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Nanotechnology and batteries

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Executive summary

From Alessandro Volta's first Voltaic pile in 1800 to the next generation of lithium batteries, this scalable device, used to convert stored chemical energy into electrical energy, has made evolved greatly. The portability of batteries has made them popular and useful for a variety of purposes. In less than two centuries, we have come from simple saline-based devices to alkaline-based, primary non rechargeable batteries. The latter is now competing with secondary rechargeable batteries, among which, the most well-known are NiCd, NiMH and Li-ion batteries. The battery has become a common power source for many household and industrial applications. By far, Li-ion has the highest share of the dry cell rechargeable market. It is replacing NiMH which has replaced NiCd in most applications due to an increase of around 100 to 150% of the storage capacity.

Therefore, most activities concerning batteries are dedicated to Li-ion technology. To widen the range of applications available for Li-ion batteries, some improvements are necessary. The main focus of R&D on battery systems is: to increase the energy or power density in order to enhance the performance of the batteries; to ensure high lifetime (mainly by ensuring durability of the electrodes under repeated charge-discharge cycles) and to reduce the size and weight of the systems.

Nanotechnologies offer promising innovations for these broad functional requirements. An increase of the power density may be possible using nanostructuring of the battery electrodes (nanowires, nanotubes …). This would increase the contact surface between electrode and electrolyte and decrease the ions (Li^+, H^+) diffusion path inside active the material. These parameters have an influence on battery power density, which is key for applications such as electric vehicles.

The improvement of the battery lifetime, which is limited by unwanted side reactions could be obtained by using nanoarchitectured materials which couple external micro- or mesoscale particle sizes to internal nanosized grains, such as nanotubes.

Nanotechnology offers also new processing opportunities. Placing of materials beneath nanoparticles could act as the basis of novel printing processes, aiding battery manufacture.

From the market point of view, batteries represent a rapidly growing sector. For example, battery companies have received over $600 million in venture capital funding in 2009, compared with $478 million garnered for 2008. Lux Research has predicted that the energy storage market will grow to become a $60 billion industry by 2013.

Concerning portable battery-driven devices, in 2009, records show that 1.1 billion mobile telephones and 169.6 million portable PCs were produced and sold. This equates to an energy capacity production level over 15 000 MWh/year.

The financial value of power grid-connected energy storage is estimated to be currently $365 million, growing to $2.5 billion by 2015. Cost reduction and an increase in the energy density of Li-Ion batteries should result in a greater market share, which has been forecast by Pike Research to be 26% of the energy storage market by 2018.

Concerning transportation, the share of EV and HEV vehicles in the total automotive market is projected to be 6% in Europe in 2015, reaching 27% by 2020. And more generally, it has been estimated that 4.1 million xEVs (HEVs, PHEVs, EVs) will be in use by 2015.

These statistics give an impression of the quantity and diversity of battery systems that will be required over the next ten years. Currently, battery production is dominated by Asian firms with a smaller market share in Europe which focus mainly on Li-Ion battery technology.

Chapter 1 Introduction

1.1 Definition

A Battery is a device that stores electrical energy in chemical form and then converts the chemical energy into electrical energy. Batteries can store a large amount of energy and release it slowly. If this conversion is a reversible process, the battery is rechargeable (secondary battery). Non rechargeable batteries (primary batteries) are not considered here.

A distinction must be made between batteries and capacitors/supercapacitors. A capacitor is a passive electrical component that stores energy in a dielectric between a pair of conductors. Capacitors generally store a relatively small amount of energy but are able to release this energy quickly. So called ‘supercapacitors’ are capacitors which are able to store a larger amount of energy and releases it more slowly than a standard capacitor, bridging the application gap between capacitors and batteries.

The properties of these devices can be summarised in the following Ragone diagram.

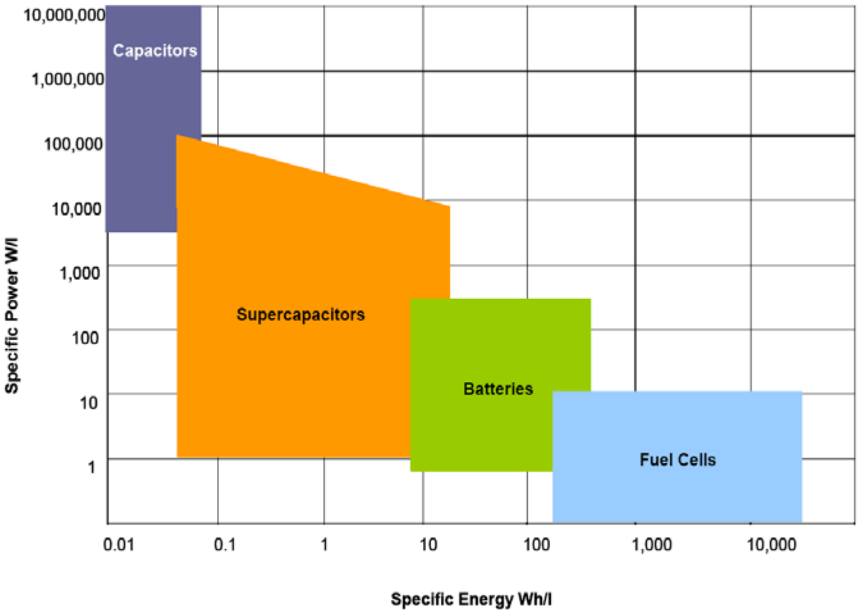


Figure 1: Ragone chart [1]

Despite the wide array of energy storage solutions, standard batteries for transport or static electrical storage remain the focus of great interest. Progress is expected in energy and power densities, lifetime, weight and volume, the use of easily available materials and environmental aspects. Battery technology is of particular interest for the automotive sector since the success hybrid and electric cars is based largely on battery performance.

Due to the developments of renewable and alternative power generation, new energy storage solutions are being sought. Batteries adapted to these specific energy production technologies are currently under development.

One of the greatest challenges for the development of energy storage systems is portability. The rapidly growing use and range of portable devices has resulted in an increase in their overall energy consumption. This is driving R&D activity on miniaturised battery technology. The main criteria for these systems are: Energy capacity, size, safety, and charging time/cost.

Thanks to their ability to deliver high power in a limited time, supercapacitors are well adapted to applications not only in public transport, but also aerospace and wind turbines. Coupled with systems providing constant energy, supercapacitors are able to quickly provide a short term peak of power when needed.

1.2 Short description

A battery is a device that converts chemical energy directly to electrical energy, consisting of one or more voltaic cells. Each voltaic cell consists of two half cells connected in series by an ion conducting electrolyte. One half-cell is the negative electrode and the other is the positive electrode (whose roles reverse when charging/discharging the cell). In the redox reaction that powers the battery, reduction occurs at the cathode, while oxidation occurs at the anode when discharging the battery. The electrodes needs to be made of 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.

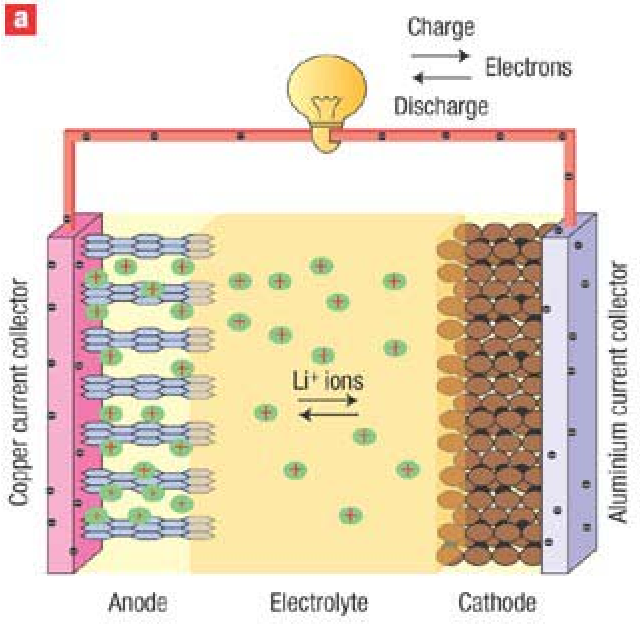


Figure 2: Li-ion battery diagram

There has been a steady development in the material choices used In batteries, from the compact rechargeable NiCd (Nickel-Cadmium) batteries to NiMH (Nickel-Metal-Hydride) and then Li-ion (Lithium-Ion) and Lithium-polymer. This evolution corresponds to a progression of the energy and power outputs and the cycling ability.

Li-ion batteries currently present the best characteristics as Li is the most electropositive and lightest metal available. A lithium layer is sandwiched between another metal oxide (manganese, nickel, cobalt oxides) and constitutes the cathode. During the charging phase, Li migrates to the anode (usually graphite) and when the battery is put under a load, Li ions are released from the anode and migrate back to the cathode. The electrolyte used is organic and therefore creates safety problems, which can be solved in Li-polymer batteries.[2]

1.3 Keywords

Battery, anode, cathode, electrolyte, electrode, energy, power

Chapter 2 ST aspects

2.1 State of R&D

2.1.1 General properties

Most activities concerning batteries are dedicated to Li batteries with a market of around 10 billion dollars per year. Li-ion batteries have proven to be the market leading technology due to an increase from 100 to 150% of the storage capacity compared to previous aqueous based batteries. The main criteria driving research to improve upon the current technology focus on power and energy density, volume reduction, safety and costs. Li-ion systems remain today the most effective technology for most applications.

Nanotechnologies can be used to texture surfaces on very small scales: the very high surface/volume ratio of nanomaterials on electrode surfaces is desirable for two main reasons: firstly, it increases the contact area between electrode and electrolyte, which is likely to increase the power of batteries by improving the ion mobility between electrodes and electrolyte. Secondly, for Li-ion systems, it improves the lithium layering properties within the electrodes.

The other main advantage of nanotechnology is associated with the use, at the research level, with new materials whose energy densities are very promising, but whose electrical conductivity is currently too low. However, the further inclusion of conducting nanomaterials may surmount this problem.

The reduction of the size[3] of active material particles could lead to significant improvments in the electrochemical behaviour which could render possible previously unavailable reversible conversion mechanisms.

The lifetime of the batteries mainly depends on their cyclability, which means the ability to preserve the performance of the electrodes over a large number of charge/discharge cycles. To increase the lifetime of batteries and to prevent low level discharge, it has been proposed to separate the liquid in the battery from the solid electrodes using nanomaterials. Many kinds of nanostructured coatings are being studied, similar to those cited previously. An alternative method consists of nanostructuring the electrode material to prevent degradation caused by the repetition of Li-ion charge and discharge cycles.

However, the application of nanotechnologies is not without disadvantages. Increasing the surface area of a compound promotes instability, especially at the electrode interfaces of batteries. This can degrade safety characteristics, which is in many sectors a dominating factor. As a consequence, and due to the fact that processing the smallest nanomaterials is technological challenging, the use of particles smaller than about 100nm is generally considered as a serious source of difficulties. As a consequence, depending on the properties expected for each application, the use of nanotechnology is not always the best solution.

The performances of the batteries strongly depends on the properties on the composition of the electrodes. The most studied materials (lithium iron phosphates, vanadium or manganese oxides, lithium cobalt oxides…), have attractive properties in terms of cost, stability, environmental impact and/or electrochemical properties.

The main drawback is that all these properties are not available in a single material (e.g. a material with a particularly low cost will be highly toxic or will have limited electrochemical performances). To combine these properties and/or create new functionalities, the association of different materials seems to be an effective solution. This can be made by coating electrically insulating particles with a conductive nanolayer or by coating materials reacting with the electrolyte with a passivating nanofilm or nanoparticles.[4] Another possibility is the inclusion of nanoparticles of an active material with high capacity and high volumetric expansion properties on a passive matrix or with a low volumetric expansion. Furthermore, nanotechnology could allow the realisation of artificial organic/non-organic composite materials.

It is also interesting to notice that the performance expected for the battery strongly depends 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 required application.

2.1.2 Electrodes[5]

Power density

The power density of a Li-ion battery depends on the ion migration rate between the two electrodes. The transfer of ions from electrode to electrolyte or vice versa (discharge and charge) is an important stage of this process, and often limits the migration rate. This rate depends on the conductivity of the electrode materials, and of the electrode/electrolyte interface. Most of the materials currently commercialised or considered as forthcoming replacements exhibit a moderate ion migration rate. To overcome this limitation, nanostructured electrode materials are being developed that provide high surface area and short diffusion paths for ionic transport and electronic conduction.

This can be achieved by nanostructuring (nanoparticles, nanocomposites, nanotubes, aerogels…)[6,7] the positive and/or negative electrodes, or coating them with nanomaterials[8,9]such as nanowires or mesoporous materials. Nanowires have an advantage in this respect over nanoparticles as they efficiently facilitate good electrical conduction paths.

Furthermore, reducing the morphological characteristic length size of electrode active materials brings several advantages. Firstly, the increase of the contact surface between electrode and electrolyte could allow high charge/discharge rates (up to 6 times the value of bulk materials without degrading the storage capacity). Secondly, the decrease of the ions (Li^+, H^+) diffusion path inside the active materials could allow the use of less conductive materials, the use of high charge/discharge rates or lead to a significant improve of the high-rate capabilities. These two points are likely to increase the power density, which is linked to the charge and discharge processes rates.

Lifetime

A better mechanical resistance of particles(electrodes?) against volume variations caused by insertion/removal of H^+ or Li^+ ions could be obtained using mesoporous materials (‘honeycomb’ structures), or by selecting materials displaying good layering properties due to their intrinsic structure. This stabilises electrodes throughout a higher number of cycles, thus allowing a longer lifetime.

The main limitation of the large area nanostructured surfaces is induced side reactions with the electrolyte, especially at high voltages and temperatures, resulting in poor cyclability. This problem could be solved by using nanoarchitectured materials with which couple external micro- or mesoscale particle sizes to internal nanosized grains. Such properties are offered by nanotubes: their diameter is around 200 nm, their length around several micrometers but the particles composing the tubes walls have sizes between 10 and 40 nm. These tubular architectures help reducing the side reactions while maintaining the benefit of nanosize effects.

Positive electrode

For several years it has also been known that the reduction of the size of the active material particles could improve the kinetics of ion insertion[10] and therefore stabilize new phases. Indeed, when approaching nanometric sizes of particles or films, the number of surface atoms could potentially become significant even dominating in comparison to volume atoms. Otherwise, the surface proximity of the particles has an influence on the constitution of the bulk material: the arrangement and the mobility degree of bulk atoms are thus modified.

Nanostructures of vanadium oxides or lithium intercalation hosts incorporating manganese oxides might also be particularly useful.[11] The storage and rate capability depends on the nanostructure morphology: coreshell nanocables exhibit better performances than nanotubes or nanorods, which in turn achieve better performances than bulk material. Vanadium oxide is a typical intercalation compound as a result of its layered structure. For Li-ion intercalation applications, vanadium oxide offers the advantages of low cost, easy synthesis, and susbsequent high energy densities. This material has been synthesised in various nanometric size structures (nanotubes, nanofibers, nanoribbons…). These positive electrode materials could contribute to an increase of power density of Li-ion batteries for various applications.

$LiMn_2O_4$ or $LiCo_2O_4$ are commercial positive electrode compounds. But they still suffer from limitations that could be overcome using nanomaterials. For instance, $LiCoO_2$ displays a moderate electrical conductivity, limiting the intercalation/de-intercalation kinetics. To improve this mechanism, it would be necessary to downsize the material to achieve short diffusion distance and large surface area.

An increase of battery power is also possible using a thin nanostructured layer at the positive electrode surface. A high active surface improves indeed the storage capacity of lithium and increases the diffusion kinetics. However, increasing the active area also increases the reactivity of the electrodes surface with the electrolyte, leading to safety concerns (one of the most critical issues for lithium batteries, especially for EV applications) and poor battery lifetime. A compromise needs thus to be found, for example by using materials with a low reactivity, such as $LiFePO_4$, which is one of the most studied material for batteries cathodes. Its relatively low cost makes it a very promising material for applications. The main drawback of $LiFePO_4$ is its low electronic conductivity, which tends to limit the capacity of the system. Many recent works try to improve this parameter by adding conductive material (such as carbon nanotubes), to obtain a nanocomposite structure or a coating of the nanosized $LiFePO_4$ particles[12,13,14,15]. These composites and coatings are synthesised by various processes[16,17], which could result in higher Li^+ intercalation capacity systems for high energy applications, like electric vehicles[18].

Negative electrode

The use of mesoporous SiO_2 is advantageous to better control the expansion/contradiction of the electrode material due to insertion/removal of Li. The mesopores act as a buffer, improving the cyclability. Si and Ge nanowires allow the improvement of the cycling performances in comparison with bulk materials as they reduce both the stress and the Li diffusion path and also improve the electronic conduction.

For the anode, the main performance limitation is due to the degradation of the electrode due to high strain induced by the high volume of lithium inserted during charge phase. Much effort is devoted to studying alloying reactions that are the subject of renewed interest following the downsizing of particles, moving to nano-textured/nanostructured composites and subsequent new electrode concepts[19].

Two other significant problems which severely limit the practical voltage and Coulombic efficiency of battery electrodes are passivation and corrosion.

Several solutions have been proposed to overcome these difficulties. One possibility is to implement silicon nanowires onto the anodes to improve the electrical storage capacity of the Li-ion battery. The lithium is inserted in Si nanowires. As the nanowires can easily inflate, absorbing positively charged Li cations during charge without being damaged, the degradation of the battery as a whole is reduced[20]. Silicon nanocomposites are actively studied for this application, since they allow a high lithium insertion capacity. Si nanoparticles (with a size down to a few tens of nanometers) are being developed with the hope that the battery capacity will be greatly improved, compared to current graphite electrode technology. The main drawback is the poor conductivity of silicon. Therefore, it is usually blended with a material that better carries electrons, such as carbon nanostructures or carbon black... This nanocomposite material can be inserted in a binder, a metallic or polymer matrix. So far, nanoparticles are preferred to nanowires as the manufacturing process is easier.

Tin is also a good candidate thanks to its gravimetric capacity, which is twice that of graphite carbon, and its moderate average working potential. However, the cyclability and large irreversible capacity of tin electrodes limit the performance. A solution is then the development of nanostructured tin oxide because these materials achieve good capacity retention and a high rate capability which mostly depends on the morphology as it is measured in hollow structures, nanowires mesopores and nanorods. For mesopores inside bulk particles, the benefit is that the pores act as a buffer layer for volumes change of the pore walls. The capacity retention is then improved and the volume expansion and contraction is controlled. As a consequence, the cycling stability is much improved and reversible change in the state of the pores without damaging the mesopore structure is possible. With a value of 95% after 30 cycles the retention capacity is better in mesoporous SnO_2 than in SnO_2 nanoparticles (63%). Hollow SnO_2 nanotubes waste the core of the particles, decreasing the volumetric density of the electrode. This irreversibility tends to limit the capacity of tin-based systems. To try to solve this problem, the mesosphere core/shell SnO_2 has been developed.[21]

Another enhancement for lithium storage technology is the use of nanocomposite materials[22]. Recently, Sony implemented a tin-based amorphous composite anode (NEXELION battery) which led to a lithium ion storage capacity per volume ratio that increased by 50%, which increases the overall battery capacity by 30%[23].

The previously discussed solutions tend to shorten the recharging time. Carbon nanotubes can also incorporate more lithium than traditional graphite electrodes.

Also for these systems, a major issue is the reversibility of the insertion mechanism, which remains a problem.

Alternative concepts

In order to increase the electrode/electrolyte surface area, other structures have been investigated, such as porous carbon based materials infiltrated with $LiFePO_4$ precursor[24], or even three dimensional structured electrodes[25,26].

Besides active materials for electrodes, other functional materials could be present in electrodes such as current collectors, electronically conductive additives and binders used to insure the cohesion of the electrode. Nanostructuring of the current collectors could improve the exchange surfaces by adding active layers and thus reduce the overall contact resistance[27] as well as possibly leading to entirely new battery architectures[28].

Three dimensional structures can be obtained by mimicking nature[29]. The most advanced study[30] of this method looks at the synthesis of a virus which has an affinity for carbon nanotubes, and is capable of nucleating amorphous iron phosphate. The use of this kind bio-inspired material system is a promising proposition for use as cathode material compounds which has been previously excluded because of its low electronic conductivity. This approach could significantly enlarge the choice of electrode materials for high power batteries[31].

2.1.3 Electrolyte

'Real' solid electrolytes are inorganic components that are either amorphous (glassy electrolyte) or crystalline. The main limitation of these electrolytes is their low conductivity at ambient temperature. These materials require either a high operating temperature or their manufacturing as thin films to properly function. Firstly thinning the electrolyte can improve performance. but this decrease of the thickness is limited by the subsequent mechanical integrity. Secondly, the creation of limited defects at the interface of the electrolyte and a second phase that allows a preferential diffusion of electrolytes ions has been proposed. The second phase could be a second electrolyte whose composition is slightly different, or the addition of a passive component. The overall conductivity of the mixture increases with the number of defects created whose number could be multiplied by the use of nanoparticles with a high specific surface or by alternating the 2 previous materials in a thin layer of around 10 nm. Thirdly, the use of alumina, silicon or zirconium nanoparticles in a non aqueous electrolyte can lead to an increase of the electrolyte conductivity by a factor of 6.

For polymer electrolytes, the use of nanocomposites can allow high efficiency, safe and green batteries. Moreover, the use of ceramic nanomaterials as separators in those polymer electrolytes leads to an improvement in ionic conductivity of 10 to 100 times.[32]

The already high ionic conductivity of liquid, gel or polymer electrolytes could be further improved with the use of nanomaterials. Solutions proposed should then bring other properties, for example new mechanical properties. As these electrolytes are not solid, unwanted contact between electrodes is possible. To avoid this, microporous separators are necessary, which should have a sufficient mechanical resistance to be handled in an industrial environment without being damaged. Nanotechnology provides new perspectives by allowing the possible increase of the porosity of the separator without decreasing the mechanical performance.

Also, to improve the safety of battery systems, avoiding short-circuit between electrodes could be achieved through the use of ceramic or polymer-gel electrolytes. Solid ceramic materials are also interesting because of their high temperature resistance. Nanoparticles added to solid polymer electrolyte (like poly-ethylene oxide-based polymers) might significantly increase the electrolyte conductivity. The further nanostructuring of these materials could improve the storage capacity of the electrolyte.

2.1.4 New processes

The use of those nanotechnologies, especially carbon nanotubes, recently led to the realisation of paper thin batteries, around size of a postage stamp. These batteries can be printed like paper, rolled, twisted, folded or cut into shapes without a reduction of mechanical integrity or efficiency[33]. However, they require protection by an encapsulation which limits the ease of recharging.

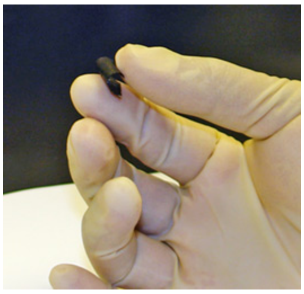


Figure 3: Example of paper thin battery

2.2 Additional demand for research

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

A compromise between electrode surface area increases and safety concerns should be addressed by a better understanding about interface processes. Various new studies are underway to better understand the behaviour of the battery during fast charging and to find the cause of the formation of metallic Li dendrites, which are a source of heating and sometimes catastrophic failure.

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

A better cooperation between material scientists, electrochemists, and battery engineers should improve the efficiency of research projects on electrochemical energy storage device developments.

2.3 Applications and perspectives

The performance requirements of batteries depend greatly on the particular applications. The following is a classification of the various applications of battery systems.

High specific energy capacity in the range of 250 Wh to 5 MWh is required for stationary applications such as the storage of alternative energy (PV, wind …) electrical production, emergency power, UPS (Uninterruptible Power Supplies) or for spatial applications. Specific energy in the range of 20 to 650 kWh is necessary for transport applications (hybrid, plug-in and full electric vehicles, tramway/subway, locomotives …). The latter application also requires high specific power. The batteries are here obviously secondary (rechargeable), mostly based on NiMh or increasingly on lithium-based technology. The lifetime depends on the certain application and is expected to be for example around 10 years for transport applications.

A mean specific energy from 2 Wh to 100 Wh is required for portable applications (cellphones, laptop, cameras, toys …) or from 100 to 600 Wh for starting lighting and ignition batteries (cars, trucks, buses, wheel chairs …). In addition, a high specific power is required for applications like power tools. The batteries used are mostly secondary (rechargeable) systems which require a lifetime in the range of 2 to 5 years. Longer lifetime is often not necessary as it could become greater than the lifetime of the device itself.

A low specific energy (from 100 mWh to 2 Wh) is required for medical devices and medical implants as well as for small applications like electric watches or calculators. The batteries used are mostly primary, non rechargeable cells whose lifetime is in the range of 1 to 2 years for small applications and up to 15 to 20 years for medical implants. The technology used may then range from simple alkaline to Li-ion batteries.

Some of the previously cited applications are very restrictive concerning safety requirements either due to the quantity of contained energy (transport or stationary applications) or because of the nature of the application itself (medical implants).

New battery developments are also expected to succeed to Li-ion and Li-polymer technology. The first technology in development is the Li-air battery. This combines a positive electrode identical to that of a conventional Li-ion battery and a negative electrode based on a fuel cell working principle. This is intended to reach a theoretical mass energy density of 3500 Wh/kg. Nanotechnology could be useful to improve the negative electrode performance the same way that has been described in this report and the positive electrode performance by reducing the quantity of catalyst used.

The second technology in development is Li-S battery. This is a secondary battery expected to deliver up to 500 Wh/kg or 600 Wh/l. However, these currently suffer from the low ionic and electronic conductivity of sulphur, difficulties to impose cycling at satisfying rates to the electrode and degradation of the electrochemical performance during cycling (polysulphide formation). Nanotechnology could address the low ionic conductivity and thus allow charging/discharging at a rate above C/10. The penetration of sulphur by capillary action into a mesoporous carbon structure creates a nanocomposite carbon/sulphur. The solidification of the composite leads to a special nanostructure.[34] The confinement of the sulphur inside the carbon structure ensures the cycling stability.

2.4 Current situation within the EU

Along with photovoltaic systems, batteries represent a challenging energy market. Large companies have understood how strategically important the development of their own high performance batteries is. Thus in mid-June 2009, General Motors officially opened a 3,000-square-meter battery lab at its technical centre in Warren, MI. This lab is being used to test battery cells and packs for the forthcoming Volt plug-in hybrid vehicle and is part of GM's strategy to develop its own battery packs, just as it now develops its own gasoline engines.

In Europe, an important linked community named ALISTORE groups academic and industrial in a European network dedicated to the development of nanotechnology for electrodes, electrolyte and current collectors and of accurate characterisation methods. The research and development are distributed among the various members.

To prove the feasibility at an industrial scale, the fabrication kg-sized quantities of materials is required. A production at a much higher rate (tons) will indeed allow the reduction of costs.

Chapter 3 Economic aspects

3.1 General market description

The market for batteries is divided into three segments; portable devices, stationary, and transportation. Of these, portable storage is the largest existing market, but transport applications – particularly in electric (EVs) and hybrid electric vehicles (HEVs) will stimulate significant market expansion in the coming decade.

3.1.1 Portable Devices

The portable device market includes batteries for mobile phones and computers. 1.1 billion mobile telephones were produced and sold in 2009, each requiring a battery with a storage capacity of around 3Wh for a total annual market of 3.3 MWh. DisplaySearch records shipments of 169.6 million portable PCs during 2009. This is projected to increase by 16% to 197.8million units in 2010.[35] Whilst the number of units is less, portable PCs require additional power, of around 70Wh per unit. This places the total market for portable device batteries (including mobile phones) at 15 200 MWh/year.

Current battery technologies for these applications are Nickel Cadmium (NiCd), Nickel-Metal Hydride (NiMH), Lithium Ion (Li-ion) and Lithium Ion polymer. Over recent years there has been a shift from Nickel MH or NiCD to Lithium based batteries, mainly because of the latter's superior energy and power densities. Higher energy density enables the use of lighter batteries, which is significant in applications – such as mobile phones and netbooks - in which the battery represents a significant proportion of the weight of the device.

3.1.2 Stationary and Grid-Connected Storage

A growing need for batteries is in stationary applications and grid connected storage. This includes energy storage systems that are connected to the electricity grid in order to perform frequency regulation, balance intermittent power source, to cope with periods of high demand, and as auxiliary power supplies for applications in case of power grid failure.

Large scale storage is currently achieved with kinetic means, including pumped hydro and compressed air storage. Also used – more often for applications with slightly lower power requirements – are sodium sulphur batteries.

Because nuclear power stations generate electricity continuously, electricity should be stored as demand varies. Equally, intermittent sources of power- particularly solar and wind – require an energy storage capacity. This need is likely to increase as these sources become more widely used. Utilities also have a need for frequency regulation. Whilst they may be able to predict average hourly levels of demands, a storage capacity is required to handle variations around the mean.

These applications typically demand very high storage power capacity. The world's largest battery at the time was installed in the city of Fairbanks, Alaska in 2003 and was designed to provide 40 MW of power for up to seven minutes.[36] The southern Californian energy company SoCal Edison is planning to build a 32 MWh battery array to stabilise electricity coming from a wind farm. If approved, the utility plans to partner with A123 Systems, a developer of nanotechnology-based battery systems.[37] The current value of grid-connected energy storage is estimated to be $365 million, growing to $2.5 billion by 2015. [38]

Reducing the cost and increasing the energy density of Li-Ion batteries should lead them to take a greater share of this market. Pike Research predicts that Li-ion batteries could represent as much as 26% of the energy storage market by 2018 (a market which they value at $4.1 billion). However, batteries developments will also compete against non-battery solutions for energy storage, including flywheels.[39]

3.1.3 Transportation

Applications of batteries in Electric and Hybrid-Electric Vehicles are the most important developing market, given the sheer amount of Wh required in these applications. Almost all automotive firms have or are planning to introduce vehicles in which some or all of the propulsion comes from electric power.

Power requirements of these applications vary. A fully electric vehicle (EV) requires 25 kWh, whereas a Plug-in Hybrid (PHEV) which also has an internal combustion engine requires 12.5 kWh. Hybrid vehicles can also be describes as full (requiring 2.5 kWh) or mild (1.25 kWh) depending on the extent to which they rely on electric power. The various types of electric vehicle are occasionally referred to collectively as xEVs.

Whilst the Toyota Prius is the best known of the current crop of hybrid vehicles, manufacturers are planning vehicles which require even more electrical power. The Nissan Leaf will be a full EV, and the company plans to produce 50 000 units in 2010, rising to 200 000 per year in 2012. General Motors is planning to sell 50 000 units of its PHEV, the Chevy Volt, in 2010.[40]

The share of EV and HEV vehicles in the total automotive market is projected to be 6% in Europe in 2015, reaching 27% by 2020. Globally, Roland Berger projects that there will be 4.1 million xEVs on the road in 2015.[41]

The predominant battery technology for transportation applications in the future is thought to be Li-ion, largely due to its technical advantages over other battery types. Most of Li-ion cells are been produced in Asia - over 95% of Li-ion cells shipped in 2009 were produced by Japanese, South Korean or Chinese manufactures. This is the consequence of several factors, including R&D subsidies from the respective governments, and the fact that these countries also have high volume consumer electronics production (for which Li-ion cells were originally intended).[42] Whilst there are European producers of Li-ion batteries, including Saft, Leclanche and Li-Tec, volumes are substantially lower than Asian competitors.

3.2 Drivers and barriers

3.2.1 Drivers of Market Growth and Technology Development

The underlying drivers behind transportation (and to a lesser extent, stationary applications) are efforts to reduce carbon emissions. This is reflected in a favourable policy framework – European governments have pledged to reach certain numbers of EVs on the road by 2020; two million (France), 1 million (Spain and Germany). In many cases EVs benefits from favourable tax conditions such as reduced value added tax at purchase, or lower road tax. Renewable electricity generation also benefits from policies such as feed-in tariffs.

Asia's dominance in Li-ion battery production is in part due to historically high public funding support for R&D. More recently the United States has made significant investments in battery production, allocating $2.4bn from its economic recovery package to support plant construction. Individual states have also contributed significant funding; Michigan, for example, has made $335 million in tax credits available.

Individual European countries have made subsidies available for Li-ion production, albeit on a smaller scale. Nissan is building battery plants alongside existing facilities in Portugal, for which it has received public subsidies of €46 M, and the United Kingdom. Daimler's purchase of a 49.9% stake in Li-Tec was supported with €60 M from the German government, and CEA has supported Renault's construction of a battery manufacturing facility near Paris.

In expectation of large and growing markets, battery firms have also received significant amounts of venture capital. Lux Research places investment at $600 million in 2009, an increase from $478 million in 2008.[43]

3.2.2 Barriers

One of the barriers to entry in this sector is the high cost of research and development and plant investment. The cost of a 100 000 unit plant is estimated to be €350 M, in addition to €50-100 M for the development of new cell chemistries. This accounts for the low number of small companies in this space, and restricts smaller firms that are unable to raise such funding to the position of technology supplier.

3.3 Functional Requirements and Boundary conditions

3.3.1 Cost

For all applications but particularly transportation, cost is a critical factor. Batteries are expected to account for a high proportion of the cost of electric vehicles, and unless reduced, this will compromise the ability of EVs to display the internal combustion engine.

However, the large amounts of investment that companies have received have led to cost reduction through technology development and production process optimisation and scaling. The current cost per kWh of a prismatic Li-Ion cell is estimated to be $650/€475 at present. This would mean the battery in the Nissan Leaf would cost 11 400€. There are indications that this price is dropping, with reports that manufacturers have signed large scale supply contracts for batteries at a cost of $400 / €290 per kWh for supply in 2011/2012.[44]

3.3.2 Energy Density

An important factor in portable and transportation applications is the energy density of the battery – for transportation, every additional gram of battery weight also increases the energy requirement. Energy density is expressed at Wh/kg, and the target for 2015 is to increase this to 200-300Wh/kg, placing the weight of the battery in the Nissan Leaf at 80kg. This requires significant technology innovation to increase power density, and is the driving force for much of the research in this area.

3.3.3 Charge/Discharge Cycles

To be suitable for use in portable or transport applications, a battery must also be able to undergo thousands of charge/discharge cycles. The target level here is around 3000 cycles – which would equate to be being charged and discharged every day for ten years.

3.3.4 Safety

To be accepted by transportation safety regulators, batteries for transportation will also need to demonstrate that they will not explode if overcharged or punctured. This has been one of the drivers for research, particularly with cell separator membranes, and is a selling point of A123's nanophosphate electrode technology.

3.4 Economic information and analysis

3.4.1 Company Revenues

Some information about the current status of nanotechnology for batteries is provided by the revenue information from publicly traded companies. A123 Systems is the most high-profile user of nanotechnology for batteries, with a technology which uses a nanophosphate electrode to increase energy density and battery stability. The company listed on the New York Stock Exchange in 2009 (the first nanotechnology linked company to list for some years) and has 1800 employees.

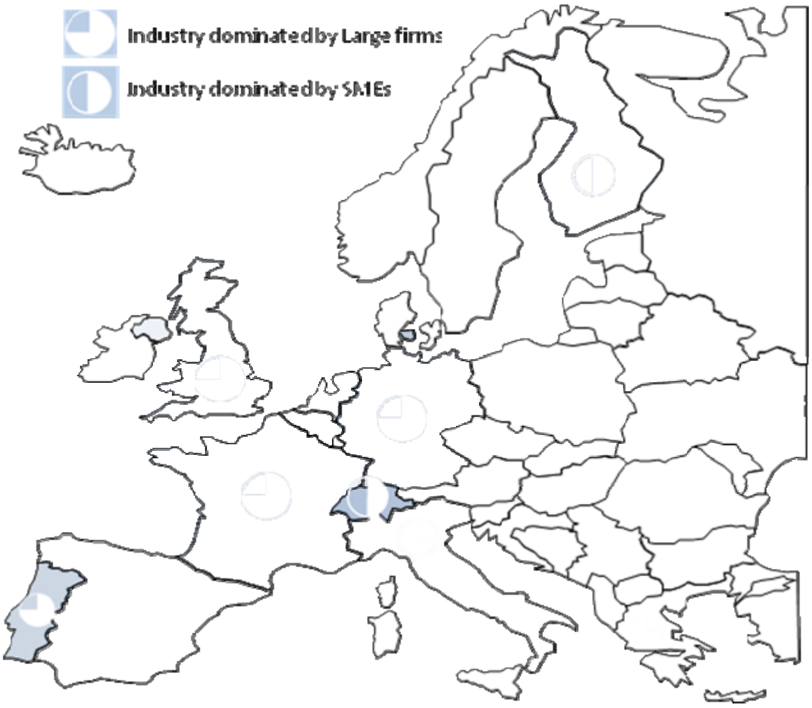
A123 Systems reported revenues of $91 million for 2009, and sold batteries to all three markets. Revenue from transportation revenue grew 359% to $45.3 million, helped by the sale of a conversion kit enabling a car to be upgrade from hybrid to a plug-in hybrid vehicle (PHEV). The company saw revenue from the provision of grid-connected storage grow 282% to $11.1 million. Revenue from consumer applications decreased by 51% to $20.1 million – one of the company's earliest applications was in battery packs for power tools, but the company is likely shifting to higher growth higher volume markets.[45]

Altair Nanotechnologies develops batteries using nanoscale titanium dioxide in the anode. The company is mainly focused on stationary and mass transportation applications, and recorded revenues of $4.4 million in 2009, dropping from $5.7million in the previous year. [46]

3.5 Selected company profiles

3.5.1 European Companies

Whist this market is dominated by Asian firms, Europe does have battery manufacturing and particularly firms working with Li-Ion battery technology. However, as the following figure shows, these are dominated by medium-sized and large firms.



LiTec, a joint venture between Evonik and Daimler, is producing Li-Ion batteries for transport applications in Germany. These use a ceramic separator membranes developed by Evonik and marketed under the name SEPARION®.[47] The membranes use Al_2O_3/SiO_2 particles which are fixed in place by a Sol-Gel-process. The primary benefit of this is to make the battery more durable, preventing explosion when it is overcharged or punctured. Evonik is also investigating the use of nanoparticles in the silicon anode to reduce the stress caused by battery cycling. The company states that “nano structured materials will play an important role in all parts of next generation Lithium ion batteries.”[48]

Company	URL	Country	Size	Technology
Johnson Controls-Saft Advanced Power Solutions	http://www.saftbatteries.com	USA / France	Large	Li-Ion batteries for electric vehicles
SB LiMotive	http://www.sblimotive.com/	Germany / South Korea	Large	Joint venture of Samsung and Bosch to create Li-ion batteries for electric vehicles
Li-Tec	www.li-tec.de	Germany	Medium	Joint venture of Evonik and Daimler. Manufacturing Li-ion cells for transportation applications, using nanotechnology-based seperator membranes developed by Evonik.

Axeon	www.axeon.com	UK	Medium	Supplier of lithium-ion battery system
European Batteries	www.europeanbatteries.com	Finland	Medium	Large scale Li-Ion batteries
Leclanche	www.leclanche.eu/home.1.0.html	Switzerland	Medium	Produces Li-ion batteries for all application sectors

3.5.2 Rest of the World Battery Manufacturers

Many companies are developing batteries for portable, transport and stationary applications, and several of these are investigating nanotechnology-based approaches. The US-based company Ener1 produces batteries for HEVs and EVs, and has a subsidiary - NanoEner – which develops nanostructured thin films for battery electrodes. The company uses a variety of chemistries with its batteries, including a hard carbon anode to increase durability.

BYD, a Chinese manufacturer of batteries and electronic components, is notable for both its scale and structure. The company, which employs 160 000 people, originally entered the battery to produce mobile phone batteries for Motorola. It has made substantial investments in Li-ion battery production to build production capacity of 4 MW, and has adopted a highly vertically integrated structure – from lithium mining to the production of EVs.[49] The company is known to be using $LiFePO_4$ as a cathode material.

Company	URL	Country	Size	Technology
A123 Systems	www.a123systems.com	US	Large	Nanophosphate electrodes
LG Chem	www.lgchem.com	South Korea	Large	Manufacturer of Li-ion and Li-ion polymer cells for portable and transport applications.
BYD	www.byd.com	China	Large	Diversified electronics manufacturer. Produces lithium-ion ferrous phosphate batteries, and has explored building own electric vehicles.
Altair Nanotechnologies	www.altairnano.com	USA	Med	Develops nano-structured lithium titanate as a replacement for graphite in Li-ion batteries.
Toshiba	http://www.scib.jp/en/	USA	Large	Has two plants producing Super Charge ion Batteries (SCIB)

GE	www.getransportation.com	USA	Large	GE's transportation division is setting up a plant to produce a high energy-density sodium-metal-halide cell, particularly targeted at rail locomotives.
Panasonic Sanyo	sanyo.com	Japan	Large	Formed after Matsushita (formerly Panasonic) aquired a majority stake in Sanyo. Manufacturers Li-Ion batteries for portable and transportation applications.
NGK Insulators	http://www.ngk.co.jp/english/index.html	Japan	Large	Manufactures Sodium Sulphur batteries for stationary applications.
Compact Power	www.compactpower.com	USA	Large	North American subsidiary of LG Chem
Maxwell	www.maxwell.com	USA	Medium	Developer of ultracapacitors
Valance	www.valence.com/	USA	Medium	Manufactures Lithium Iron Magnesium Phosphate batteries
NanoEner, Inc., (wholly owned subsidiary of Ener1)	www.nanoener.com	US	Large	Production of nanostructured coatings
Amprius	www.amprius.com	US	Small	Silicon nanowire anodes

Annex: Expert Engagement

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