European Commission

ObservatoryNANO

Report on
Energy

Draft Version

Term 1/2008

Authors: Odile BERTOLDI, Sébastien BERGER

Version: 06.08.2009

Description of the workpackage structure; segmentation into 10 technology sectors

http://www.observatorynano.eu/

5 Energy

5.5 Batteries and Supercapacitors

5.5.1 Definition

Batteries and supercapacitors are devices that store electrical energy.

Battery stores electrical energy in chemical form and thus converts chemical energy into electrical one. It stores a large amount of energy and releases it slowly. When this conversion is a reversible process, the battery is rechargeable. Non rechargeable batteries are not considered here.

A capacitor, a passive electrical component, stores energy in the electric field between a pair of conductors. It stores a small amount of energy but releases it quickly.

A supercapacitor is a capacitor that stores a larger amount of energy and releases it more slowly than a simple capacitor.

This can be sum-up in the following Ragone diagram.

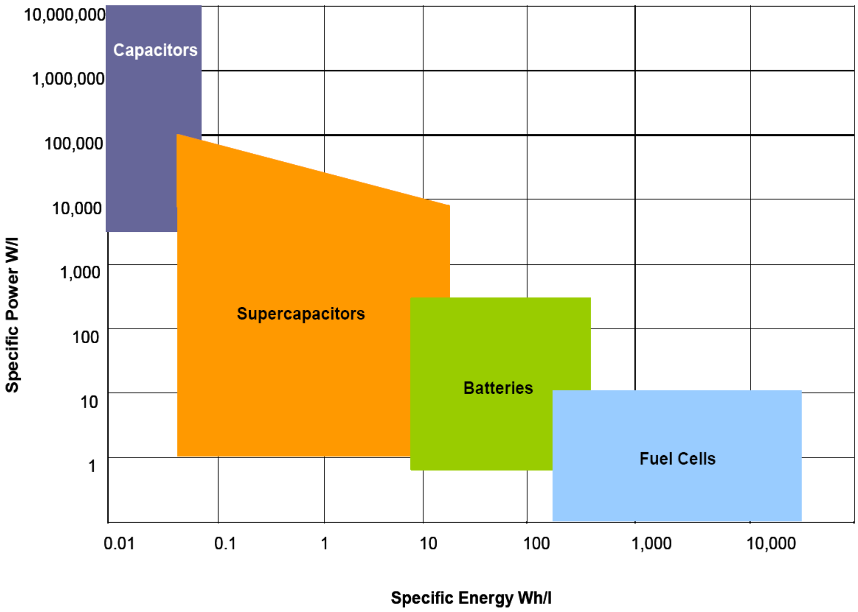

Figure 1: Ragone plot [1]

Different kinds of batteries are developed. Classical batteries for transport or static electric storage are still of great interest, and the main expected progress concern their storage capacity, the life time, the weight, the use of materials available and environment-friendly aspects. This topic is of great interest for automotive since hybrid and electric cars are under development.

Due to the developments of renewable and alternative energy sources, like photovoltaic systems, new storage solutions are also required. Batteries adapted to these specific energy production means and management are under development.

One of the greatest challenges for storage systems development is mobility. The exponential use of portable devices results in an increase of the amount of functions and of energy consumption. That is what drives R&D activity on miniaturised batteries. The main criteria for these systems are: autonomy, size, safety, charging time and cost.

Thanks to their ability to deliver high power in a limited time, supercapacitors are well adapted to applications for public transports, but also aerospace or wind turbine. In complement of systems providing constant energy, supercapacitors are able to quickly provide a peak of power when needed.

5.5.2 Short description

5.5.2.1 Batteries

A battery is a device that converts chemical energy directly to electrical energy. It consists of one or more voltaic cells. Each voltaic cell consists of two half cells connected in series by a conductive electrolyte. One half-cell is the negative electrode (the cathode) and the other is the positive electrode (the anode). In the redox reaction that powers the battery, reduction occurs in the cathode, while oxidation occurs in the anode. The electrode needs to be from different materials. The electrodes do not touch each other but are electrically connected by the electrolyte, which can be either solid or liquid. In many cells, the materials are enclosed in a container, and a separator, which is porous to the electrolyte, prevents the electrodes from coming into contact.

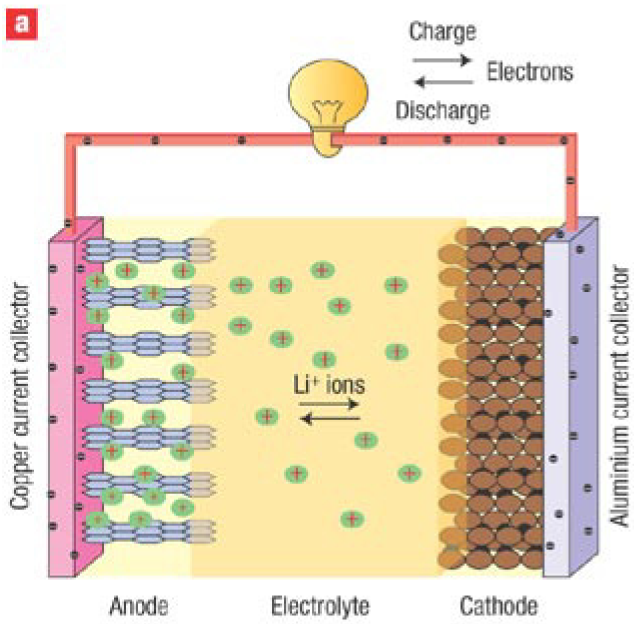

Figure 2: Li-ion battery diagram

There has been constant developments in cell chemistries from the aqueous rechargeable NiCd (Nickel-Cadmium) 1.2V batteries to NiMH (Nickel-Metal-Hydride) and then to 3.6V organic electrolyte Li-ion (Lithium-Ion) and Lithium-polymer cells.

This evolution corresponds to a large progression of the energy densities (40, 90 and 205 Wh/kg respectively)

Li-ion battery presents the best electrochemical performances as Li is the most electropositive metal. Lithium is intercalated in another metal oxide (manganese, nickel, cobalt oxides) and constitutes the cathode. During the charging step, Li inserts in the anode (usually graphite, in this case at around 80mV/Li/Li^+) and when the battery is put under a load, Li ions are desinserted from the anode and migrate back to the cathode. The combination of organic liquid electrolyte and high voltage positive electrodes may create safety problems, which can be solved by the use of new electrolyte composition, safe active material (for ex. $LiFePO_4$), or by dry Li-polymer batteries.[2]

5.5.2.2 Supercapacitors

A supercapacitor, variously referred to by manufacturers in literature as “supercapacitors” or “ultracapacitors”, is a device that stores energy as a charge (concentration of electron) in an electrochemical double layer on a surface of a material. Consequently, they are also quite properly referred to as electric double layer capacitors.

The energy density is therefore 100 times higher than in a traditional capacitor and the power density is 10 times higher than in a classical battery. Because supercapacitors move electrical charges between solid-state materials with no chemical or phase changes taking place, the process is highly reversible and the discharge-charge cycle can be repeated over and over again, virtually without limit.[3] Until now, when high power was required, two solutions were offered: the use of higher battery capacities than the one really needed for the applications or the use of the battery outside operating specifications, slowly degrading the battery performance. Even with Li-ion, batteries are a poor solution for high power density applications. Supercapacitors are now in continuous development because they offer relative long life combined with high power density.

A supercapacitor is composed of two electrodes and current collectors, most of the times identical. These electrodes are immersed in an electrolyte and are separated by a dielectric separator.

The electrolyte can consist of water solution of potassium hydroxide (KOH) or sulphuric acid (H_2SO_4), for example. This limits then the voltage to 1V because above this value, water is decomposed in hydrogen and oxygen. Typically, the electrodes are made of porous carbon.

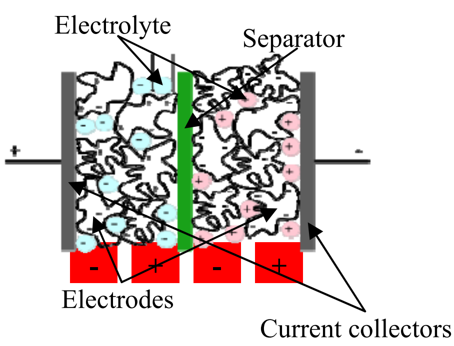

Figure 3: Parts of a supercapacitor[4]

When a voltage is applied between the electrodes, negative ions from the electrolyte flow to the positive electrode. In the same time, positive ions from the electrolyte flow to the negative electrodes. The separator prevents the charge to reach the concerned electrode creating indeed a double layer of charge. It acted like a double capacitor.

5.5.3 State of R&D

5.5.3.1 Batteries[5]

The general purpose of R&D is to increase the energy or power density in order to enhance the performance of the batteries, to improve their safety, to ensure high lifetime, mainly due to a good durability of the electrodes under discharge-recharge cycles and to reduce the size and weight of the systems. Nanotechnologies are used for the shape they are able to give to materials: the very high surface/volume ratio of nanomaterials is here the main driver.

The performances of the batteries highly depend on the properties of the materials chosen for the electrodes. The most studied materials (lithium iron phosphates, vanadium or manganese oxides, lithium cobalt oxides…), have interesting properties regarding their cost, stability, small environmental impact or electrochemical properties. The main drawback is that all those properties are not available in the same material (a material with a particularly low cost will be highly toxic or will have limited electrochemical performances). It is also interesting to notice that the performances expected for the battery highly depend on its application: the lifetime of a battery should be around 4 years for a laptop but around 7 to 10 years for an electric car. This implies that the material chosen mostly depends on the aimed application.

The enhancement of the battery capacity can be afforded by increasing and structuring the surface area of the electrodes. Then a higher current flow between electrode and chemicals is possible, the charge and discharge rate is increased and the amount of ion stored on the electrodes is higher. It also allows reducing the amount of materials used;

This can be achieved by nanostructuring (nanoparticles, nanocomposites, nanotubes, aerogels…)[6,7] the anode or the cathode or coating them with nanomaterials[8,9]such as nanowires or mesoporous materials like silica. Nanowires have an advantage compared to nanoparticles: they ensure more easily electric conduction path. So, for the negative electrode, intercalation materials like vanadium oxides or manganese oxides are particularly useful.[10]

On the negative electrode side, the main limitation is the degradation of the electrodes using Li-alloyable materials due to high strain induced by the higher volume of lithium inserted during the charge of the cell. Several solutions have been proposed to overcome this difficulty. One possibility is to implement silicon nanowires onto the anodes to improve by 30% the electrical storage capacity of the Li-ion battery. The lithium is stored in the middle of Si nanowires. As the nanowires can inflate without degrading when they absorb positively charged Li atoms during charging, the degradation of the battery is reduced[11]. The main drawback is the poor conductivity of silicon. Therefore, it is coated with black carbon, a more conductive material and inserted in a binder. So far, nanoparticles are preferred to nanowires as the preparation process is easier. The first commercialisation of battery using nanoparticles is expected for mid-2010.

Another way for lithium storage enhancement is the use of nanocomposite materials[12]. Those previous solutions tend to shorten the recharging time. Carbon nanotubes can also incorporate more lithium than traditional graphite electrodes.

At least, some compounds as $LiMn_2O_4$ or $LiCo_2O_4$ are also usually employed, in a mesoporous or nanostructured form or as nanoparticles.

On the cathode side, the increase of the power might be obtained thanks to a thin nanostructured layer as an electrode. A high active surface improves indeed the storage capacity of lithium and increase the diffusion kinetic.

The intercalation materials like vanadium oxides or manganese oxides might also be particularly useful.[13]

Concerning the electrolyte, its efficiency might also benefit from nanotechnologies. To improve also the security of the batteries, by avoiding short-circuit between electrodes, the use of ceramic materials or polymer-gel has been proposed. The addition of nanopowders of compounds such as Al_2O_3, SiO_2, and ZrO_2 to non-aqueous electrolytes can enhance the conductivity by a factor of six. Solid ceramic are also interesting because of their good temperature resistance. Nanoparticles added to solid polymer electrolyte (like poly-ethylene oxide-based polymers) might increase in the useful range of electrolyte conductivity. The nanostructuring of the matter might improve the storage capacity of the electrolyte.

In order to increase the available interface between electrodes and electrolyte, various kinds of 3D architectures are studied as well. They are combined with the previously mentioned solutions for increasing the surface.

Nanostructuring might also be considered for the current collectors in order to improve the exchange surfaces.

The lifetime of the batteries mainly depend on their cyclability, which means the ability to preserve constant properties of the electrodes through a large amount of charge/discharge cycles. To increase the lifetime of batteries and to prevent low level discharge, it has been proposed to separate liquid in battery from solid electrodes by nanomaterials. Many kinds of nanostructured coatings are studied, similar to those cited previously.

The use of those nanotechnologies, especially carbon nanotubes, recently led to the realisation of paper thin batteries, the size of a post stamp. These batteries can be printed like paper, rolled, twisted, folded or cut into shapes without mechanical integrity or efficiency damages[14] but they require to be protected by an encapsulation which limits the recharging possibility.

Figure 4: Example of paper thin battery

5.5.3.2 Supercapacitors

The general purpose of the research is to enhance the performance of the supercapacitors and to reduce the costs, consequence of miniaturisation.

The performances considered are the energy density, the operating voltage and the lifetime.

The increase of the amount of energy stored is achieved by giving the electrode an enormous surface area (combined with a high charge storage capability of the electrochemical interface). The capacitance per weight of carbon (the material used for the electrode surface) is the dominant criterion. Carbon is generally coated on a metallic substrate like aluminium. Structuring of this substrate allows a high surface/volume ratio for the carbon. The size distribution of the pores made in the substrate and the particle size of carbon need to be optimised.

Several solutions have been developed. It is for example possible to coat the electrodes with activated carbon (a teaspoonful of the porous, sponge like material has about the surface area of a football field).[15]

Another solution consists in the process of carbonization and/or activation of polymer/SWNT (single wall nanotubes) composite films. Carbonization, indeed, leads to an increase in pore volume and this subsequently leads to an increase in the specific surface area of the electrode.[16,17]

There has been also research on the use of carbon aerogel that has high electrical conductivity and controlled ultra fine pores producing a highly usable surface area.[18]

To increase the amount of energy stored it is also possible to use better charge-storing materials. Materials like manganese oxide and conducting polymer have been proposed. Nanotechnology solutions consist in the use of, for example, nanoflowers of manganese oxide connected to the current collectors by carbon nanotubes.[19]

To improve the operating voltage, the electrolyte has to be improved. Research is then focusing on solid electrolyte such as organic one.

5.5.4 Additional demand for research

5.5.4.1 Batteries

The main limitation of the use of nanotechnology in battery is the cost related to the method used to prepare materials at a nanoscale and to the layout used to avoid aggregates.

Some works are awaited concerning the membrane. The current one used (PVDF) suffers problems regarding its pores: they tend to get blocked. The future membrane will need to have a porosity low enough to avoid short circuits but sufficient to allow diffusion.

A work is needed concerning the managing of the batteries. To increase the lifetime of a battery, it might be possible to design a battery with a high capacity but which capacity is managed as to be not completely used during charge and discharge phase in order to reduce the solicitation of the material.

5.5.4.2 Supercapacitors

To enhance the performance of the supercapacitors, it has been possible to realise supercapacitors using graphene. For the moment, they have shown storage abilities close to those of supercapacitors already on market. A challenge is stack sheets of graphene to increase energy storage and possibly double the current capacity.[20] [21]

The positive and negative ions of the electrolyte are always of different size (e.g. K^+ and OH^-). Therefore, an electrode, which nanopores fit the size of one of the electrolyte ions will almost certainly not fit the other electrolyte ions. R&D on tailored material is needed.

5.5.5 Applications and perspectives

5.5.5.1 Batteries:

- Transport
  - hybrid and electric vehicles (car, bus)
  - wheelchair – electric bicycles
  - tramway, subway …
- Portable applications (cellphones, laptop, cameras …)
- Medical devices
- Medical implants
- Power tools
- Spatial applications
- Storage of electrical production of alternative energy (PV, wind …)

5.5.5.2 Supercapacitors:

When a large rapid pulse of energy or high power and quick repetitive recharging is required

- Power back-up in electronic devices
- Automotive:
  - quick burst of power over short streches & braking replenishment
  - catalyst preheating
  - hybrid-electric and fuel cell powered vehicles (to start them)
- Weatherproof power sources

- Electronic devices for rapid charge (laptop, cellphones …)
- Military projects (starting the engines of battle tanks and submarines or replacing batteries in missiles)

5.5.6 Current situation within EU

Concerning batteries, there is an important linked community in Europe named ALISTORE (Advanced lithium energy storage systems based on the use of nano-powders and nano-composite electrodes/electrolytes) , which groups academic and industrial in a European network of excellence dedicated to the development of nanotechnology for anode, cathode, electrolyte and current collectors and of precise characterisation methods. The research and development are distributed among the players.

To prove the feasibility at an industrial scale, the fabrication of kg of materials is required as the project Plateforme Nanomill tends to attempt. A production at a much higher rate (tons) will allow reducing the costs.

5.5.7 References & Literature

---

[1] A Case Study in Commercialising Nanotechnology: A. Kongats, Cap-XX – Nanotech Northern Europe 2008 – http://www.cap-xx.com/

[2] Road Maps for Nanotechnology in Energy; The Institute of Nanotechnology (2006) – http://www.nanoroadmap.it/

[3] Nanotechnology helps solve the world's energy problems (2004) – http://www.nanoforum.org/

[4] http://www.supercapacitors.org/

[5] Nanomaterials for Rechargeable Lithium Batteries; P.G. Bruce, B. Scrosati, and J.M. Tarascon: Angewandte Chemie International Edition **47**, 2930 (2008

[6] Electrochemical Performance of Sol-Gel Synthesized LiFePO4 in Lithium Batteries; Y. Hu, M.M. Doeff, R. Kostecki & R. Finones: Journal of the Electrochemical Society **151** A1279 (2004).

[7] Cathodes for Lithium Ion Batteries; The Benefits of Using Nanostructured Materials: F.F.C. Bazito & R.M. Torresi: Journal of the Brazilian Chemical Society **17**, 627 (2006).

[8] Review paper, e.g.: Nanostructured materials for advanced energy conversion and storage devices; A. S. Arico, P. Bruce, B. Scrosati, J.-M. Tarascon & W. van Schalkwijk: Nature Materials **4**, 366 (2005)

[9] http://www.a123systems.com/#/technology/

[10] Developments in nanostructured cathode materials for high-performance lithium-ion batteries; Y. Wang & G. Cao Advanced Materials **20**, 2251 (2008)

[11] High performance lithium battery anodes using silicon nanowires; C.K. Chan, H. Peng, K. McIlwrath, X.F. Zhang, R.A. Huggins & Y. Cui: Nature Nanotechnology **3**, 31 (2008)

[12] Si/C composites for high capacity lithium storage materials; J. Yang, B. F. Wang, K. Wang, Y. Liu, J. Y. Xie, & Z. S. Wen: Electrochemical and solid-state letters **6**, A154–156 (2003).

[13] Developments in nanostructured cathode materials for high-performance lithium-ion batteries; Y. Wang & G. Cao Advanced Materials **20**, 2251 (2008)

[14] Flexible energy storage devices based on nanocomposite paper; V.L. Pushparaj, M.M. Shaijumon, A. Kumar, S. Murugesan, L. Ci, R.Vajtai, R.J. Linhardt, O. Nalamasu, P.M. Ajayan: Proceedings of the National Academy of Sciences **104**, 13574 (2007).

[15] Nanoflowers Improve Ultracapacitors – A novel design could boost energy storage; P. Patel-Predd (2006) - http://www.technologyreview.com/Energy/21375/

[16] PAN/SAN/SWNT ternary composite: Pore size control and electrochemical supercapacitor behaviour; C Zhou, T Liu, T Wang & S Kumar: Polymer **47**, 5831 (2006)

[17] Carbon nanotube research; S Kumar, Georgia Tech School of Polymer, Textile and Fiber Engineering – http://www.ptfe.gatech.edu/faculty/kumar/kumar.html

[18] Carbon Aerogels and Ultracapacitors; G. Allen (2008) – http://www.ultracapacitors.org/

[19] Growth of Manganese Oxide Nanoflowers on Vertically-Aligned Carbon Nanotube Arrays for High-Rate Electrochemical Capacitive Energy Storage; H. Zhang, G. Cao, Z. Wang, Y. Yang, Z. Shi & Z. Gu: Nano Letters **8**, 2664 (2008)

[20] Graphene - The New Ultracapacitor Breakthrough; G. Allen (2008) – http://www.ultracapacitors.org/

[21] Graphene-Based Ultracapacitors; M.D. Stoller, S. Park, Y. Zhu, J. An, and R.S. Ruoff: Nano Letters **8**, 3498 (2008)