \tag{7}$$

where $0 < x < 2$. With this type of electrode, the specific capacitance over $700F/g$ [31]. However, due to rarity and high cost, the commercial applications of RuO_2 supercapacitors have been limited. For this reason many researcher started to investigate others oxides that may provide the same performances with a lower costs. Manganese oxide (MgO_x) has been an interesting candidate because of its low cost, nontoxic and large theoretical maximum capacitance about $1300F/g$.. However the poor electronic and ionic conductivity, low surface area and difficulty to achieve long term cycling stability are some of the issue that need to be addressed before to make Manganese oxide usable in practice [31, 66]. Other metal oxides including (but not limited) NiO, $Ni(OH)_2$, Co_2O_3, IrO_2, FeO, TiO_2, SnO_2, V_2, O_5 and MoO can also be applied [23].

Utilization of conducting polymers as the electrodes (polymer EPC) is also investigated. Since the polymer EPCs are based on a bulk process, a higher specific capacitance respect to carbon based capacitors can be achieved, and thus an expected larger energy density [36]. Furthermore conducting polymers are more conductive than the inorganic materials, thus, the reduced ESR and consequently the increased power capability respect to standard battery can be obtained [60]. Conductive polymers, as their name suggest are organic polymers that conduct electricity, are able to combine both advantages of metals (such as high conductivity) polymers (such as low cost, flexibility, low weight). They are made by doping conjugated polymers [21]. The synthesis of conjugated polymers can be done by chemical oxidation of the monomer or electrochemical oxidation of the monomer [21]. Polymer EPCs have three basic configurations depending on the type of the polymer used [60]:

- Type I: Both electrodes use the same p-doped polymer (symmetric configuration).
- Type II: Electrodes use two different p-doped polymers with a different range of electro-activity (asymmetric configuration).
- Type III: Both electrodes use the same polymer ,with the p-doped for the positive electrode and the n-doped for the negative electrode (symmetric configuration)

Among the three configurations, TYPE III is the most promising one for commercialization [36, 60]. Despite it is possible to synthesize many types of conductive polymers, three in

particular are commonly used for polymer EPCs as listed below (the relative structures are shown in fig.8) [60, 66] :

- Polyaniline (PANI)
- Polypyrrole (PPy)
- Thiophene-based polymers (PTh)

PANI has shown a high specific capacitance (around 800 F/g [66]) and a good life cycle stability ($\approx -20\%$ in capacitance after 9000 cycles) [60]. Polymer EPCs based on PPy and PTh are also successfully fabricated [36, 60, 66] with a specific capacitances between 200 and 300 F/g.

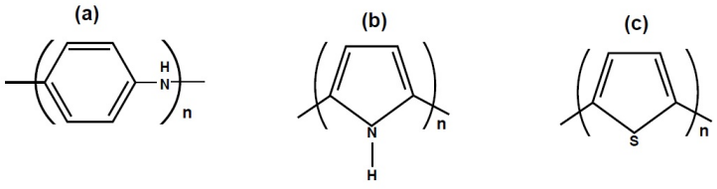

Figure 8. Polymers structures: polyaniline PANI(a), polypyrrole PPy(b), polythiophene PTh (c); adapted from [60]

In general, polymer EPCs suffer of poor cycle stability. The rapid performance degradation is due to the mechanical stress derived from the volumetric changes during the doping/dedoping process. (Swelling and shrinking)[16, 20, 27, 66]. For this reason further research is needed in order to improve performance of polymer EPCs.

3.3. Hybrid supercapacitors

Hybrids supercapacitors are a class of devices that attempt to combine the advantages of both EDLC and EPC, which are able to exploit at the same time both Faradic and non- Faradic processes for storing energy. The idea is using the propriety of EDCL for obtaining high power and the propriety of EPC for increasing the energy density [59]. According to Halper & Ellenbogen [20], the hybrid supercapacitors can be classified, based on the electrode material, in:

1. Composite
2. Asymmetric
3. Battery type

In composite supercapacitors, each electrode is formed by a combination of a carbon material as the frame and a metal oxide material or a conductive polymer deposited on top of the carbon material (e.g. [67, 68]). BBy doing this the carbon material create a large surface area for a large capacitance. Furthermore the polymer material further increases the capacitance with a result of high energy density and cycling stability comparable with EDCL [20]. For example, in the case of Carbon/PPy based electrode, the high cycling stability is due to the carbon frame below the polymer that mitigates the polymer stress for increasing life cycle. Very recently

Wang et al. [67] has reported one interesting example of this class of supercapacitors. The electrodes were made by graphene/RuO_2 and graphene/$Ni(OH)_2$. The device has shown an energy density $\approx 48Wh/kg$ at a power density of $\approx 0.23kW/kg$. Furthermore a high cycling stability has also been achieved. After 5000 cycles of charging and discharging at a current density of 10 A/g it has shown 8% reduction of the original capacitance. Another example of using carbon electrodes coated by conductive polymers was reported by An et al. [2]. They used polypyrrole-carbon aerogel for the capacitor electrodes.

For the Asymmetric supercapacitors, carbon material for one electrode and metal oxide or polymer material as second electrode are applied. One example of this technique is reported by Staiti & Lufrano [61], which uses manganese oxide and activated carbon.

The battery type supercapacitors are the most interesting candidates for the relative high energy density. Similar to the asymmetric, in this type of supercapacitors one electrode is made of carbon material, and the second one is made of a typical battery electrode material (such as Lithium). In particular one lithium- intercalated compounds (Nanostructured $Li_4Ti_5O_12$ also known as LTO)has been extensively studied [4, 10, 38, 41, 42, 46], which can enable the cycling stability during Li intercalation/ deintercalation processes [38]. When coupled with carbon electrode, the charge storage can be realized by the mechanisms of a Li-ion battery at the negative electrode and a supercapacitor at the positive electrode [10]. The energy density for battery like electrode is very high compared to capacitors. Naoi et al. [41] reported an energy density for as high as 55 Wh/Kg. However the power density for the battery type supercapacitor is in general lower than the other classes and, faradic principle leads to an increase in the energy density at the cost of life cycle. This is one major drawback of hybrid devices (when compared with EDLCs), and *"'it is important to avoid transforming a good supercapacitor into a mediocre battery"'* [59]

4. Conclusions

Tracking a clear path for the future energy storage systems is not easy. Fuel cells in the near future can became mature enough to be used as primary energy source for large vehicles. However, despite small fuel cells (in particular the direct methanol fuel cells) can also be used for supply laptop or other small electronic device, it is believed that battery will continue to lead this market for several years. Microturbines and internal combustion engines are also very promising technology but further research is needed for improving current prototypes. Supercapacitors have a great potential to play an important role in future energy storage systems, in particular to all the application that require high peek powers. Nowadays then can be used as secondary energy storage system, for example, in vehicle applications they can be used in parallel with fuel cells or batteries for overcoming the power peaks during acceleration [4]. Supercapacitors will be able to be full recharged in a very little time and this provides the key advantage that the customers and the market are waiting for.

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