

STRATEGIC ENERGY TECHNOLOGY PLAN

Scientific Assessment in support of the Materials Roadmap enabling Low Carbon Energy Technologies

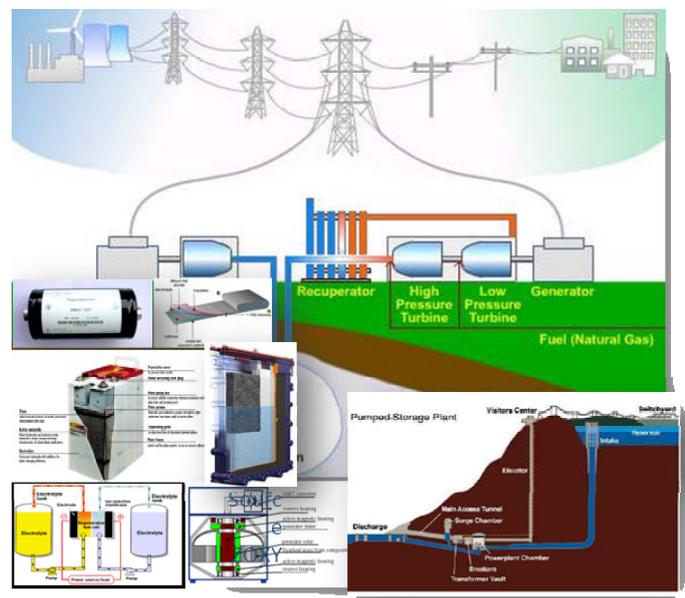
Electricity storage

Authors:

M. Rosa Palacin, Anne de Guibert, John Collins, Marcel Meeus,
Gerd Schumacher and Florence Fusalba

JRC Coordination:

A. Perujo, E. Tzimas



EUR 25143 EN - 2011

The mission of the JRC-IET is to provide support to Community policies related to both nuclear and non-nuclear energy in order to ensure sustainable, secure and efficient energy production, distribution and use.

European Commission
Joint Research Centre
Institute for Energy and Transport

Contact information

Address: Adolfo Perujo
E-mail: adolfo.perujo@ec.europa.eu
Tel.: +39 0332785175
Fax: +39 0332785236

<http://iet.jrc.ec.europa.eu/>
<http://www.jrc.ec.europa.eu/>

Legal Notice

Neither the European Commission nor any person acting on behalf of the Commission is responsible for the use which might be made of this publication.

***Europe Direct is a service to help you find answers
to your questions about the European Union***

Freephone number (*):

00 800 6 7 8 9 10 11

(*) Certain mobile telephone operators do not allow access to 00 800 numbers or these calls may be billed.

A great deal of additional information on the European Union is available on the Internet. It can be accessed through the Europa server <http://europa.eu/>

JRC 68159

EUR 25143 EN

ISBN 978-92-79-22606-9 (pdf)
ISBN 978-92-79-22605-2 (print)

ISSN 1831-9424 (online)
ISSN 1018-5593 (print)

doi:10.2788/401 (online)

Luxembourg: Publications Office of the European Union, 2011

© European Union, 2011

Reproduction is authorised provided the source is acknowledged

Printed in the Netherlands

Preamble

This scientific assessment serves as the basis for a materials research roadmap for Electricity Storage technology, itself an integral element of an overall "Materials Roadmap Enabling Low Carbon Technologies", a Commission Staff Working Document published in December 2011. The Materials Roadmap aims at contributing to strategic decisions on materials research funding at European and Member State levels and is aligned with the priorities of the Strategic Energy Technology Plan (SET-Plan). It is intended to serve as a guide for developing specific research and development activities in the field of materials for energy applications over the next 10 years.

This report provides an in-depth analysis of the state-of-the-art and future challenges for energy technology-related materials and the needs for research activities to support the development of Electricity Storage technology both for the 2020 and the 2050 market horizons.

It has been produced by independent and renowned European materials scientists and energy technology experts, drawn from academia, research institutes and industry, under the coordination the SET-Plan Information System (SETIS), which is managed by the Joint Research Centre (JRC) of the European Commission. The contents were presented and discussed at a dedicated hearing in which a wide pool of stakeholders participated, including representatives of the relevant technology platforms, industry associations and the Joint Programmes of the European Energy Research Associations.

Table of Contents

Preamble.....	3
Table of Contents	5
Context of electricity storage	7
Technologies and Systems State of the Art and Challenges	7
Why focusing on storage for stationary applications?	8
Second life concept: storage for both mobile and stationary applications.....	9
What are the main drivers for energy storage?	10
Reference technologies for stationary applications.....	11
Sorting energy storage technologies by stationary power levels	11
Why focusing on battery technologies?	11
Key materials.....	12
Technology and manufacturing processes challenges	12
Lead acid.	12
Li-ion.....	12
Sodium high temperature.	13
Flow batteries.....	13
Super capacitors.	13
Material Supply Status and Challenges.....	13
Electrochemical storage systems.....	13
Cobalt has a special position for batteries.....	14
Materials supply	14
Sodium-Ion.....	15
Ni-MH.....	15
Graphite.....	15
Vanadium	15
Zinc.....	16
Cerium.....	16
Catalysts (Precious metals)	16
Membranes	16
Current and Future Supply Status	16
Recycling and Substitution.....	16
Risk Analysis.....	17
On-going Research and Actors in the Field of Material Research for Energy Technology	
Applications and Challenges.....	18
Current Research on Batteries.....	18
Lead-acid manufacturing companies	18
Ni-MH metallurgic companies.....	18
Li-ion.....	18
Flow batteries	19
Super capacitors (SC).....	21
Flywheels	21
Superconductors	22
Hydrogen Energy Storage	22
Other systems	23
Main programmes at EU and Member State levels.....	23
Focus on European Union.....	24
In member states.....	25

On-going efforts in other developed countries.....	26
Material's Specification Targets for Market Implementation in 2020/2030 and in 2050.	29
Specification targets for Market Implementation in 2020	30
Objectives for cost of materials.....	31
Energy segment.....	31
Power segment	32
Specification targets for Market Implementation in 2030 to 2050 (or 2030 and beyond)...	32
Synergies with other Technologies	33
Level 1.....	33
2 steps: before 2025 and after 2025.	33
Level 2.....	34
Synergies between consumer electronics, automotive and storage (i.e. metal air).....	34
Especially regarding Li ion technologies	34
Post Li-ion tank of new ideas	34
Level 3: Today	34
Between materials on different technologies (i.e. Super capacitors and batteries and Fuel Cells...)	34
Between manufacturing processes	35
Needs and Recommendation of Activities addressing 2020 and 2050 Market Implementation	36
Needs and recommendations for Market Implementation in 2020/2030.....	37
Related to Battery Materials: @ EU and MS (Member State) vehicle level	37
Related to Super capacitors (EDLC): @ EU and MS (Member State) vehicle level.....	42
Related to Hydrogen/Fuel Cells: @ MS (Member State) vehicle level (not fully detailed because drafted in Hydrogen and Fuel Cells Chapter).....	42
Related to Flywheels: @ EU and MS (Member State) vehicle level.....	43
Related to SMES: @ EU and MS (Member State) vehicle level.....	43
Related to CSP Thermal: @ EU vehicle level	44
Related to manufacture designs and processes (needs new smart materials) for batteries and super capacitors or others: @ EU and MS (Member State) vehicle level.....	44
Related to pumped hydro: @ EU and MS (Member State) vehicle level	44
Related to CAES: Demonstration @ EU and MS (Member State) vehicle level	44
Electric Vehicles (EVs), advanced control systems and power electronics for efficient grid connection [31]: @ EU vehicle level.....	45
Safety organizations	45
Main research Challenges	45
Excellence	46
Needs and recommendations for Market Implementation in 2050	46
To conclude.....	47
Road-mapping process (See Material Roadmap document)	49
ANNEX I: References.....	50
ANNEX II: Figures and Tables.....	52
ANNEX III: Safety, cost, feasibility and environmental aspects additional parameters to be considered when selecting a system for a given application.....	63
APPENDIX: More detailed data on electrochemical storage technologies and their evolution	66

Context of electricity storage

The evolution of the electricity sector (economic, environmental, institutional and technical) and technology development (chemistry, electronics, materials ...) are forcing an increasing role of energy storage in our current society. More flexibility will be needed in the system, especially if the integration of massive renewable energies takes place and storage is one of the solutions to bring about such flexibility.

The present technology roadmap focuses on materials which are key drivers in the development of energy storage. Considering only a single revenue stream for a unique application is most of the time insufficient to balance the costs of the device and reach energy storage profitability. To maximize the energy storage benefits, all the applications need to be taken into account and the market design must enable aggregation of different streams revenue. To validate these, R&D studies, dedicated simulation tools and demonstration projects will be needed at the European level.

Besides, while the storage requirements in the power systems, from centralised to distributed to the customer, remain to be more precisely defined, energy storage must also be able to fulfil the requirements in electricity markets.

Technologies and Systems State of the Art and Challenges

Energy storage systems include different technologies, with different sizes and different levels of development. They can roughly be classified according to how much energy they can store, for how long and how quickly they can release it (storage capacity, available power, discharge time, efficiency, durability, autonomy...) Additional parameters to be considered when selecting a system for a given application (see Annex III) are safety, cost, feasibility and environmental aspects.

Some of the main technologies are reported below with their strengths and weaknesses:

- Electrochemical storage (Batteries and super capacitors): Proven technologies in consumer electronics and automotive, large storage systems in the initial phase of deployment [1]; Different systems based on different chemistries and processes offer high versatility in performance.
- Pumped Hydro: GW storage capability, lowest cycle cost but high capital costs; need of suitable geographical locations
- Compressed Air Energy Storage (CAES): Energy from various sources can be stored. Different versions are today available : Diabatic CAES (> 100MW, > 1GWh), based on the two first Huntorf and Mc Intosh systems and which need extra-heat during discharge (55% of efficiency expected); Adiabatic CAES (> 100MW, > 1GWh) which are new concepts based on both compressed air and heat storage would enable to reach 70 % of efficiency: heat storage is the key point with today low technical maturity; Isothermal CAES (~1MW, ~4MWh) are low capacity and power storages based on an isothermal compression and expansion that lead to 70-75 % of efficiency (taking into account 95% of efficiency for each compression and expansion and others losses). LAES or CES for Liquid Air Energy Storage or Cryogenic Energy Storage (~50 to 100 MW, ~200 to 500 MWh) are studied in order to store liquid air: efficiency is in the same scope of CAES for higher cost due to its complexity. CAES needs suitable geographical locations. LAES or CES do not have the same constraint.
- Flywheels: Fast response in storage and release, (but technology not yet matures for large Systems discharge time at rated power in the range seconds to 15 minutes to date, expected to reach the hour in the years to come. Several noticeable advances have been announced over the past few years; for instance, as part of the DoE ARPA programme, Beacon Power is

installing a 20 MW / 15 minutes flywheel plant in New York State, U.S.A. Industry is less developed in Europe than the U.S. EU companies have concentrated on automotive and UPS applications so far, but are now paying increasing attention to the stationary market. Several UK have developed automotive flywheel technologies as kinetic energy recovery systems (KERS) for Formulae 1 racing, but are transferring the technology to domestic vehicles. (Flywheels are power systems needed for grid energy management delete). In power systems, flywheels could perfectly match the requirements of power (<15-30 minutes), high cycling applications such as primary frequency control or fluctuation mitigation of renewable.

- Superconducting magnetic energy storage (SMES): Electrical current is kept circulating in a coil under short-circuits conditions and so electromagnetic energy is stored. An associated power conditioner system allows fast charge and discharge of this energy. SMES and Flywheels are systems complementary to the existing electrochemical storage systems.

- Inertial energy storage (INES): A flywheel rotates under levitating conditions with a self-stable magnetic bearing including bulk superconducting materials and magnets and so kinetic energy is stored. An associated power conditioning system and a vacuum vessel is required for the whole system.

In both systems, SMES and INES, the energy density which can be achieved is limited by the stress, electromagnetic in the case of the SMES, and mechanical, due to the high speed of rotation for the flywheel. The energy density values which can be achieved are intrinsically low as compared to the present state of the art electrochemical batteries, however, the specific power which can be developed is very high, as well as the conversion efficiency¹ (>95%). Hence, SMES and INES systems should be more compared to super capacitors in terms of performance.

Major characteristics of the above mentioned energy storage systems (Key Technologies for Energy Storage, Challenges to Technology, Materials and Processes) are given in Table 1 [2] ANNEX II (Technologies performances and costs).

So far there is no universal storage solution. Various supply storage technologies allow responding different energy profiles depending on requested power rating and discharge time, as shown in Figure 1 ANNEX II. Indeed, priorities in criteria to be taken into account for the selection of a given energy storage systems are rather application dependent. While for portable electronics energy density is the prime factor, cost increases its impact when moving to larger scale applications.

Why focusing on storage for stationary applications?

So far, in terms of storage for the GRID the cost/benefit analysis blocked the adoption of new storage technologies. However storage is fostered by the huge increase in generation from renewable (solar and wind) which will require significant storage in order to be able to keep grid output quality. With the integration of the renewable energy, peak demand shaping, power quality and grid load have to be fully managed. Moreover, auto consuming becomes a reality when the electricity purchase incentive is revised, as happened in Germany (auto consuming grant). However, cost is still a major problem for tomorrow's deployment. Therefore, if the industry's growth in the vehicles is substantial there are huge manufacturing

¹ Authors note: conversion efficiency is usually used only to define the energy efficiency of the power electronic converters. For all storage medias, it is required to talk about "round trip" efficiency, which can be considered either on the storage side ("DC round trip efficiency") or calculated directly at the AC connection point ("AC round trip efficiency"). Roughly, we have: AC r-t eff. = DC r-t eff. X conversion efficiency² (the square is required because the conversion efficiency applies two times per cycle: during charging and during discharging). Moreover, the overall efficiency of storage systems must take into account the energy consumption of ancillary equipment such as heaters, air conditioning, vacuum pumps, etc.

economies of scale expectable and storage (even Li-ion) will find its way into grid applications. Also, development of second life applications (in the long term) will act as decisive parameters.

Even if so far there is a lack of agreed deployment and market frame, assuming an increase in generation from renewable together with improved power quality and expecting auto consuming, there is a feeling today that grid storage will be supplied by a combination of technologies at varied stages of development. These technologies can be classified in several ways but at least splitting it into two broad categories:

i) Energy applications involving storage systems discharge over periods of hours (typically one cycle per day). The strategy consists of adjusting and optimizing energy generation including reducing the large fluctuations that occur in electricity demand by storing excess electricity during periods of low demand for use during periods of huge demand. For instance in PV systems energy storage has to ensure a quasi-permanent energy supply no matter what the level of sunshine. A regulator enables management of the energy between the module, the battery, and the charge consumer. While many technologies have been proposed for electrical energy storage applications, only a handful have actually been used such as pumped hydro and CAES. In terms of batteries we can refer lead-acid, nickel/cadmium, sodium/sulphur, vanadium-redox flow batteries and some advanced batteries.

ii) Power applications involve comparatively short periods of discharge (seconds to minutes and many cycles per day). Faults, dynamic operations, or nonlinear loads often causes various types of power quality disturbances such as voltage sags, voltage swells, impulses, notches, flickers, harmonics, etc. In the field we can mention advanced batteries, flywheels, ultra capacitors and SMEs.

While focusing on stationary applications, there are several reasons indicating that storage for stationary and mobile applications are strongly linked: i) vehicle market is foreseen to rise up before grid; ii) because of economies of scale, similar storage solutions for both automotive and stationary markets will help decreasing cost; iii) regarding Li ion batteries, materials are generic; iv) one can start thinking in smart energy management concepts including the use of the battery car as storage back up for stationary applications; v) second life concept introduced to decrease battery pack cost of ownership in electric vehicles induces the need for a storage technology sized for both applications.

Second life concept: storage for both mobile and stationary applications

Electric vehicles (EV) and plug in hybrid vehicles (PHEV) arouse as a big hope but, in view of the high cost and of the weak life cycle of their batteries, their purchase seems difficult to pay off for a private individual. In this context, some car manufacturers make a commitment to spread vehicles equipped with Li-ion batteries which will have to find another use to guarantee a cost of usage of the electric vehicles comparable or lower than thermal vehicles. The concept of " Second Life" for Batteries from EVs thus consists in using the system of storage successively for the mobility of vehicles then for the applications susceptible to supply a complementary source of income to shorten the time of return on investment. Stationary applications are such "Second life" opportunity for batteries after electric vehicle usage. However, this role of car battery capacities for stationary application is still debated. There is a consensus that, in the near future, the car battery capacity will act only as an energy sink (possibly until 2020). Second life applications i.e. a use of a car battery in a stationary application is envisaged in this time frame, providing a possibility to amortize the usage cost between the two applications. In a longer time frame, it is expected a more dynamic use of car batteries (charge and discharge) with respect to grid applications. These applications will

imply more stringent requirements on materials, for instance, shortened battery lifetime due to high cycling.

Therefore, whatever the storage solution, energy storage is a key enabling technology for the penetration of clean vehicles (HEV, PHEV and pure EV) on one side, and use of intermittent renewable energies such as wind and solar energy [3].

However, one must consider that the underlying assumption of strong synergies between the requirements of storage solutions for stationary and mobile applications reported in this exercise is not a unanimous shared assumption. Especially if one can point out that today, there is no basis for believing that Li-ion technology should be preferred to other battery types in stationary grid applications.

Moreover, there are distinctive requirements of stationary applications with respect to automotive applications. While synergies do exist, in particular common material composition, technical aspects such as life duration, product life time or safety, reliability & low maintenance requirement are predominant for technology developments in stationary applications. While unit mass/volume is a major parameter for mobile applications, it is less important for stationary ones. Unlike the portable and automotive applications that are mainly based on purchasing cost concepts, the electrical storage cost analysis will be based on Total Cost Ownership concepts and on the cost evaluation of the discharged kWh/KW for the duration of the application. Reasonable cost of storage systems for grid applications can vary largely being strongly dependent on foreseen TSO, DSO and end-user major benefits.

Today, automotive storage is a very well defined application, on the contrary in the grid there are many different storage needs (e.g., power quality, UPS, ...) that differs for rating, size, performance, location, etc. Indeed, energy (electrical and thermal) storage is of great interest for efficient grid applications whereas EVs focus on electric storage only. Finally, grid-connected storage systems need today interfacing, monitoring and advanced control systems (SOC, SOH, ...) as it will be needed for V2G in future (dynamic bidirectional energy flows).

Today, the stationary utility energy storage market is very much in its nascent stages. However, most energy industry participants believe that energy storage technologies have to play a **large** role in the **electricity grid** of the **future**. It is generally estimated that storage will be necessary when intermittent energies share reaches 25-30 % in a grid. Market forecasts vary largely between different market researchers but all agree “**billion € markets**” will be made in the next **10-15** years (see Figure 1 ANNEX II).

What are the main drivers for energy storage?

Grid quality issues will probably be the first driver for the introduction of storage into the grid, i.e. rapid reaction time of the storage system is required.

Stationary energy storage enables the improvement of transmission efficiency from existing and new renewable energy sources by management of peak demand, by shaving peak load and shifting to off-peak hours, improving of overall power quality and smoothening out of fluctuations in the electricity transmissions.

It also serves as a temporary off-grid power solution (back-up.)

Summarized, the main functions of energy storage are:

- 1) Stabilization of intermittent renewable energy allowing an increased absorption of renewable distributed power in grids;
- 2) Emergency power supply as ancillary services;
- 3) Standalone isolated system in remote areas.

Therefore, stationary applications include storage of energy from renewable sources, UPS and load levelling to compensate fluctuations in demand (day/night or seasonal).

As already mentioned, the development of the electricity storage market is based on requests for the grid flexibility due to the increase of peak loads on one hand and the increase of intermittent renewable energy sources on other hand. Thus, contributions could be various and performed at different locations as shown in Table 2.

Energy Storage represents one possibility among others to improve the grid flexibility through flexible generation systems, grid (Transmission/Distribution) upgrades and demand side management. It will contribute to **achieve** the **EU Climate and Energy targets** “20-20-20” to be met by **2020** and will help to **realize** the Strategic Energy Technology Plan (**SET**) projects related to **grid** initiatives and thus dedicated research and industrial developments are required.

Reference technologies for stationary applications

Lead/acid (LA) is the current battery technology of choice for stationary applications on the grounds of availability and price, although Na/S is achieving much success in Japan and is also starting to be implemented in the US. Though lithium batteries are also being proposed, both their high cost together with the safety concerns over the use of large lithium-ion batteries are severe drawbacks to be taken into account. Diverse examples of installed large scale battery energy storage systems are given in references [1, 6], Pros and cons of batteries for these applications compared with other electricity storage techniques are discussed in [7]. Super capacitors demonstrate also their interest especially when associated to intermittent energy sources such as flywheels (while electric buses are currently operating with these systems).

Otherwise, as already discussed, a wide spectrum of energy storage **solutions** does already **exist**, and it is **needed** as no single storage technology option will ever meet the needs for all applications. Energy storage requirements span orders of magnitude in power and in discharge time: seconds for regulation, minutes for smart grid integration, and hours for peak shaving (see Figure 1 – ANNEX II: [4, 5]).

Sorting energy storage technologies by stationary power levels

- Large bulk energy (GW): pumped hydro, CAES, Hydrogen Energy Storage (large scale >100MW, up to weeks)
- Grid storage systems (MW) able to provide:
 - Power: super-capacitors, SMES, flywheels
 - Energy : batteries such as LA, NaS & Flow batteries
 - Energy & Power: Li-ion batteries
 - Hydrogen Energy Storage (small scale, 10MW < P < 100MW, hours to days)
- End-user storage systems (kW):
 - Power: super-capacitors, flywheels
 - Energy: batteries such as LA & Li-ion
 - Energy & Power: Li-ion batteries

Why focusing on battery technologies?

Energy storage in batteries is being developed in both types of applications – mobile and stationary – through adaptation of products to the applications. As mentioned above, major

parameters (specific or volumetric energy, cost, cycle and calendar life, safety issues, power/energy ratio, etc...) do not have the same weight according to the applications, but **battery designs rely on a common bank on materials knowledge and economy of scale due to automotive expected growing market which will promote lower costs storage solutions**. Therefore, synthesis, scale-up, industrialisation and inexpensive materials is joint key programs able to facilitate the penetration of SET-plan technologies.

Especially, electrical-electrochemical storage is technology of interest because batteries – and above all – lithium-ion batteries have excellent energy efficiency. Lead-acid batteries can reach 78 % and alkaline batteries 75% energy efficiency at each cycle. Li-ion global efficiency can be above 90 % (the coulombic efficiency is 100%).

We will therefore consider in this chapter the rechargeable battery technologies existing today and introduced in the above mentioned applications:

- lead-acid for standby (also for the micro-hybrid application if associated with super capacitors)
- nickel metal-hydride batteries (also for hybrid cars or larger vehicles such as tramways)
- lithium-ion
- high temperature batteries (Na-S and Na-NiCl₂)
- flow batteries for grid scale storage (includes Metal (Li) air batteries also for automotive)
- super capacitors for application as peak power smoothing device in fuel cell (PEM) powered electric vehicles and, as a second option, in delocalized energy production (e.g., CHP = Combined Heat and Power Production) plants using PEMFC

Key materials

- Key Technologies for Energy Storage and the corresponding Challenges to Technology, for Materials and Processes are listed in Table 3, ANNEX II.
- More details on Electrochemical Storage Materials Status is given in Appendix

Technology and manufacturing processes challenges

Lead acid.

Despite the fact that lithium batteries are threatening to dominate the market, lead batteries continue to compete: several companies aim to improve this technology for standby applications and micro hybrid vehicles by making them more enduring while keeping low cost. Advanced lead batteries come in three categories with different manufacturing processes:

- bipolar lead batteries (developed notably by Effpower);
- compressed lead batteries (developed by Exide);
- hybrid batteries combining lead batteries and a super capacitor in the same accumulator (the concept of the Ultrabattery developed by CSIRO – Commonwealth Scientific and Industrial Research Organization – in Australia and the Japanese battery company, Furukawa).

Li-ion.

A significant new trend in manufacturing is to take in account the environmental impact of both manufacturing process together with product safety and disposal. For instance, reducing solvents contents during electrode coating process, an alternative consists in extrusion,

already introduced in some manufacturers. Such process gives rise to electrodes with similar characteristics than coated ones after calendaring step. Indeed, today, the manufacturing goal is to reduce the exhaust of non-friendly component (solvent, gas,) and propose a battery and processes with a maximum waste reduction.

Sodium high temperature.

All developers have adopted a similar design approach for sodium sulphur cells in stationary applications which involves the use of self-contained modules each with 10 to 50kW of power and 50 to 400 kWh of energy. Independent modules are manufactured that consist of various series-parallel configurations of cells within a thermal enclosure. The cells are built in a tubular thin shape to maintain structural and mechanical stability. Attempts to manufacture flat plate cells with satisfactory quality (tolerance to freeze-thaw cycles and vibration) have been unsuccessful. Electrolyte membranes are manufactured in cost-effective processing operations from spray-dried powders formed into tubular shapes by automatic isostatic pressing and a subsequent sintering/annealing step.

Flow batteries. Production and cost engineering of flow battery technology is critical to reduce the installed cost. For example it may be cheaper to mass produce many smaller battery systems (10 to 50 kW) than to incur the expense of scale up engineering and produce fewer units.

Super capacitors.

This technology is today quite mature however still expensive. Electrolyte is a key material to succeed in this search. Typically, super capacitors use aqueous electrolytes, which are often unstable at high voltages, or organic liquid electrolytes like acetonitrile, which are highly toxic and flammable.

Material Supply Status and Challenges

Although raw materials are essential for the EU economy, their availability is increasingly under **pressure**. Moreover, the majority of raw materials needed for building batteries are not available in Europe. Skills for manufacturing some components (separators, thin metallic collectors) are also limited, especially for Li-ion systems.

The European Commission in its report on Critical Raw Materials (June 2010) [8] defined Antimony, Beryllium, Cobalt, Fluorspar, Gallium, Germanium, Graphite, Indium, Magnesium, Niobium, PGM's, Rare Earths (RE), Tantalum and Tungsten are most **critical** ones mainly due to geopolitical-economic reasons that impact on the supply and demand of these raw materials. Lists of materials assessed as critical are available from European [9] or US documents [10]. Specific studies have also been made on rare earth materials [11]

Risks on materials have different origins:

- Materials in low quantity in the earth crust
- Materials submitted to geopolitical constraints (Co in Congo, Rare Earths in China) or exploitation difficulties (strikes of workers, climatic problems such as floods)
- Materials relatively abundant but with insufficient exploitation to be able to satisfy an increasing demand. This is of particular importance during recovery periods after economic crises. The need of 5 to 10 years to open a new mine causes periodic tensions
- Materials subject to speculation (Li, Co, RE, even Ni...)

Electrochemical storage systems

Related to Energy Storage, **Cobalt** (Li-Ion batteries), **Platinum** and **Palladium** (Fuel Cell catalysts) can be withheld as well as **Rare Earths** (magnets and Ni-MH).

In the future there will be a high demand on Cobalt and Lithium for the Lithium-Ion Batteries. **At the moment only Cobalt belongs to the fourteen so called “critical raw material” of the EU working group.**

System	Raw materials	Geographic origin	Production	Critical materials	Comments
Lead-acid	Pb, Sn	Many for Pb		Sn	
Ni-MH	Rare earths (RE), Ni, Co	. RE come from China Co from Congo, Australia	Co : 54 000 tons/y (2009)	RE Co	Speculation on Co, Ni
Li-ion	Li ₂ CO ₃ Co, Ni, Cu, Al, Fe,	Li salts from South America	23 000 tons/y of Li	Co	Speculation on Co

Cobalt has a special position for batteries

Batteries are ranking n°1 or n°2 for the use of cobalt metal worldwide. In these, cobalt is important for both lithium-ion and alkaline systems.

A few per cent of cobalt (3-8%) are used in positive electrodes of alkaline batteries and additional cobalt is also found in hydride alloys of Ni-MH.

LiCoO₂ was historically the first and only material used as cathode material for portable devices using Li-ion batteries. Cobalt has been replaced by mixes containing also manganese (lamellar or spinel) and nickel, but generally all cathodes for those applications contain at least 20% cobalt.

For industrial applications using larger batteries lithium iron phosphate is also well introduced, in competition with mixes of materials.

Challenge is of course to reduce the cobalt quantity and to improve performances of alternative materials in terms in power, life, safety and energy.

Materials supply

Taking the high degree of “substitutionality” into account, the fact that a wide array of energy storage systems exist, following comments on material supply status can be formulated:

- (i) So far, there are no specific issues related to Pb-acid and Ni-Cd. Regarding Li-Ion, Cobalt will not be used as most of the development work tends to LiFePO₄, LiNi_{0.33}Mn_{0.33}Co_{0.33}, LiMn₂O₄, Li₄Ti₅O₁₂, i.e. lithiated iron phosphates, manganese and titanium oxides; *See Cobalt special position, above*
- (ii) Due to the wide spread usage of Li-Ion, concerns arise about the availability of lithium and its dependency on Latin American resources;
- (iii) We believe that based on many assessments, supply of lithium will not be a major concern in the first decades, after which battery recycling and lithium recovery will be fully rolled out.

Combining further brine exploitation (Brine exploration : extraction of lithium from seawater²) and providing timely the necessary Li_2CO_3 manufacturing plants with efficient recycling processes should be enough to match the demands of automotive and stationary storage needs and loosen geopolitical risks.

Sodium-Ion

The working principle being similar to Li-Ion, lithium substitution by sodium is investigated by many researchers with the aim to offer an alternative to lithium's availability and cost price evolution [12, 13].

Ni-MH

Concerns exist on the supply side of the misch metal hydrides (RE) but again Li-Ion is believed to take over most of its markets and the recycling of the metal hydrides is addressed in many processes. In addition there is a high price increase of neodymium but some others are much more stable and can replace Nd in batteries.

Graphite

The concern could be its dependency on China. Research aims to substitute graphite as anode material by Si, Sn... containing intermetallics for specific capacity increase. Sn is among identified critical materials. For flow batteries bipolar plates, generally, these are carbon based and the EU is well served by the manufacturers who have invested in bipolar plate development for fuel cells.

Vanadium

There are abundant sources of Vanadium worldwide with 92% of the production of V_2O_5 (100,000 MT/yr) going into the steel industry and long term there should not be supply problem. However if the installed capacity of vanadium batteries were to increase rapidly then short supply shortages of the high purity grades required for electrolyte manufacture will occur as 1 GWh of storage requires almost 7.5% of the 2009 V_2O_5 production. Thus, very few primary mines coming on line in the next decade would lead to a delicate supply/demand situation so vanadium would be classified as a crucial raw material.

Additionally vanadium electrolyte is not easy to manufacture from the cheaply available chemicals (vanadium pentoxide or ammonium metavanadate). Vanadium pentoxide's solubility in sulphuric acid is limited and it must be reduced by chemical, electrochemical or thermo-chemical means to get it into solution. Once in solution the correct oxidation states need to be obtained. If rapid increases in vanadium flow batteries did occur then this could be a bottleneck until new capacity was built.

The relatively high price of vanadium ore and the expense of processing it, make the electrolyte of vanadium batteries quite expensive at around \$250/kWh at current prices. Vanadium price fluctuations could adversely affect the take up of this technology but these effects could be mitigated by: (i) long term supply contracts and (ii) lease of the electrolyte (it is entirely recoverable and has a real value which can be easily achieved. Due to cost and availability issues, vanadium is likely to be superseded as a storage medium.

Vanadium is therefore considered as not critical due to the possibility of substitutions (other electrochemical compositions for flow batteries) and its abundance on earth but crucial if the installed capacity of vanadium batteries were to increase rapidly.

² This process is not realistic today and in the near future, its concentration could be far too low (0.1 - 0.2 ppm)

Zinc

Used in flow batteries, no supply problem is envisaged. It will probably give the lowest cost at \$10/kWh.

Cerium

It is the most common rare earth metal but is significantly more expensive than Zn and there is unlikely to be significant spare production capacity if demand increases for Ce in flow batteries.

Catalysts (Precious metals)

On PGM's for Fuel Cell, provided that collection and channelling through the recycling chain can be improved, metal recovery processes exist (e.g. Umicore). In a complementary manner, regarding flow batteries, if bipolar air electrodes require PM catalysts at a high loading then this will both affect the system price and drive up the PM price, assuming it becomes a significant storage technology.

Membranes

In flow batteries, membranes are typically a significant portion of the stack cost and are often the lifetime limiting factor. Significant increases in membrane usage could cause supply problems.

The default membrane option for many systems is Nafion, which is produced at a single factory in the USA. Prices for small quantities of membrane can be high (\$1000/sq.m). However, it is known that Regenysis³ negotiated significant discounts for large quantities. Production costs are estimated at around \$10/sq.m. EU based manufacturers such as Fumatech (D) are also active in the market and are starting to introduce credible Nafion competitors. Many flow battery developers are currently developing their own membranes or modifying commercial membranes. Today, Nafion has other competitors such as Solvay in Italy (aquivion) or Asahi Glass in Japan.

Current and Future Supply Status

In 2006 the worldwide cobalt reserves are estimated to be 7 Mio. t. Relating to this number, the statistical reach amounts to 100 years. In 2009, 52 % of the global reserves were concentrated at the Democratic Republic of Congo, followed by Australia (23 %) and Cuba (8 %). In 2006, world primary production was estimated to be 67 500 t. The main producers were the democratic republic of Congo (40 %), Zambia (15 %), Australia (10 %) and Russia (10 %). An estimate for the Cobalt consumption for emerging technologies shows a rise from 12 800 t in 2006 to a need of 26 860 t of Cobalt per year in 2030.

The lithium reserves are estimated 9.851 Mio. t. They are mainly located in Chile (76.1 %), in Argentina (8.1 %), in Australia (5.9 %) and in China (5.55 %). It is assumed, that there are also large reserves in Bolivia. Portugal and Spain are European lithium producers. The most important Lithium importers for the EU are Chile, USA and China.

Recycling and Substitution

The European recycling rate for cobalt is estimated about 16 %. Recycling of alloy and hard metal scrap is operated by super alloy and metal carbide sectors. Recycling of catalysts and batteries is also done by the cobalt industry. Cobalt recycling from applications in pigments, glass, paints, etc. is not possible because of the dissipation in these usages. At the moment

³ Regenysis does not exist anymore

there are no equivalent substitutes for Cobalt. The use of substitutes results in a reduced product performance.

Lithium Recycling is done in the field of batteries, but the recycling rate is almost 0 %. The EU set a recycling rate of 45 % of batteries in portable electronics up to 2016. There are possible Lithium substitutions in batteries, ceramics, greases and manufactured glass.

The electrolyte used in flow batteries can readily recycle to recover the metals. The cell stack can also be easily disassembled to yield the individual components which can be split into the various polymers, metals and composites for recycling.

Regarding, batteries, the EU directive 2006/66/EC (“Battery Directive”) sets clear targets on *collection rates* and *recycling efficiency*: by 2016, a minimum of 45% of the tonnage of batteries put on the market has to be collected: the recycling efficiency should be > 50%.

Several industrial recycling initiatives were started (e.g. at *Umicore*) where a dedicated process for recycling of rechargeable batteries is developed and built: CO₂-release for Co, Ni is only 1/3 that of virgin metals, for precious metals even better. The metal content is maximally recovered and transformed into new battery materials. The next step in the valorisation process is the recovery of lithium for which active research programs have been put in place. The net cost of battery recycling will depend on the chemistry of the cathode materials and the processing cost and it is obvious that LCO or NMC type materials position themselves better than LMO or LFP in this respect.

Complementary to battery recycling, is to further **development of second life** applications for rechargeable batteries. An electric vehicle (EV) battery is considered to have reached its end of life when it can no longer provide 80% of the energy or 80% of the peak power of a new battery. Stationary energy storage applications often do not have these severe requirements. Considering these “end of life” electric vehicles batteries, in a second life for energy storage, the process requires the acquisition of used electric vehicles batteries, their testing and their reconfiguration for this stationary use by preference but not limited to small residential type systems (see Figure 2 ANNEX II) [14]). Industrial initiatives already exist like a Nissan/Sumitomo (4R process). It is recommended to further foster research and economic assessment of second life applications. The supply chain of batteries is illustrated as an example in Figure 3 ANNEX II.

Risk Analysis

There are no cobalt reserves in the EU. Europe completely depends on Cobalt imports; which in present mainly comes from the Democratic Republic of Congo. The DRC is economically and politically unstable, so it exists a supply risk for Cobalt. Cobalt is although critical because of its poor substitution possibility and the high economic importance.

Lithium does not belong to critical resources. It has a high economic importance, but the supply risk is low. The environmental country risk is similar low as for cobalt. A detailed forecast elaborated by Fraunhofer ISI for Lithium until 2015 shows in the worst case scenario (e.g. assuming a market penetration scenario in which electric cars make up 85 per cent of all newly registered private vehicles world-wide by 2050) the lithium resources are not exhausted by 2050. However, those supplies which can be extracted using today’s technologies and at today’s lithium prices will be completely exploited, meaning that new reserves would have to be tapped. There is one mining project for lithium minerals in Europe (Finland) and there have been discovered pegmatite containing lithium minerals in Austria, France, Ireland, Spain and Sweden. A new way to extract lithium from salt lakes (Salar de Atacama, Chile; salt lakes in Bolivian) has been developed. And finally there are no export restrictions for lithium for the main source countries like Chile, USA and China.

On-going Research and Actors in the Field of Material Research for Energy Technology Applications and Challenges.

As there are so many different energy storage technologies and materials, on-going research is different from one system to another. Present chapter tries to summarize the main trends and actors in some of them.

Current Research on Batteries

Battery technology can be divided into three main parts: Consumer batteries, stationary energy storage and batteries for E-mobility. Research in the EU is focused on stationary energy storage and batteries for E-mobility.

For stationary energy storage Redox-Flow-batteries are of interest. For E-mobility there are several battery types currently under research: On-going Research in the field of materials concerns:

Lead-acid manufacturing companies

Lead-acid companies enter the market of micro-hybrid cars on the one hand, and plan to keep their position on standby battery. Due to weight of lead, they are not competitive for more electric vehicles (even HEVs), but the market of stop-and-start has a huge potential growth in South Europe for small cars in the 5-10 years.

For both applications, they need to improve cycle life of their batteries:

- Improved alloys for lead grids more resistant to corrosion
- Ability to cycle in partial state-of charge through better conductivity of electrodes (specific additives)
- New structures of electrodes
- Building of large integrated demonstrators for life tests

Ni-MH metallurgic companies

The objectives are:

- to improve specific capacity of hydridable alloys through the use of light metals (Mg) and new structures
- to study the properties of alloys not using the critical rare earths neodymium Nd and praseodymium Pr ; build and improve Sm containing alloys because Sm is not used and piled as scraps (not used in magnets or optics)
- In stationary applications, NiMH is the natural substitute of NiCd for ELU (Emergency Lightning Units) for people not accepting lithium in safety devices.

Li-ion

Applied research

Among the different rechargeable battery systems, *Li-Ion* has become the system of choice first for portable electronics and then for electric vehicle applications. Research is now focused on the development of an advanced Li-ion batteries exploring the capacity limits of the system through the development of new cathode and anode materials in combination with higher voltage (up to 5V) necessitating new electrolytes and binders. Breakthroughs are expected from the combination of so called 5V or high capacity (and lower voltage) new positive electrode materials and intermetallic new anodes [14]. These systems are only options among others. Research on Power batteries (fast charging, high rate & high power capability, long life cycle materials in specific cells designs) is at the same level as high

energy in applied research while it finds application in several large scale mobile (public transport) or stationary (charging stations) applications.

Status of advancement

For lead-acid as well as lithium-ion or sodium-sulphur, research continues in parallel with storage demonstration projects. Pb or Li-ion batteries in 20 feet standard containers have been developed with their autonomous electronics and management system and presently tested in the field. While large lead-acid or Li ion batteries have already been installed, more than demonstration status has been reached already.

For lead-acid, actors in the field are companies such as Johnson Control, Exide, EnerSys or Xtreme Power. For lithium-ion, Li-tec (Kamenz, Germany), A123, SAFT, Samsung and the Chinese BYD are among the actors. For high temperature batteries, NGK has already numerous systems in exploitation in Japan and has begun exportation to USA and Europe ; GE has also presented projects, but not at the same stage of advancement. Those batteries-in-a-containers can be assembled in series and parallel to obtain multi MWh systems, according to the needs.

The roadmaps leading to Advanced Li-Ion and new battery systems, as developed for portable electronics and automotive applications, will also have impact on energy storage in general as many of these developments will also once find their usage in storage. See Figure 4 and 5 in ANNEX II. On-going lithium-ion research is extremely vast in academic and industrial laboratories everywhere throughout the world (See Appendix for further details)

Basic research

- compounds with poly anionic frameworks allowing to reach high capacity are presently in infancy
- other compounds able to exchange more than one lithium ion per mole with a sufficient voltage (time scale > 7 years)
- Li ion system in aqueous media in a very prospective manner find its interest in a green approach perspective (introduce the need of protective layers)

Work is currently carried out on alternative technologies to Li ion such as Li-organic, Li-air, Li-S technologies... Significant breakthroughs should be carried out before any practical application of rechargeable Li-air battery can be achieved. The Li-S system has an intrinsic protection mechanism from overcharge, providing safety wide temperature range of operation and the possibility of long cycling. This is a closed system where chemistry is controlled, compared with the open Li/air. However, despite several works under progress the self-discharge remains an issue (as long as you will have an overcharge protection, self-discharge will remain a problem). Despite this system exhibits high mass energy density, its volumetric energy is rather low. While this makes this technology less interesting for embedded applications, for stationary applications where volumetric energy density is less important than for transportation, Li-S technology remains a promising candidate.

Flow batteries

Applied research

The requirements for a membrane or separator are: high conductivity, long term stability, low permeability to the charge storing species and low cost. At present membrane performance is often the limiting factor in flow batteries due to high cost, too short lifetime and performance limits (ohmic drop and poor selectivity). Membrane replacement must be factored into the operating cost. Nafion is still the choice in many systems but it is expensive and redox flow

specific grades are not available. Membrane development is a key area to reduce cost and increase performance, at high operating temperature of the technology (>100°C).

Current membrane technology is also strongly biased towards cation ion transport i.e. acidic systems. The development of cheap and stable anion membranes opens up the use of a number of interesting alkali electrolyte systems with the potential benefits of low cost chemicals and high energy density. Membranes are not commercially available for non-aqueous systems.

Electrodes provide both the surface upon which the electrochemical reactions occur, separate the cells in a bipolar stack and conducts current from one cell to the next. It must combine electrical conductivity, stability, mechanical strength and sufficient fast kinetics / low over-potentials for the required electrochemical reactions.

Most current systems use electrodes based on carbon polymer composites, many of which were developed for use in fuel cells. The type of electro-catalytic surface required will depend upon the specific chemistry being used and will be the subject of proprietary development. The mechanical and conductivity developments will probably follow fuel cells with the introduction of carbon nano-tubes for conductivity and strength and the use of metal electrodes. After membranes they are the most significant stack cost, so cost reduction is important. Metal electrodes based on stainless steel are potentially much cheaper but the acidic conditions of many current systems prevent their use.

Because, low technology membrane seems mature for low temperature, it is the platinum content, which prevents an affordable cost (increased speculation on the price of raw material due to a very narrow market - South Africa and Russia being the only providers) ... and not the electrolyte membrane itself. Much research has helped to optimize its cost (reduction of production cost + reduction in the thickness ...) to reach approximately 750 € / m² (75 € / kW).

Basic research

Optimisation of existing electrolytes along with other system components will bring about improved performance. Step changes in performance are only likely to be brought about by radically different electrolytes from the acidic metal systems currently dominating. Possible areas for development include:

1. Synthetic ions with high solubility and fast kinetics.
2. Non aqueous electrolytes i.e. organic solvents or ionic liquids with higher cell voltages than are possible in aqueous systems and high concentrations of active species.
3. Aqueous alkali systems which could have high solubilities for active species and be very cheap. Lack of suitable membranes has limited development of alkali systems.
4. Slurry based systems where slurry of electrolyte and solid phase reactant is pumped around the system. This is similar to a conventional alkaline battery but without the capacity being limited by the inter-electrode gap. Pumping costs are likely to be very high and engineering will be challenging.

While these approaches will certainly give much higher energy densities, this may not be required for stationary grid storage applications and non aqueous electrolytes are unlikely to be cost competitive with aqueous ones.

Challenges

The main challenge is the reduction of the system total system cost (Capex and Opex).

Super capacitors (SC)

Research is currently strongly focused to improve capacitance while controlling pore sizes and PSD (Pore Size Distribution) in EDL capacitors, improving energy density ($> 10\text{Wh/kg}$) by working on hybrid/asymmetric systems to improve cycle life, on pseudo capacitive (oxides) systems to improve charge-discharge symmetry. In synergy with batteries, increasing energy also deals with increasing the operating cell voltage thus investigating new electrolytes solutions (solvents/salts/Ionic Liquids). As for high power batteries, low internal resistance devices are needed for high rate capability with high thermal dissipation designs.

Applied research

Super capacitors technology is today quite mature however still expensive. The issue of acetonitrile (ACN) as solvent for electrolyte is not solved. It induces some safety issue and it is difficult to be managed at the plant level. Japanese companies propose propylene carbonate to replace ACN but with higher solution resistance and 2.5V electrolyte window.

Basic research

Work on modified carbons is therefore still under progress: While graphenes are currently under the flash lights, they exhibit high oxygen contents that make them difficult to be foreseen as super capacitors electrodes. Several carbons processes are under investigation such as carbon template (using a silica matrix), functionalizing of carbons, bio polymers manufacturing (mesoporous carbons for high power)... Asymmetric systems use a faradic electrode such as carbon/PbO₂ (see Axion Power) or C/Li₄Ti₅O₁₂ or AC/LiMn₂O₄. This gives rise to synergies in R&D with lead acid or Li-ion batteries (see the issue of current collector corrosion at high voltage or in aqueous media...) used and piled as scraps (not used in magnets or optics).

Flywheels

Flywheel systems have traditionally been developed for high power (UPS and frequency stabilisation) rather than high energy applications. Both steel and composite flywheels have been developed for stationary applications the latter allowing higher rotation speed, i.e. higher energy density. Mobile applications require high strength composites. The high cost of carbon fibre means that its application is limited to high value applications such as those above. Penetration into stationary applications, which require higher energy storage, will need considerable cost reduction (current \$4000/kWh) to make them competitive. New low cost but high strength fibres will need to be developed along with production technologies to implement them. High temperature superconductor (HTS) bearings are currently used to balance some flywheels but do not have enough magnetic strength to be used to support the flywheels. Increased HTS performance will allow reductions in the losses. EU companies involved are: Stationary – ATZ (Switzerland), KST (Belgium), Rosetta Technik (D) and Mobile – Flybrid Systems (UK), Compact Dynamics (UK) and Williams Hybrid Power (UK). R&D activity on High Temperature Superconductors (HTS) could allow the development of innovative FESS and SMES devices⁴ (fast ramp rate, very large cycle life ...). Small 100 kW / 5 kWh FESS prototypes with low-friction, high efficiency HTS magnetic bearing have been already successfully tested by Boeing (US) in the framework of a US DOE funded program.

⁴ Examples on Flywheels Energy Storage Systems (FESS) and SMES projects:

FESS - funded project to use advanced fibre technology to develop a low-cost, extremely high energy-density, high-efficiency flywheel technology for energy-storage (Boeing).

FESS - Development of a 100 kWh/100 kW Flywheel Energy Storage Module (Beacon Power Corporation)

SMES - Superconducting Magnet Energy Storage System with Direct Power Electronics Interface (ABB)

Superconductors

Applied research

All these superconductors systems were based on low temperature (LTS) or 1st generation High Temperature superconductors (HTS) because these were the only ones where long length tapes were available. The present trend is, however, to substitute these tapes by the second generation HTS tapes with composition $\text{YBa}_2\text{Cu}_3\text{O}_7$ (YBCO). The performances of YBCO coated conductors are much better adapted to the requirements of achieving high magnetic fields at high temperatures and the energy density of a SMES is proportional to the square of B, the magnetic induction, so the expected efficiency and size which should be reached is much higher. The YBCO coated conductors are now available in km lengths (even if they are not yet commercial products) and so several new, high performances, SMES projects are underway all around the world.

Hydrogen Energy Storage

The integration of renewable energy especially of wind power requires high storage capacities and high power solutions. In this context storage must be able to take surplus energy and to provide energy for days and weeks, which can be translated in a capacity demand starting at a low single digit GWh range to a higher triple digit GWh range per unit. Hydrogen offers a high energy density. It is very simple to produce via electrolysis, easy to store in pressure tubes or tanks and to reconvert into electrical energy within a combined cycle power plant. Almost all required components are available today or could be made available soon (3-7 years) if the market requests it. Furthermore hydrogen offers many additional links to other infrastructures e.g. mobility and industry e.g. chemical industry.

Today, hydrogen based storage solutions are not commercially available. The following bullets will focus on an implementation road map how this solution could be made available without taking high financial burdens.

- Installation in distributed grids at community level at a power level of ~50MW and a capacity of up to 2 days at full load (capacity of ~3GWh), achievable with 3 to 5 years
- Installation in transmission grids at a power level of >>100MW and a capacity of weeks (capacity of 100GWh to 200GWh), achievable in 5 to 8 years.

Research

R&D needs are structured along the conversion chain of that storage solution which consists out of an electrolyser (conversion in), a storage (above ground / underground) and a combined cycle power plant (conversion out).

§ Electrolyser converts surplus electrical energy into hydrogen at high pressure (>25bar)

- Validation of very dynamic load change operation and its impact on the auxiliary systems (e.g. cooling, water supply, power electronics), gas quality and life time consumption
- Overload capability and its impact on invest cost and H_2 production costs
- Pressure control of hydrogen and oxygen gas streams during different operation schemes

§ Hydrogen gas storage can be structured in above ground and underground storage. Above ground storage is suitable for applications with capacity demands lower than 10GWh and for locations without the option for underground storage. Underground storage in salt caverns are suitable for high energy capacities >>10GWh up to 300GWh per storage.

- Above ground storage are steel vessels (spheres or tubes) in which hydrogen is stored at pressure.

- Evaluation of potential health and safety related aspects and measures to overcome such impacts
- Material selection to maintain tightness and to minimize life time costs
- Dynamic operation of such systems in regard of fast charge / discharge limits
- Underground storage is artificial cavities in salt formations of volumes starting at 100.000m³ up to 1.000.000m³ each
 - Evaluation of potential health and safety related aspects and measures to overcome such impacts
 - Underground regional planning procedure for storage (as part of the legislation, give storage a priority)
 - Dynamic operation of such systems in regard of fast charge / discharge limits
 - Alternative geological options (e.g. saline aquifer)

§ Hydrogen combined cycle power plant reconverts the hydrogen into electrical power. The topping cycle (steam cycle) is very beneficial to the overall system efficiency as it make use of the exhaust heat of the gas turbine.

- Major R&D topic is to adapt the gas turbines fuel supply and combustion system for the use of hydrogen as fuel (w/o or with minimal dilution).
- Validation of material substitutes within the fuel supply system and the combustor to cope with hydrogen
- High dynamic operation and special grid services such as frequency support / control mode, phase shift or black start capabilities

§ Storage system

- Evaluation of the balance of plant requirements in terms of load dynamic and cost optimization
- Identification of system efficiency improvement levers
- Determination of a realistic storage operation scheme based on real grid data or close to reality grid model data

Hydrogen as storage solution is often discussed as so called seasonal storage which is just one option. This storage offer also peak power on a daily or even sub-day interval as done today in peak load power plants. This has to be considered for the economic discussion. Also often neglected are its grid service capabilities such as frequency control / stabilization, phase shift (reactive / active power) black start options and its independency of power input / output in regard of state of charge. Most alternative technology options have a state of charge power dependency. Also its scalability from >10MW into the higher 500MW class provides a very universal storage technology for various grid levels.

Other systems

On-going research addresses the key issues of storage systems: Size and weight, capital costs, per cycle cost, maintenance, life efficiency, environmental (CO₂-emissions).

Main programmes at EU and Member State levels

The lithium battery technology has emerged as the major technology option to power first portable electronics and later both Plug in Hybrid Electric Vehicles (PHEVs) and Electric Vehicles (EVs). This philosophy has led major companies to almost abandon other battery technologies, public institutions to fund battery research almost exclusively focussed on lithium and finally also the academic battery research community to adhere to this. Despite

the vertiginous progress achieved by lithium battery technology and the speed at which it enlarges its field of applications, we must, owing to Li availability and cost, pursue researches in parallel systems.

Even if fundamental research has been mostly focused in lithium, there have been some remaining activities in the field of nickel based batteries and more recently efforts in fundamental research are being redirected from lithium ion to lithium/air and lithium/sulphur. Moreover, since the basic science related to intercalation chemistry that was at the origin of the lithium ion concept was developed in parallel for lithium and sodium, embracing these alternatives should be plausible. With respect to high temperature solid electrolyte sodium a battery, research is almost abandoned in Europe even if there's a company (MES-DEA) fabricating ZEBRA (Na/NiCl₂) cells. This contrasts with the situation in Japan where the concept was never abandoned, and the US where GE is building a plant to produce these cells. Today, a lot of work is currently done at the level of **industrial prototyping**. Public systems foster the gathering of private actors (See Table 4 Annex II). Therefore, high temperature batteries are already commercialised in Japan and the US due to a specific market demand. So far such demand does not exist in Europe.

Compared with the US and the Far East, the flow battery field is relatively poorly served in Europe. The only systems that are truly commercially available from an EU manufacturer are from Cellstrom (Austria) and REDT (UK and Ireland). Both supply all vanadium flow batteries. At the European level, technology development is being currently carried out mainly by organisations.

Regarding superconductors, INES systems which have been developed up to now are in the range 5kWh/250 kW for a rotor of about 600 kg [15] and it is expected to extend the system characteristics by a factor 10 by increasing the rotor size and mechanical performances. Europe is particularly well placed in this field [16]. Several SMES systems have also been developed and used to improve the power quality locally. They behave as uninterruptible power supplies (UPS) in the range of MW and several units have been tested and/or connected to the grid in Europe.

Focus on European Union

In the 6th EU Framework, projects relating to E-mobility were already funded. Within the 7th EU Framework several battery projects were funded in the 1st to 3rd call, such as: SUPERLION, SIMBA, ORION, PolyZion, MAHEATT, and MERGE. The European Commission initiated in 2008 the "European Recovery Plan". In the automotive sector the public-private partnership "Green Cars" (GC) was funded to secure competitiveness of the European automobile industry. To establish the topics for the European Commission the "Green Cars Advisory Group" was initiated. The involved partner whose are mainly members of the European technology Platforms ERTRAC, EPoSS and SmartGrids.

Basic Research

With respect to fundamental research related to battery materials, activities within the ALISTORE-ERI (Advanced Lithium energy STORAge systems) deserve a special mention. Started in 2004, it is a contractual European network of excellence with unincorporated body federating 23 European research organisations structuring R&D on lithium storage systems, promoting nano materials and strongly involved in education (Erasmus Mundus European master) [17]. This durable integrated structure was created within the **FP6 NoE "Advanced lithium energy storage system based on the use of nano-powders and nano-composite electrode/electrolytes"** coordinated by the CNRS (contract number 503532, 2004-2008) Research within ALISTORE-ERI is cooperatively organised within the framework of six thematic groups, one of them being devoted to new chemistries and new materials for

technologies alternative to lithium. In order to favour better creativity/innovation and efficiency in moving from ideas to products while contributing to fund the ALISTORE-ERI Federation, an associated European Industrial Club was settled in December 2007 which is currently composed of 14 members, including SMEs and large companies, with common interests in materials for energy storage. The budget raised from industrial memberships is fully invested in boosting the integrated common research activities, which has strongly contributed to maintain and reinforce the achievements made in structuring of the European Research Area in the field of materials research for battery applications and has granted ALISTORE-ERI scientific recognition not only at the European level but also internationally. There is no parallel institution in Japan or the US, though two of the six DOE funded EFRC do have activities in the field of battery materials. Several FP7 programs are currently running emerging from ALISTORE (HELIOS, EUROLION...).

The KIC Inno Energy was designated as a Knowledge and Innovation Community by the EIT's Governing Board on the 16 December 2009 in Budapest. The priority area which this KIC addresses is sustainable energy. The goal is to change the European energy system through innovation, running like a business through a flexible and effective organizational structure. 13 companies, 10 research institutes and 13 universities are involved [18].

According super capacitors at the European level, while FP7 ILHYPOS - Ionic Liquid-based Hybrid Power Super capacitors ended in 2008, programs such as AUTOSUPERCAP-Carbon for High Energy / High Power Density Super capacitors for Automotive Applications started in 2010. Usually super capacitors are included in "energy storage" thematic together with batteries as in ALISTORE (see above) or in COST Action 542, an European Co-operation, Scientific and Technical Research focused on the development of high performance energy storage systems and their implementation is screened for both mobile and stationery applications in transportation and energy technologies.

Applied research

In Europe there has been development of SMES systems for use as pulse power sources using 1st generation HTS tapes, so there is enough knowledge to extend the development to the new 2nd generation HTS conductors. The possible success of SMES systems is linked to the progress in enhancing performances at high magnetic fields and reducing the cost of YBCO coated conductors.

In member states

France

At a French level, to fast rate batteries innovation & developments in the industrial sector, a research and technological network was created. The Alliance Nationale de Coordination de la Recherche pour l'Energie (ANCRE) is gathering main academic and industrial actors in the field. The main goal deals with reducing transfer delays from laboratories to industry. This national network is supported by 2 R&D centres: One for fundamental research (CNRS) and the second for technological developments (CEA with IFP, INERIS and INRETS support), working in close partnership. 8 french laboratories are involved including LRCS (Université de Picardie Jules Verne/CNRS). 3 main actors in the field of batteries are already involved in this network: SAFT, Batscap (for batteries and super capacitors & SVE).

Spain

Academic research takes place either at universities (e.g. Universidad de Córdoba), CSIC institutes (e.g. ICMAB) or in newly created technologic or fundamental research centres (e.g.) CIC energiGUNE, IREC. ZIGOR Research and Development is involved on Vanadium flow

batteries and a large engineering company is known to be developing a system using novel chemistry.

Austria

Cellstrom (Vanadium) flow batteries system ranging 10 kW - 100 kWh has been available for a few years.

Germany

The German project “LiB 2015” gathers the efforts of battery, chemical and automotive industries with universities from the institutional side. Furthermore, within the German Recovery Package II, two main competence clusters have been funded to set up competence in electro mobility: one of Fraunhofer Research institutes and the other one of universities plus Helmholtz Centers.

Flow batteries developments are thought to be at **lab and pilot scale**.

- Fraunhofer ISE Freiburg - Vanadium
- Fraunhofer Institute UMSICHT – Vanadium & Non aqueous Vanadium
- Fraunhofer Institute ICT - – Vanadium & Non aqueous Vanadium
- RWTH Aachen (Vanadium)

The Netherlands

KEMA (V-air and novel alkali systems) are available at **Lab scale only**.

Unite Kingdom

Several groups and companies are working on flow batteries as the following

- University of Southampton (Walsh, Pletcher and Wills): Polysulphide-bromine, Soluble lead, vanadium, Zn-Ce and Zn air
- RE-Fuel Ltd (Vanadium) – 5 kW stacks are **in production and development** work continues on 100 kW stacks. The company has significant **scale up plans**.
- C-Tech Innovation Ltd (Soluble lead & Zinc air) – **pilot scale**.
- Plurion Ltd (Zn-Ce) – stacks up to 60 kW but the company is now in administration

On-going efforts in other developed countries

Switzerland

ReVolt – (Zn-air flow battery using Zn slurry as the electrolyte). Their main market is consumer electronics batteries but **development** of a flow battery is being carried out by the company in the US under DoE ARPA GRID programme.

Russia

ESMA **sells** a wide variety of EDLC modules for applications in power quality, electric vehicles, and for starting internal combustion engines.

USA

The DoE (US Department of Energy) has major funding programmes in battery development (1.5 bn. US\$): it has invested in **fundamental applied research** via the BATT program, which involves universities and national laboratories, and in the development of the battery pack via the USABC program together with car manufacturers. Today, the main topics in the

USA are Metal-Air batteries and Lithium-Ion batteries, covering as examples, high capacity, and high voltage, fast charging batteries... All the current trends are in the scope...

FY 2011 DOE budget includes a 14% increase for the electric drive-specific programs, which are established in a separate line item "Batteries and Electric Drive Technology" - formerly Hybrid Electric Systems - in the Vehicle Technologies budget. Program goals include reducing battery kWh costs to \$300/kWh by 2014 and reducing total electric drive costs. The request for the program is \$120,637,000 compared to last year's (activity) total of \$101,405,000. A 12% increase in the DOE's Office of Science Basic Energy Science program is also proposed. The \$1,835,000 total would include funds for 2 new innovations hubs, "Batteries and Energy Storage" and Fuels from Sunlight. In Electricity Delivery and Energy Reliability's Research and Development Programs, \$39.3 million is requested for **Smart Grid Research and Development including the development of systems to support plug-in vehicles. The Energy Storage program, focused on stationary energy storage is budgeted at \$40 million.** US is also currently investing >\$100M as part of their stimulus package in flow battery technology administered by DoE, particularly in its ARPA programme. Several US companies commercialize flow batteries (ZnBr: VBB and Premium Power, Soluble lead: General Atomics, Hybrid fuel cell / flow battery using hydrogenation / dehydrogenation of an organic: General Electric or Enhanced Metal-Air Energy Storage System with Advanced Grid-Interoperable Power Electronics Enabling Scalability and Ultra-Low Cost: Fluidic Energy, Inc. & Chevron) or components (Low-Cost, High Performance 50 Year Electrodes (Metal bipolar electrodes and Zinc Chloride): Primus Power and Novel unspecified cell design: United Technologies) with Funding Pacific North West Labs as a centre of excellence for flow battery development and Hydrogen-Bromine Flow Batteries for Grid-Scale Energy Storage developed at Lawrence Berkeley National Laboratory or Low-cost Grid-Scale Electrical Storage using a Flow-Assisted Rechargeable Zinc-Manganese Oxide Battery by CUNY Energy Institute. **Demonstration systems commissioned** include: 1 MW 8 MWh VFB, 5 x 500 kW 2.5 MWh ZnBr, 25 MW 3 hr ZnCl and 250 kW 1 MWh FeCr. Most of these systems are targeting costs of less than \$100/kWh and feature major energy companies. Regarding super **capacitors manufacturing** in U.S.A, Epcos, ELNA, AVX, and Cooper produce components, while Evans and Maxwell produce integrated modules that include voltage balancing circuitry. Kold Ban International markets a super capacitor module designed specifically for starting internal combustion engines in cold weather.

SMES systems have been developed and used to improve the power quality locally under the auspices of DOE to demonstrate powers in the range of 10-100 MVA and energies above 10 MJ. The final goal is to use them for stabilization purposes of micro grids, stabilization against sags or load fluctuation compensations.

US have also heavily subsidized new plants on their territory for having "home-made" materials cells and batteries. Information about Advanced Research Projects Agency-Energy (ARPA-E) (US DOE) projects on Grid-Scale Rampable Intermittent Dispatchable Storage can be found at <http://arpa-e.energy.gov/ProgramsProjects/GRIDS.aspx>.

China

China is one of the world largest battery suppliers. The main competence is in the field of Lithium-Ion batteries. **Battery research** is addressed in the 11th five-year-planning of the Chinese government. In China, 863 programs of the Ministry of Science and Technology (MOST) Priority Projects conduct R&D in 19 subjects that range over 6 high-tech priority fields in the civil sector including Advanced Materials Technology; Advanced Manufacturing and Automation Technology; Energy Technology; Resource and Environment Technology... Renewable energy in China continues to play an increasingly important and strategic role in

the country's energy development. Total renewable power capacity in China reached 226 GW in 2009, including 197 GW of hydro, 25.8 GW of wind, 3.2 GW of biomass, and 0.4 GW of grid-connected solar PV. **This total was more than one quarter of China's total installed power capacity of 860 GW.** And, significantly, during the five-year period 2005–2009, wind power grew thirty-fold, from just 0.8 GW at the end of 2004. An update of 2005 Renewable Energy Law occurred summer 2010 and grid-based electricity storage and smart-grid operation will become important. Nonetheless, China's renewable industries have hardly suffered from the recent global economic problems, and the period 2010–2020 looks promising. Several Chinese **commercial suppliers** for flow batteries equipment (Vanadium) are reported as Dalian Rongke Power, Prudent Energy, Golden Energy Fuel Cell.

Japan

Japan is traditionally very strong in the battery sector. Japan is world leading in the visionary field of Metal-Air batteries and Redox-Flow batteries. There are **strong private research** activities ongoing and a good cooperation between industry and academia, which is coordinated by NEDO (New Energy and Industrial Technology Development Organisation). Japan's strength is the implementation of new technologies. Sumitomo licensed the generation 1 vanadium battery technology and **installed systems up to the MW scale.** They pulled out of the market in the late 1990's but are reportedly intent on re-entering. While today a number of companies around the world currently manufacture **Electric Double Layers Capacitors (EDLCs) in a commercial capacity:** NEC and Panasonic have been producing EDLC components since the 1980's.

Several SMES systems have been developed and used to improve the power quality locally in Japan. One of the most emblematic is that promoted by NEDO under the M-PACC (Materials and Power applications of coated conductors) program. As in USA, the first step in this program is to demonstrate powers in the range of 10-100 MVA and energies above 10 MJ and the final goal is to use SMES for stabilization purposes of micro grids, stabilization against sags or load fluctuation compensations.

Korea

Korea has two leading companies in Li-ion batteries, Samsung and LG. and is increasing continuously its research efforts in the battery field. The main focus is on Li-ion improvement and Lithium Sulphur Batteries. Korea's leading research institute is the Energy Research Institute in Ulsan. Robert Bosch GmbH and Samsung founded in 2008 a joint venture SBLiMotive. Ness Capacitor Co. **commercializes** a range of capacitors components. SMES systems as uninterruptible power supplies (UPS) in the range of MW have been tested and/or connected to the grid in Korea.

Australia

In Australia, ZnBr flow batteries are manufactured by Redflow (and part of ZBB) and Vanadium Gen 1 and Gen 2 by V-Fuel Pty Ltd (Original inventor Maria Skyllas-Kazacos). 'Low cost' 5 kW pilot stacks are available and 50 kW units under development. Cap-XX offers a range of super capacitors components.

Canada

In Canada, Tavrma manufactures a range of capacitors modules. PhosTech is a well-known supplier of LiFePO_4 .

Thailand

In Thailand, Vanadium pilot systems with novel cell designs are displayed by Cellenium.

Material's Specification Targets for Market Implementation in 2020/2030 and in 2050.

Stationary energy storage by batteries, most probably, will go parallel with materials and system development roadmaps developed for e-mobility.

Indeed, materials themselves are the first step in determining the cost of each technology and their performance. This requires the control of intrinsic properties, processing and production, taking into account potential impacts on health, safety and the environment throughout their entire life cycle. The criteria to choose the most suitable technology (and hence the materials involved) for a given application are performance and efficiency (both in terms of energy and power), durability, safety and cost. The relative importance of each criterion is rather application dependent. At the scale needed for electrical grid applications cost is much more important than for lower scale applications, while the global specific energy or energy density are not essential factors as in portable electronics or electric transportation, since the systems will be stationary and ground-based.

Cost is determined both by raw materials and manufacturing process. The emphasis on potential cost reductions is hence achievable by using (i) readily available affordable materials and (ii) low cost manufacturing processes. Thus, only materials for cost effective safe technologies should then be considered for lifetime and performance evaluation. Alternatively, even if cost effective electrodes with high capacity and performance can be achieved, control of interfaces both within manufacture and assembly process but most importantly during operation, is a crucial issue to ensure extended lifetime. While voltage, capacity, specific energy and energy density are governed by the properties of bulk electrode materials, cycle life is mostly dependent on the quality and the stability of the diverse interfaces present.

The above mentioned requirements places already constraints within the technologies considered: while some definitely fall out of the scope (e.g. Ni/MH due to scarcity and high price of rare earths used at the anode) others fall well within the scope (super capacitors, sodium based batteries) or lie in between (lithium based technologies). Indeed, for lithium ion the very high cost of cathodes and the high cost of Li_2CO_3 raw material itself [19] render the cost prohibitive (see an example of cost estimations in [20]). Alternative lithium systems avoiding the use of expensive cathodes (e.g. Li/air or Li/S) would also fit well within the scheme. The maturity of these systems being radically different, the latter being much less developed, and the difference in materials targets for 2020/2030 and 2050 is necessarily technology dependent. The cost of lithium-air will depend on the catalysts used in air electrodes and on the materials used in ceramic separator. Lithium-air and Li-S use metallic lithium for the anode (they are not Li-ion batteries) and, due to the poor cycling performances, need 4 times more lithium than Li-ion.

Part of the German innovation alliance LIB2015, founded by the BMBF in 2007, is the Foresight Process to set up a Lithium-Ion Battery Roadmap [21]. The Roadmap focuses on lithium based cell components and cell types and also compares to complementary and competing technologies with respect to lithium-ion batteries in the time frame between 2010 and 2030.

In order to clarify what is meant by market implementation it is important to distinguish between the levels of battery cells, battery systems and the use of batteries for various applications (stationary and electro mobility). As an example, while the developments described in the Lithium-Ion Battery Roadmap [21] address the materials developments up to the level of battery cells, the working groups of the national platform for electro mobility also include the other two levels and point to a time gap between the market readiness of battery

cells and battery systems as well as battery systems and their use (of several years). In parallel, a recent report issued by DOE on advanced materials for stationary electrical energy storage applications [22], also addresses storage device optimization through advances in materials research in the near (<5 years), mid (5-10 years) and longer term. Priorities are defined according to each technology and key targets in performance and cost are defined. The latter are mostly defined due to economy of scale for all technologies and roughly evaluated to be ca. 50% of the current price in 2015 and 25% of the current price in 2020.

Finally, referring to the technology penetration scenarios for the materials roadmap (low and high) as presented in the SET-PLAN (Figure 6-7 ANNEX II), huge capacities of electrical storage have to be provided to smoothly integrate the renewable energy production installed, necessitating industrial and economic storage solutions. A clear industrial vision for Europe needs to be developed for each technology and to include as a KPI the projected cost of service as a relevant indicator for grid applications.

Focusing on technology penetration high scenario for the Materials Roadmap as shown below (Table extracted from figure 7 ANNEX II), one can estimate expected costs relative to economy of scale for 2020 and 2030-2050 (See 1.4.1 and 1.4.2 paragraphs) for various power sources:

Energy Source	Capacity			Installed per year	
	2010	2020	2030	2010-2020	2020-2030
Nuclear (GW) ⁺	127	198	297	8.9	11.9
Wind (GW) ⁺	86	230	400	14.4	17.0
Solar PV (GW) ⁺	15	360	630	35	27
CSP (GW) ⁺	0.5	30	60	3.0	3.0
CCS (GW) ⁺	0	20	80	2.0	6.0
Biofuels (Mtoe)	15	48.9	72.7	3.5	2.5
Fuel cells non-automotive (GW _e)*	0	22	75	Max 6	5.3
Hydrogen (Mcars)	0	5	25	Max 1.8	2.0
Efficient buildings (energy consumption reduction %)	0	30	80		

⁺ expressed in terms of electricity production capacity
* incl. fuel cells using other fuels than hydrogen

Specification targets for Market Implementation in 2020

Referring to stationary storage with figure 7 ANNEX II (High scenario level) costs are calculated and each technology is checked in order to give insights regarding affordable prices related to economy of scale. In 2020, 33000MW of storage (worldwide installed) with 45% Li ion penetration gives rise to 14000MW. Today, stationary storage costs ca. 500€/kWh. Future cost targets for stationary storage will probably not be different from the automotive meaning ca 200 €/KWh by 2020, in other words less than 40% of 2010 prices.

Which materials can fit costs? It is believed that all Li Ion chemistries will allow reaching those costs in the longer run as they are also supposed to do for the automotive. Cost and safety are advantages for LiFePO₄ (LFP) but cycle life (>2000) is still to be improved for each of the different chemistries. What matters for utilities in large storage units is €/KWh/cycle and roughly for LIB this comes down to 25cents€/KWh/cycle (based on 2000 cycles) in other

words to come down to e.g. 10 cents€ there is still some way to go. There come Titanate-based negative electrodes, while a bit more expensive, such materials are expected to greatly improve cycle life. Moreover, in stationary applications, the lower energy density induced by these higher voltage negative electrode materials is not limiting as for electric vehicles.

Objectives for cost of materials

Negative active materials:

1. Carbon : basis 5-6 €/kg ; additional value possible for surface fonctionnalization
2. Advanced materials (Si, Sn or other) : not more expensive in terms of Wh/kg obtained by a battery using the same positive
3. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) : for high power systems < 10 €/kg

Positive active materials :

1. lamellar oxides <20 €/kg ; will be indexed according to the cost of metals at LME (as it is already the case for lead in lead-acid batteries
2. phosphates (Fe, Mn) : <<10 €/kg

Separator :

<1 €/m² ; additional value possible for surface fonctionnalization (to confirm)

Copper : unpredictable due to the copper evolution and the thickness decrease of collector (process for very thin collectors increasing price)

Energy segment

A steep upscale in production of today's technology is needed and also progress in materials research is needed to pave the way for the next generations of storage systems.

Regarding batteries, one can underline that as the 1st Li ion technology generation still under development for large scale applications (electro mobility and photovoltaic), LFP (130Wh/kg) positive electrode is selected as very promising due to its high intrinsic safety, but at the same time its energy density is lower than in NCM (175 Wh/kg) or LMO (life time has to be improved) and NCA (seems too unsafe). Pay attention : at this level of size of battery, the safety must be ensured at battery level whatever the cathode.

The further development of cathode materials together with improved anode materials (graphite and modifications thereof as well as LTO as alternative, from 2017 on also hard/soft carbon) (hard carbon is more expensive) are expected to lead to improved battery cells and battery systems (1st and 2nd Generation), which could be ready for market entry not only in electric vehicles but in stationary field in 2015 (see Figure 8 in ANNEX II: Lithium-Ion Roadmap together with Battery Roadmap of the NPE).

High Energy-Batteries (2nd & 3rd Generation), including high capacity positive electrodes (lamellar...) and high voltage positive materials in combination with high voltage electrolytes could improve the energy density of battery cells before 2020 (e.g. 5V cells) and be available as battery systems for electric vehicles from 2020 and therefore for stationary storage (see second life concept in section 1). *See Figure 8-10 ANNEX II. The key issue for 5 V cells is life increase even in their first life*

Regarding the negative electrode: Carbon based materials will be the key material at least until 2020. In the long-term, high capacity negative electrode materials such as silicon-carbon based systems for instance are very promising. Research efforts in high capacity negative electrode materials are needed to improve specific energy. Alternatively, research in high voltage negative electrodes is also interesting as, for instance, LTO for fast charging, high power capability and if possible improving the material capacity ($\text{TiO}_2\text{-B}$...).

In summary, materials research will determine the limits in capacity of the storage systems and hence the achievements in performance.

Since Li ion technology is already part of many ongoing research actions of the EU member states, EU research funding should focus on post-lithium ion systems (Li-S, metal air, others...). For such systems, while fundamental research is still needed to improve materials and components, and fully understand mechanisms, EU funding beyond proof-of-concept could be implemented, involving small demonstrators (cells and systems).

Further key components for battery development that should be addressed by EU research activities are electrolytes and additives. These will also be crucial for improving battery life time and safety aspects and should be cost effective. In addition to new solvents, the use of highly stable salts deserves to be investigated as well as new current collectors protected against corrosion... Finally, even if inherent thermal properties of electrolytes and electrode materials are important, cell designs must also be considered for safer battery developments.

Power segment

Power cells design targets $>5\text{kW/kg}$ but with an energy density of $80\text{-}100\text{Wh/kg}$ and lifecycle $>15\text{years}$. Innovative designs would allow a reduced internal resistance for the whole battery and most important a lower heat generation (Rl^2) and better heat dissipation that makes the cell behaviour against abusive tests very safe...

Specification targets for Market Implementation in 2030 to 2050 (or 2030 and beyond)

Post-Lithium batteries, such as Li-S, Na-ion, Metal-Air, Solid State Batteries or Liquid batteries (See MIT batteries composed of two molten metals)... (around 2030) could be available on the cell level until 2030 and would lead to significantly improved energy densities (Li-S, Li-air) or improved safety (solid state batteries). Alternatively, paying a small penalty in energy density which is fully tolerable for stationary applications, the Na-ion technology would lead to much reduced costs basing on readily available non strategic materials. (see Figure 6 ANNEX II).

For the market readiness of these systems in large scale versions again a time gap has to be considered. In accordance with the Japanese Battery Roadmap (see METI-Report on Target Values of Rechargeable Batteries for Vehicle Use) such innovative batteries would be expected beyond 2030 for electro mobility market. This one could again drive stationary storage perspective with experiencing those new technologies or not, if one considers these technologies better designed for large systems in a stationary use manner (Flow managements, lower volumetric energy, low power capability...). This is also in agreement with forecasts by DOE [22].

Beyond these dates, other storage systems (merging several technologies or involving new concepts), would have to be assessed in order to introduce a real breakthrough in performances.

As to the other mentioned energy storage systems, key materials development are further required for the super- and pseudo capacitors increasing their energy performance while maintaining maximum power, for SMES (Superconducting magnetic energy storage) improving its cost and developing superconductors at higher critical temperature and for CSP improving heat transfer media and salts.

Going from systems to applications, further research should be carried out on Vehicle-to-grid (V2G) concepts, connecting the electric vehicles onto the interconnected power network with facility for the transfer of energy between vehicle and grid. It is agreed that such approach is a long term concept to be explored.

Home area networks (HAN), advanced metering infra structures (AMI) have to be further developed to integrate automobile communication with emerging energy management requirements related to efficiency, pricing, messaging ... The battery pack could communicate both to the car computer and directly to charging/quick drop stations... New autonomous powered electronic devices (sensors with long distance communication for instance) using low cost processes (see organic electronics and printing technologies) would have to be developed introducing here energy harvesting and storage, thin film batteries technologies... and fully integrated in the mobile product. This means a decentralized power distribution in the car structure.

The impact of V2G operation on battery lifetime is a critical issue so it has also to be further examined.

Synergies with other Technologies

Today, few European programs regarding storage for pure grid systems are reported, thus, such projects would need to be further pushed. However, one must care to develop this thematic in full agreement with linked other ones such as electro mobility for instance. So three synergies levels associated to various time frames are proposed as listed below:

Level 1

2 steps: before 2025 and after 2025. Year 2025 is suggested as the boundary beyond which generalised implementation of electric mobility will be in force

As already discussed, stationary Renewable Energy (RE) systems require storage systems in order to maximise and load level the electricity production and to improve the quality of electricity delivered from the grid. Introducing new technologies means to demonstrate their effective cost related to their life time and reliability. However, there is no simple model for the global evaluation of the emerging storage technologies according to the different user profiles and a lack of appropriate data base allowing the comparison of these implemented storage technologies. For clean Vehicles, the reliability of the storage system is also the bottleneck of their massive development. In a similar approach to stationary applications, lifetime prediction and global costs evaluation are of worth interest among the problems to be solved. Moreover, battery management systems can find their interest when stationary and automotive are combined. However, before 2025, because no sufficient operational electric to grid is expected to be available, we believe that there is no need to separate materials R&D for storage which can be used in both applications (i.e. room temperature batteries) in two categories: stationary and electro mobility. Of course, one must consider differences in materials specifications priorities for each application. For instance, stationary applications require first low cost, safe and years life time technologies before high energy densities. While these specifications may differ, one must also underline that these technologies draw from common materials feed. Alternatively, the scope of materials research for grid applications could be broader than that considered for electro mobility since some technologies are only suitable for the first (Na/S batteries, flow cells, etc...). Therefore we believe, for all the above mentioned reasons, that there are synergies for programs merging grid systems with electro mobility. After 2025, after a preliminary practical sorting in storage systems for stationary applications, these programs could be revised.

Level 2

Synergies between consumer electronics, automotive and storage (i.e. metal air)

Consumer electronic devices are in the forefront of the race towards energy density increase. As such, they are pioneers and models in the search of new materials and processes to use them. Today, they are a fish tank of new ideas available for energy increase.

Especially regarding Li ion technologies

The Li-ion technology is already the reference solution for portable battery and is becoming also the reference solution for clean cars such as EV & PHEV. Even if there are a lot of synergies between both applications, the difference in specifications leads to different technologies and different products. Therefore, the Li-ion technology used for the electrical storage will benefit from synergies with portable and automotive applications but is expected to have specific features due to the requirement differences:

- Electrical storage: emphasis on life duration
- Automotive: emphasis on energy density

Furthermore, the V2G concepts and the second life battery scenarios must be checked carefully:

- The best application for a second life battery seems to be the second hand vehicle
- The battery use for two different applications is expected to decrease the life duration for both applications

Different electrical storage products based on Li-ion technologies are already available and marketed in some areas such as US and Asia. However, a continuation of the R & D effort is mandatory to decrease its TCO, according to the second challenge:

- Life duration increase
- Material cost decrease
- Energy density increase
- Safety improvement
- Improvement of temperature operating windows

Assuming that the Li-ion technology family will be used in the next 10 years (at least), the Li-ion program must be launched to position the European Li-ion network (R & D, material supplier, battery manufacturer, energy storage operators,...) in front of the US and Asian competitors.

Post Li-ion tank of new ideas

Mobile applications with increasing functions are mandatory to search for energy storage technological breakthroughs based on the use of new materials. Such systems like metal air face some strong technological barriers to-day so it seems difficult to forecast their market introduction. However, research programmes must be launched to first solve those barriers and second assess the compatibility of these new systems with the market requirements.

Level 3: Today

Between materials on different technologies (i.e. Super capacitors and batteries and Fuel Cells...)...

Synergies between **super capacitors with flow batteries, Li ion batteries, Li-S and metal-air technologies**, exist as shown with few relevant topics listed below, in a non exhaustive manner:

- Development of Carbon-Carbon super capacitors controlling pore sizes (and Pore Size Distribution) and **increasing voltage** thanks to surface treatments (Functionalized hydrophobic carbon) to reach energy density >15Wh/kg with similar charge-discharge rates (salts like LiEt₄NBF₄) in synergy with Li-S and metal-air negative electrode stabilization (passivation) or with very prospective aqueous Li-ion system.
- Further work on Ionic liquids (ILs) for higher voltage ranges with wide operational temperature range and high conductivity. Or working on ILs-solvent mixtures with high voltage solvents as developed in Li ion batteries (additives/new solvents), keeping in mind that so far ILs are already less worked as solvents for direct battery application.
- Li Ion Capacitors (LIC) asymmetric systems need further work to improve life cycle (LTO or other oxides-Carbon...) and improve symmetry of charge-discharge rates to achieve 20-25 Wh/kg in synergy with high Power Li-ion batteries.
- Existing synergies between fuel cells and metal-air batteries should be taken advantage of... For example, the air electrode of a fuel cell can be used in metal-air systems. Air electrodes developed for metal-air batteries can be used in alkaline fuel cells and vice versa.
- Flywheel systems need further work to increase the energy of the system through the development of cost effective high strength materials (fibre composites and mixed metal/composite structures) to allow high speeds and the further development of advanced magnetic bearings (superconducting magnetic bearings or fully passive bearings) to reduce losses and provide self-balancing thus allowing higher operating speeds. From the technical point of view, the existing products seem viable and have been demonstrated on the field for a few years; a huge challenge is the development of integrated products for stationary applications with reduced capital and O&M costs.

One can identify key technologies that compete with energy storage for similar materials (either as raw materials or intermediate stage) and rely on similar manufacturing capacities as for instance on:

- Rare Earth metals:

- synergy between Ni-MH batteries (Ce, La) and permanent magnets for electric motors or wind turbine (Nd, B).

- PGM catalysts:

- synergy between water electrolysis catalysts, fuel cells catalysts and air electrodes catalysts (in Li-Air/Zn-Air however most of research is based on non-PGM catalysts).

- Si nanopowders and inks:

- both for thin film printing in PV as for Li-Ion anodes.

- Hydrogen storage by metal hydrides:

- in Ni-MH batteries and other storage systems.

Further, regarding the need of materials that can sustain extreme conditions (high voltage, corrosion, high temperature...), expertise in nuclear materials science would be of help

Between manufacturing processes

Regarding manufacture and fabrication processes, working to decrease environmental impact (reducing solvent contents) and production costs, several techniques already employed in traditional manufacturing such as extrusion or printing are foreseen to be implemented in batteries manufacturing. Cross links with traditional industries (textile, paper...) that already manage the use of these techniques would be of interest.

Manufacturing principles for fuel cell stacks technology are somehow very similar to the production of battery cell stacks. One can note that Flow batteries exhibit especially strong synergies with fuel cell technologies.

- Bipolar plates: Bipolar architecture also introduced in Li ion batteries in order to increase the cell operating voltage (Technology under development in very few battery manufacturers –Nissan, Daimler for instance)
- fuel cells architecture
- Stack construction has much in common with fuel cells and electrochemical cells in general
- Membranes
- Bipolar Air electrodes – metal air electrodes and unitised regenerable fuel cells

Capacitors also use some similar physical-chemical processes to batteries (especially when one thinks about hybrid capacitors) and sometimes common manufacturing equipments (i.e. winding machines).

In addition to the synergies above highlighted, one must emphasis communalities between thin film technology / nanotechnology and manufacturing processes for ceramic as well as heat storage between adiabatic air storage and concentrated solar power.

Needs and Recommendation of Activities addressing 2020 and 2050 Market Implementation

Europe being well positioned within the Renewable Energy field and having a strongly interconnected electric grid, success when implementing storage for stationary applications should contribute to the establishment of strong strategic positions for European science and technology in these key emerging areas. In particular, efforts should be directed in parallel to (i) exploration of radically new paths leading to highly innovative, high risk, long term research in the field of materials for energy applications and (ii) parallel prototype validation and demonstration projects for more conventional technologies. These storage systems could be used in the central grid generation and distribution facilities for load-levelling and area regulation as well as improved line stability and voltage regulation. More importantly, it also opens for the possibility of local energy generation based on renewable energy sources in remote areas, or in locations where connection to the main grid may be impractical or too costly, potentially making clean energy production accessible to a new group of users. Cost, safety, reliability and ease of use are imperative for successful implementation of relatively small scale localized energy generation systems supporting the energy demands of, for example, a village.

At this stage, a priority ranking of the different storage systems seems difficult. Indeed one must stress that, to date, there are no consented scenarios on the requirements for additional storage capacities in Europe. Several market uncertainties are currently hindering reliable prediction on the need for electricity storage such as uncertainties on the energy technology mix (and the related needs for flexibility) that will be implemented by 2020 and 2050 or uncertainty on the learning potential of advanced storage technologies. These scenarios are essential inputs for framing the needs for material developments and bottlenecks. Therefore, **in this roadmap exercise the approach followed consists in the scientific assessment -a time-dependent technological performance level analysis at technology level or technology open approach-** as a way forward. Authors agree that there is a need to advance further the analytical framework of storage at European level as a pre-requisite for prioritising research for storage. Deployment and market frame would have to be addressed based on

dialogue with all the actors in the supply chain within additional work, well beyond the mission of this group.

Needs and recommendations for Market Implementation in 2020/2030

Key materials long-term funding of research and chemistry are recommended for market implementation in 2020/2030, as sorted below starting from technologies top priority:

Related to Battery Materials: @ EU and MS (Member State) vehicle level

Improvement of current storage systems or those already in development phase [23] (Applied research)

- Redox system:

- Improvement of energy density; development of new chemistries which give faster kinetics, higher voltages and higher energy densities;
- Improvement of membranes (long duration materials, (acid, alkali and inorganic);
- Investigation of redox systems that do not require membranes (which will have impact on price), e.g. soluble lead system
- Development of bipolar air electrodes;
- Study organic based flow systems (higher cell voltage); - likely to be too expensive for static grid applications: The main issues of aqueous systems are the corrosion of pumps and tanks as well as leaks between analyte and catalyte (which leads to pollution). Moving from aqueous to organic solubles, despite a likely increase in system price, would give rise to a better conductivity that may in turn lead to longer cycle life. A prototype using a non-aqueous soluble would be a logic starting point.
- Study V (V_2O_5) supply;
- Cost reduction through engineering and migration to cheaper electrolytes than V. (With regard to existing VRBs, it should be noted that if the amount of vanadium dedicated to redox-flow batteries were to increase greatly, its price would increase because already today 94% of vanadium is dedicated to steel manufacturing)

For the higher energy demands of longer-term grid applications, redox-flow batteries seem to offer better potential than conventional battery types. There are many possible chemistries and it is suggested that a whole-life cost/benefit analysis should be made of all these chemistries to predict which has the best potential for grid applications. Having made this assessment, the most promising should then be supported strongly.

Overall a medium priority is assigned for redox systems with respect to the recommendations.

- Na-S system:

- One claims Na to be more abundantly present than Li and lower in cost. Na is found for instance in France. There is seawater elsewhere but indeed, France is probably the unique best high quality Na producer for electrochemistry applications. Study of the economics further required;
- Role of β -Alumina is critical: risk for breakdown. Study of new electrolytes;
- Corrosion risks of container materials prevent the use of cheap packaging;
- Improving wetting between liquid Na and electrolyte.
- More work on Zebra batteries in Europe is needed.

Due to the dominant position of Japan on this front, it is considered that this technology is probably **not a top research priority**. Field testing using this commercially available technology would improve knowledge on potential business cases of storage applications (e.g. grid support). It was nevertheless reminded that such large scale battery is limited in terms of power capacity, which is probably the main market in Europe in the short term. However, NaS battery technology and particularly its tolerance to higher numbers of cycles with low cost seems an attractive option today. European industrial policy should address the issue of whether some local manufacturing is needed and whether to promote joint ventures between European manufacturers and the Japanese leaders in NaS (NGK). Indeed, to succeed in Na-S stationary industrial level, one can imagine an EU Company taking a license from NGK or a partnership to produce in Europe. There surely is some patented IP held by some European companies...

- Li-Ion system:

- Research should further focus on those parameters important for stationary energy storage i.e. development of low cost positive electrode materials (improved LFP, LMO, LTO, and silicate...), negative electrode materials (substitution of Carbon - based by new materials) and safe electrolytes (allowing higher charging voltages, wide operating temperature ranges, less fluoride for safety issue...);
- Materials that allow reaching the theoretical specific energy of Li ion technology
- High power Li ion systems: Materials and cells architecture, design & integration for high rate capability with high power sustainability and very long life cycle (in synergy with super capacitors)
- Conversion materials versus insertion materials: modeling, C-rate capabilities...
- Novel positive electrode architectures (3D, ...), suitable separators to cover such 3D electrodes and process to obtain such positive architecture;
- Novel negative electrode architectures (3D,), suitable separators to cover such 3D electrodes and process to obtain such negative architecture
- Additives to support conversion reaction and increase efficiency
- Material that can supply lithium ion by in situ means and enable use of non prelithiated positive materials
- New cells architectures introducing components for high design performances (Low internal resistance, high thermal dissipation, high life cycle...) as for instance new current collectors
- Cycle life targets to be set as >10.000 cycles;
- New processing technologies such as nanotechnologies and functionalized coatings should be maximally exploited;
- Materials that allows new cells and batteries architecture constructions;
- Safe and non-flammable electrolytes; solid electrolytes;
- Improvement of temperature operating window (-20, +70°C).

Concerning Li-ion systems, there is a strong need in the short term for demonstration operations of this technology to gain technical field experience and develop business knowledge, a pre-requisite to further attract private investments. As example, in Germany, in the LIB2015 LESSY project of the German Research Ministry, Evonik is testing a 1 MW lithium ion storage device to help buffering electric power produced by the Fenne power plant. Following, to introduce Li ion for stationary applications and to establish a European industry, based on our knowledge in Europe, EU Demo projects for large systems (>1MW)

and field testing projects in smaller residential ones are requested. Additional research funding seems a secondary priority compared to the funding of demonstration projects. As for second life applications, which can play an important role in the short term, it was emphasised the need to address issues such as testing procedures and life expectancy. **Thus, it is clearly believed that the near-term focus for Li-ion should be on demonstration (with power electronics) rather than on basic/applied research.**

Explorative work on new battery systems once such as:

- **Na-Ion system:** development of suitable negative and positive electrode insertion materials and highly conducting room temperature electrolytes are needed for Na ion systems;

Enabling practical use of sodium insertion materials should involve a huge decrease in battery cost (~40%) when compared to lithium, mostly derived from the much higher abundance of sodium. Moreover, the widespread availability of sodium resources (sea brines) has both life-cycle sustainability and socio-political strategic advantages, especially for lithium, since the lithium resources in the EU are almost non-existent.

Na ion technology is mainly considered for replacing Lithium (and not to achieve a better performance). Nevertheless, Na ion is today a very attractive research topic as a good candidate for storage applications due to lower expected cost compared to Li ion.

Activities on Na ion should be ranked second in terms of recommendations.

- **Metal-Air system:**

Generally:

- Research should focus on the rechargeability of the anode (Zn-Air, Li-Air), without dendrite formation and risk to shortage;
- Work on air electrodes (Air flows engineering, hydrophobic membrane...), porous electrode design; Air electrodes that work with air rather than pure oxygen or enriched air should be the focus
- Electrolyte composition for Li-Air, stability, O₂ solubility, O₂ diffusivity, properties, and Li₂O₂ stability are of prime importance
- Work on selective membranes (CO₂ and H₂O barrier membrane)
- Aqueous/Organic/Hybrid versions comparison...
- Nanotechnology is required to define the most appropriate material content
- Air catalysts (MnO₂, NiO, PGM's ...). Mechanism, morphology, surface area investigation... New catalyst with low over potential for O₂
- Cyclability and safety for Li-Air are still major concerns

Indeed, there are two types of metal-air systems with different requirements: the aqueous and non-aqueous systems. Synergies exist between the two, but they should be separated:

For non-aqueous Li-air systems what is needed is:

- An electrolyte stable to the super-oxide (O₂⁻) ion that is produced during discharge at the cathode
- An electrolyte that is Li₂O₂ soluble
- An electrolyte with low evaporation
- A barrier membrane for H₂O and O₂ for the anode
- A barrier membrane for H₂O and CO₂ for the cathode
- A good catalyst for oxygen reduction in organic electrolyte

- A good catalyst for Li_2O_2 oxidation

For aqueous Li-air systems:

- Ceramic membranes with high room temperature conductivities ($> 10^{-3}$ S/cm)
- Ceramic membranes which are stable in contact with lithium metal
- Ceramic membranes which are stable in contact saturated aqueous LiOH solution
- Composite membrane electrolytes that are water tight but Li^+ conductors and pliable
- Composite air electrodes with CO_2 barrier membranes
- Stable reversible air electrodes (ie for both ORR and OER)
- Stable bifunctional catalysts for both ORR and OER

For aqueous zinc-air systems

- High area specific capacity zinc electrodes with good cycle lifetime
- Reversible air electrodes for alkali electrolyte
- Low cost, high performance bifunctional catalyst for high current density positive electrodes (> 300 mA/cm²)

Focus on Future alternative lithium-air system [24- 28]

Promises have been made to reach up to 2000Wh/kg with lithium-air batteries. Nevertheless, a long term challenge of 500Wh/kg for rechargeable system remains extremely motivating. Primary lithium-air (= semi fuel cell)

While there are several started research initiatives (as in the German LIB2015 HELION project Bosch is addressing this issue and in the German STROM initiative where metal-air batteries research will be carried out), results are still on an early and academic state. Indeed, present projects have evidenced that several basic issues need to be improved before having the possibility to assemble true operational prototype cells. So, we recommend carry out research on the following scientific domains and objectives:

- to manage delusive electrode technologies to handle precipitated reaction products
- to develop ceramic and glass membranes with 10 times higher conductivity, improved mechanical strength (Lisicon, Nasicon...)
- to improve air electrode to make it less sensitive to poisoning by S, CO, CO_2 or organic polluting agents
- new generation of catalysts with limited ageing and no precious metals (MnO_2 based for instance)
- development of composite lithium electrodes or structured to avoid metallic dendrites and short-circuits
- membranes for air electrode, packaging ; handling air circulation

Labs from AIST (Japan), US (Polyplus company, Wright Patterson Air Force, Pacific North West National Laboratories), Israel, are among the noticeable projects. In Europe, P. Bruce team at University of Saint Andrews heads a European cooperative project as well as EdF at the French National level.

The projected cost of metal air systems is low (even lower than lead acid today), which makes it interesting for electricity storage. Using Zn in large storage installations might be feasible (and is market ready). Also Li air is a candidate, even though Li air today allows for only 50

cycles. The key problem of Li air is the electrolyte, where aqueous, organic and mixed Li air systems are under research

- **Lithium-sulphur** [29, 30]

The Li-sulphur battery is a relatively low voltage system but sulphur has a potentially very large capacity. The objective would be to reach 350 Wh.kg in standard use.

At room temperature, in organic electrolyte, the sulphur electrode behaves very differently from the high temperature Na-S battery. From sulphur, discharge takes places through four steps of polysulphides, electronically conductive down to Li_2S_4 .

The major issues to solve and the future work to achieve deal with:

- short-circuits due to metallic lithium dendrites during charge
- self-discharge through polysulphides dissolution
- ageing (corrosion, heterogeneous behaviour...)
- safety (solid polymer electrolyte, volatile, low boiling temperature electrolytes)
- suitable structures for electrodes

From patent and publications it is noticed that the first active teams are Sion Power (Israel &US), Matsushita, BASF (Germany), or small companies such as Oxis (UK) or Universities (for instance in Europe in the frame of ALISTORE European network).

The Li-S system does not have a high priority as it does not reduce the need of lithium.

- **Lead system:**

- Established storage technology, not needing additional key materials development except if one considers hybrid systems (Energy/Power-SC type) or Pb flow batteries for stationary application... At least low cost technology that is still under improvement...
- Axes for improvement in the lead-carbon batteries (high energy carbon electrodes).

- **Ni-Cd system:**

- Established storage technology, not needing additional key material development.

- **Ni-MH system:**

- Same, no immediate research needs with the exception of the RE critical materials sourcing and recycling.

- **Zn-Br₂ system:**

- No specific research needs on materials.

In this sense, research at this stage should target projects dealing novel knowledge-based materials for energy applications to develop efficient energy storage systems with drastically reduced cost. The achievement of the proposed objectives is expected to bring about a breakthrough in key areas where energy technology benefits are to be expected as for both automotive and electric grid applications. **It must be stressed that research for new materials requires research in very sensitive characterization tools** (ex and in situ) in order to fully understand reaction mechanisms as well as mechanisms high throughput

modelling tools to be used in combination with chemistry, crystallography and electrochemical testing.

Related to Super capacitors (EDLC): @ EU and MS (Member State) vehicle level

Similarly to the previous section, materials research is an important issue to tackle, some of the key points are listed below:

- Possible **substitution** of traditional carbon type materials by **carbon nanotubes**
- Development of pseudo-capacitors (redox-based) by the use of metal oxides (Ru-oxide, MnO₂ ...), nitrides or polymer films;
- Development of hybrid capacitors: 1 electrochemical electrode + 1 battery electrode in aqueous media for low cost system (c€/F) and low impact materials (Acetonitrile replacement) but still with low energy density: Carbon/MnO₂, C/NiOH (see Saft technology)...
- Development of Carbon-Carbon controlling pore sizes (and PSD) and increasing voltage thanks to surface treatments (Functionalized hydrophobic carbon) to reach energy density >15Wh/kg with similar charge-discharge rates (Salts like LiEt₄NBF₄) in synergy with Li-S and metal-air negative electrode stabilization (passivation)
- Development of aqueous electrolytes to be used with carbon-carbon systems
- Further work on Ionic Liquids for higher voltage ranges with wide operational temperature range and high conductivity. Or working on Ionic Liquids-solvent mixtures with high voltage solvents as developed in Li ion batteries (additives/new solvents)
- LIC asymmetric systems: improve life cycle (LTO-Carbon...) and improve symmetry of charge-discharge rates to achieve 20-30Wh/kg in synergy with high power Li-ion batteries
- Electrical capacity (ESTORE technology): So far no proof of concept
- Aqueous Hybrid systems for very low cost and low environmental impact using activated carbons...

For supercaps, new forms of carbons (e.g. porous carbons) might be promising, whereas Ru oxides are relatively expensive. The combination of modelling with in situ experiments is very important (also for batteries) to understand interaction with pores.

Supercapacitors (EDLC) are likely to have a role in power quality applications (power applications at large), particularly combined with batteries and power electronics converters. However, super capacitors should be considered independently of hybrid systems in the assessment. Many applications of supercaps are already in place (in UPS and cranes) and grid integration and application in cars have been demonstrated. The EU research is leading the development in this field. Europe has an opportunity to reap the industrial benefits of this excellence in research. However, this will require an industrial strategy at EU level that brings together researchers, manufacturers and possible users to form a nucleus for the expansion of this technology. EDLC science and technology is in its infancy and still has much potential for improvement, particularly with respect to energy density. **EDLC should be prioritised at basic and applied research level and hybrid systems at applied research and pilot/demonstrator level.**

Related to Hydrogen/Fuel Cells: @ MS (Member State) vehicle level (not fully detailed because drafted in Hydrogen and Fuel Cells Chapter)

- Catalysts H₂O electrolysis;

- Electro-catalysts improvements in fuel cells (reduction of PGM content and development of new, non-corrosive substrates);
- Durability of the MEA's.

COMMENT – low round trip energy efficiency. Not for stationary applications except in special circumstances. Examples: APU for remote sites with combined system PV-Low Temperature FC, micro-Combined Heat and Power, see the on-going Japanese field testing program with Proton Exchange Membrane technology...

For very high energy storage, hydrogen is a very interesting storage medium. **Priority should be given to applied research and pilot/demonstration actions** of "hydrogen-based" electrical energy storage technologies.

Related to Flywheels: @ EU and MS (Member State) vehicle level

- Continuous improvement of the magnetic bearing;
- HTS magnetic bearings represent a step possible improvement for FESS;
- Development of low cost and high strength composite materials coupled cost engineering of the system.
- Research opportunities as new materials for friction reduction and joint durability or new design

Flywheels are used when high power density is required for disruptions lasting seconds to minutes. They are simple forms of kinetic energy storage, proportional to its mass and square of its rotation speed. In general, we can classify them as low-speed (made from steel for high power output) and high speed (made from high strength composite materials).

The technology is somehow between demonstration and commercial maturity with two major research avenues: passive magnetic bearings and improved wheel materials. Like many other mature technology, other important areas are of coarse cost reduction in terms of rotor manufacturing and improved motor generator materials fabrication efficiency.

The US today has a dominant industrial position with respect to flywheel developments. Limited research and industrial developments are currently taking place in Europe. The level of research to be performed in Europe is dependent on the industrial strategy pursued (i) EU as importer or (ii) build-up of an entire industry. Such strategy is not available today. As a result, recommendations on flywheels are limited in the assessment:

Materials-related improvements in flywheels could come from lighter polymeric composite wheels to increase rotational speeds and magnetic or superconducting bearings to reduce frictional losses. Advances in bearing materials are likely to come from materials research focused on other applications, but there may be a case for applied research and demonstration projects under "electrical storage".

Related to SMES: @ EU and MS (Member State) vehicle level

- Reduce cost of superconductors;
- Develop high critical temperature superconductors
- Development of second generation HTS conductors with high critical current density at high magnetic field will allow for highly improved SMES devices
- SMES do not look to be viable for mass-roll-out energy storage any time soon

Related to CSP Thermal: @ EU vehicle level

- Further definition of best storage medium (molten salt, concrete ...) and best transfer medium (oil, H₂O, steam ...) Materials for electric heaters is a real problem limiting storage of surplus wind energy in these systems...

Related to manufacture designs and processes (needs new smart materials) for batteries and super capacitors or others: @ EU and MS (Member State) vehicle level

Towards innovative environmental, low cost storage processing and innovative cells and modules/pack designs

New architectures of cells, modules or packs for safe, efficient, low cost, high life time storage systems will have to be considered. Very high power designs (Low internal resistance, high thermal dissipation, long life cycle...) will also have to be addressed. Manufacturing of equipments necessary for an automated assembly to demonstrate the reproducibility and the robustness of the new design as well as an economic evaluation/environmental impact of its manufacturing will have to be fully investigated. Demonstration of the performances associated with this new design of storage system and simplified manufacturing are some of the topics to be closely checked. The goal deals with earnings in costs and delay of manufacturing. Besides the technical aspects of manufacturing, the choice of the sizing of the storage system to preserve its modularity and therefore enable economy of scale addressing several markets will have to be imagined. In addition new materials for innovative integration will have to be proposed: composites, electronic conductors, materials with thermal dissipation properties, integration of materials for cooling/heating, multi energy sources/conversion materials, reversible sealing materials, bio (compatible) materials, functionalized packaging, smart materials to manage safety (overcharge, overheating), multi-functional materials, full recycling materials... self-diagnostic systems... hybrid systems (energy/power/safety/storage/production...).

Related to pumped hydro: @ EU and MS (Member State) vehicle level

For very high energy in the >GWh range, the best candidates are variants of the conventional technologies like pumped hydro storage (PHS). There are materials development issues as for example, PHS combined with off-shore wind farms might be required to use sea water. For such use, radical redesign (with new materials) of mechanical and hydro mechanical equipment would be needed. Material research is also needed on some critical components such as power electronics.

Related to CAES: Demonstration @ EU and MS (Member State) vehicle level

Compressed air energy storage (CAES) is relevant for very high energy in the >GWh range. Specific materials developments would be needed on some critical components such as thermal storage for adiabatic CAES. Energy from various sources can be stored and thus different versions are today available:

- Diabatic CAES (> 100MW, > 1GWh), based on the two firsts Huntorf and Mc Intosh systems and which need extra-heat during discharge, will lead to new demonstrations in the USA that will reach about 55% of efficiency.
- Adiabatic CAES (> 100MW, > 1GWh) which are new concepts based on both compressed air and heat storage would enable to reach 70 % of efficiency: heat storage is the key point with today low technical maturity.
- Isothermal CAES (~1MW, ~4MWh) are low capacity and power storages studied by Sustain-X or General Compression in the USA and based on an isothermal compression

and expansion that lead to 70-75 % of efficiency (taking into account 95% of efficiency for each compression and expansion and others losses).

- LAES or CES for Liquid Air Energy Storage or Cryogenic Energy Storage (~50 to 100 MW, ~200 to 500 MWh) are studied in the UK and USA in order to store liquid air: efficiency is in the same scope of CAES for higher cost due to its complexity. CAES needs suitable geographical locations. LAES or CES do not have the same constraint

It is recommended to launch some R&D programmes on materials suitable for high temperatures compressors in order to ensure the economic viability of Adiabatic CAES systems:

- materials suitable for high temperature thermal energy storages devices (High temperature resistant and stable, cheap, high heat capacity, good conductivity, low degradation)
- materials for compressed air salt cavern storages (corrosion resistant and cheap)
- development and demonstration of huge thermal energy storage that take into account new media for thermal storage and container able to resist to both pressure and thermal stresses.
- development of materials suitable for high pressure and temperature compressors for Adiabatic CAES issues

There is overall a general agreement (in line with the assessment findings) on the limited needs for material research for pumped hydro (PHS). Regarding compressed air energy storage (CAES) beyond current efforts (business as usual); materials research is needed while high temperature compact thermal storage materials need to be assessed. The thermal storage also needs to deliver the heat with high power densities and therefore needs good thermal conductivities.

Electric Vehicles (EVs), advanced control systems and power electronics for efficient grid connection [31]: @ EU vehicle level

- EV's are also considered as a potential future energy storage technology.
This domain is sufficiently described in EV roadmaps (e.g. in German Platform for E-mobility);
- Study effect of V2G concept on ageing and life time of the battery.
- The interfacing to the grid by the use of power electronics is crucial to success. Any storage technology that is being researched should have correspondence with power electronics at some level. However, Care have to be taken while the preference for balanced (ES / power electronics) projects in FP7 risks too little effort being assigned to overcoming the critical challenges of the storage technology.

Therefore, there is a need for advanced experimental activity to assess performance stability and ageing problems related to number of charge/discharge cycles and to lifetime of batteries, also in view of second life and V2G applications. Applied research as well as pilot and demonstration actions on batteries and small EV fleets are certainly needed to take into account all possible use cases (fast charging, environmental effects ...).

Safety organizations

Safety organizations(@ EU vehicle level) are needed at European level with a specific infrastructure to test storage for stationary application, an example of such is INERIS for automotive in France.

Main research Challenges

To perform knowledge transfer from lab to industry in term of processing or manufacturing and accelerate the competitiveness of the industry with introducing innovative technologies,

especially for sensitive materials, the technological platforms models looks relevant. Practically, technological platforms would cover a wide spectrum of actors from basic and applied research to large industrial firms and inventive start-ups, through prototyping line and seem value-added and efficient chain to set out to provide industry with a full range of R&D resources for basic research, battery prototyping, assessing safety performance, and certification.

Projects involving cross cutting issues of several scientific programs have to be promoted. Programs that require multi-disciplinary competences on very advanced materials such as for energy and nuclear energy for instance could work to imagine innovative storage systems in order not only to increment performances but introduce real breakthroughs. Mixing other competencies such as polymers, mechanic, electro technical, power electronic, economic, safety & legal policy for instance could also help to solve some of the problems encountered working to introduce (or at least to promote) new technologies at an industrial level.

Excellence

Finally, preparing technologies for market implementation in 2050 requires strong efforts and excellence in fundamental research. Especially, European brain gain in the field of electrochemistry, through support to young scientists in the area of energy storage research, would be relevant. In addition, Education to strengthen the scientific competencies (training and education for electrochemistry, electrical storage experts) is identified as a long term needs (2020+).

Needs and recommendations for Market Implementation in 2050

Within the framework of research with a longer term perspective aimed at accelerating technology development, specific importance of integral knowledge-based cross cutting approaches is increased. The necessary synergetic integration of materials science and energy involves a wide range of industrial production sectors from manufacturing and chemical processing to engineering, electronics and device production, testing and validation. Curbing the current trend and strengthening the competitiveness of the European energy sector, in the face of severe global competition is an important objective, providing the capability for European industry to attain leadership in key energy technologies and create growth and employment. This will benefit both new, high tech knowledge-based industries (e.g. small SMEs) and big established companies whose global competitiveness is largely dependent on their capacity to integrate and exploit new knowledge and new technologies, as done by other industrialised countries such as US and Japan.

Examples of emerging storage technologies or any other new revolutionary technology to be addressed are given below, in a non-exhaustive manner:

1. Aqueous Li ion systems

2. Future alternative battery systems based on Na or pluri electron exchange (Mg, Al) [32] (includes Al/Mg-Ion, sulphur or air type)

Those systems could be useful to consider on the long term only in case of lithium shortage.

Sodium batteries: High temperature sodium systems exist but batteries need to be maintained around 300 °C..

The research projects should examine the feasibility of room temperature systems. Their main advantage would be the lower cost of the systems, while the main drawbacks would be the lower energy density when compared to lithium-ion battery.

With respect to multi electron systems, as few attempts were made in the past more on rechargeable Mg than on Al, but no components are available to date. The capacity of those

materials is as high as lithium but power limitations are expected due to slower diffusion of higher charge cations.

3. Solid State Batteries: To improve the current technologies (sodium based) or introduce real innovation involving all solid state lithium ion batteries, risky projects introducing brand new materials for large scale applications demonstration at a representative scale will be very welcome.

4. Study of liquid metal batteries as developed by Prof. D. Sadoway of MIT (2009) [23]

5. Dreamed Ultra capacitor (beyond 2050): Electrolyte with 4.5-5V stability window using materials with 3000m²/g active surface area (Theoretical value of Graphene) for 600F/g capacity

6. System integration: smart grids, Implementation of V2G (vehicle to grid) such as, by 2050, estimated EV penetration of 40 – 50% reached.... Needs in advanced power electronics to reliable grid integration.

7. New demo and field testing

8. Develop creative technologies with disruptive performances merging several know ledges as for instance electrochemistry, organic (bio), and optical, thermal and nuclear energy ..., therefore, working to imagine storage systems in order not only to increment performances but introduce real innovation as for instance targeting life time given in years rather than in kilometres or miles.

Projects crossing new energies for transport program, ICT program, Nuclear program and Renewable energy in a multi-disciplinary approach that requires competences on very advanced materials, on energy, electrotechnic, power electronic, economic, safety & legal policy... will have to be considered for energy storage breakthrough.

It is difficult to envisage none battery technologies with real promise on a 2050 timescale but possibilities include:

- Enhanced flywheels where improvements would arise from using very high strength materials and HTS bearings for support rather than just balancing to reduce losses.
- Compressed gas storage where the gas is stored on very high surface area materials such as zeolites, allowing high capacity storage for mobile applications without the need for high pressure tanks.

To conclude.

Generally, the European R & D program must be composed of the three following parts:

- Materials and technology developments in order to optimise or develop new energy storage technology for the specific needs of electrical storage dedicated to RES & grid integration
- Methods and solutions of grid integration in order to enhance the RES integration
- Large demonstration projects in order to establish and confirm future business models

The material SET-Plan is a key part of the technology development plan and must contribute to the strengthening of the European Electrical/Energy Storage Network:

- European Electrical/Energy Storage Industry
- European Electrical/Energy Storage Suppliers
- European Electrical/Energy Storage Operators
- European R & D centres

Needs and recommendation addressing long term markets deal with:

- Long-term funding of materials research and chemistry, in particular post-lithium and alternative systems (like redox-flow-batteries...). As materials represent a key cost driver of the different electrical storage systems, the launching of European initiatives to find new materials will contribute a lot to the positioning of electrical storage.
- Basic research into any storage materials technology for grid application supported on the basis of evidence that it has the potential to offer a significant cost/performance improvement over existing solutions
- Development and system understanding along the whole process chain (e.g. implementation and cooperation of industrial consortia from relevant sectors)
- Interface design is very important and integration with detection and control is a key as integration into the grid is very complex. This means that cost for interfaces has to be controlled and that storage technology can not be considered a separate technology. Integration into the grid has to be done at the right timing (otherwise resources might be wasted).
- The combination of different storage technologies (e.g. Na-S combined with flywheel) into storage systems could offer potential and demonstration of such mixed systems might be interesting.
- As the electrical storage can be located at all places along the value chain and can provide some value simultaneously to different stakeholders, the first challenge is related to the value materialization because of the following reasons:
 - No compensation scheme for storage among stakeholders
 - No clear ownership and operating models
 - No models for materializing value streams

So, the launching of R & D studies dedicated to simulating tools and the launching of large European demonstration projects could contribute a lot to establish and confirm future business models.

- European brain gain in the field of electrochemistry, support of young scientists in the area of battery research; Education: strengthen the scientific competencies (training and education for electrochemistry, battery experts) as long term needs (2020+)
- Better approach to influence international standards for battery technology (need EU regulation like for UL (independent safety science company offering expertise across five key strategic businesses: Product Safety, Environment, Life & Health, University and Verification Services))
- A strong cooperation between academics and consortia of industrial companies (not only from a vertical supply chain point of view) is crucial for the development of the next generation storage solutions in Europe. This could be achieved by the establishment of dedicated industrial development partnerships at EU level. It also should be considered that it takes at least 10 years to bring a new electrochemistry to the industrial market.
- Production/ Industrialization: needs in manufacturing plants funding (See US DOE), upscale, advanced manufacturing equipments developments (new architectures) and solutions for mass production. It is recommended that EU further fosters the set-up of storage demonstrations (RE plants, EVs convergence...) and stimulates to create in Europe maximum manufacturing capabilities (e.g. for battery cells and systems) as US DOE programs currently running together with excellence research /education : Need integration platforms, funding for technological research and upscale processing

Road-mapping process (See Material Roadmap document)

The present draft includes already an extensive and detailed list of the areas of research (topics), which need to be further prioritised in terms of timing when in the next 10 years to implement the proposed programmes or action with the preferred actors. This is essential to be able to build a roadmap that goes beyond a strategic research agenda. Hence this last section of the report targets includes this type of information.

The material SET-Plan must be divided into 2 main parts:

- First part related to technologies able to be marketed in the next 10 years:
 - New Li-ion families
 - CAES improvements
 - Power technologies such as super capacitor & SMES
- Second part related to the prospective technologies that must overcome some technological barriers before to be used in demonstration projects:
 - Post Li-ion systems: Metal-air, Li-S, Na-ion,...

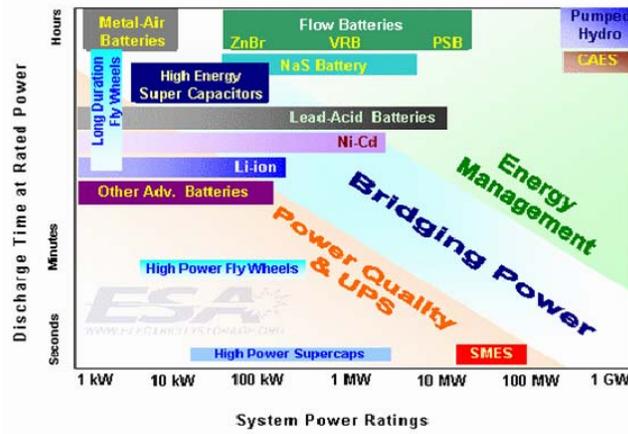
ANNEX I: References

- [1] D.H. Doughty, P.C. Butler, A.A. Akhil, N.H. Clark and J.D. Boyes, *Interface*, 19 (3)2010, 49
- [2] J.K. Kaldellis et al. *Renew. Sust. Energy Rev.* 2009, 378, 392
- [3] Bottling Electricity : storage as a strategic Tool for managing Variability and Capacity Concern in the Modern Grid, Report by the Electricity Advisory Committee (US DOE), December 2008
- [4] Sandia report 2002-1314: Energy storage opportunities analysis: Paul Butler, Jennifer L. Miller and Paula A. Taylor.
- [5] Sandia report – July 2008
- [6] http://www.electrochem.org/dl/interface/fal/fal10/fal10_p049-053.pdf
- [7] H. Ibrahim, A. Ilinca, J. Perron. *Renewable and Sustainable Energy Reviews*, 2008, **12**, 1221
- [8] EU commission report on Critical Raw Materials – June 2010
- [9] Defining critical materials for the EU, Mai 2010
- [10] DOE Critical Materials Strategy, Draft Document, December 2010
- [11] Lanthanide Resources and Alternatives, A report for Department for Transport and Department for Business, Innovation and Skills, May 2010 (UK)
- [12] Na-Ion Batteries, The Electrochemical Society (2010): Komaba et al, Tokyo University of Science
- [13] New Sodium-Ion cathode materials: www.research.waterloo.ca
- [14] Developments in battery chemistries: 2009 European Energy Fair Zürich: www.investorrelations.unicore.com
- [15] P. Tixador, *Physica C* 470 (2010) 971
- [16] P. Tixador; IEEE/CSC & ESAS EUROPEAN SUPERCONDUCTIVITY NEWS FORUM, No. 3, (2008), www.esas.org
- [17] <http://www.u-picardie.fr/alistore>
- [18] <http://eit.europa.eu/kics1/kic-innoenergy.html>
- [19] *US Geological Survey 2007*
- [20] *Cost of lithium-ion batteries for vehicles* L. Gaines, R. Cuenca. ANL/ESD-42 report under US-DOE contract
- [21] “Technology-Roadmap Lithium-Ionen Batterien 2030”, Fraunhofer ISI, 2010, <http://www.bmwi.de/BMWi/Navigation/Service/publikationen,did=370076.html>
- [22] *Advanced Materials and Devices for Stationary Electrical Energy Storage Applications*, http://energy.tms.org/docs/pdfs/Advanced_Materials_for_SEES_2010.pdf
- [23] MIT (DMSE) website: <http://dmse.scripts.mit.edu/news>
- [24] Alistore-ERI White Paper, 2010
- [25] K.M. Abraham, *J. Electrochem. Soc.* 143, 1, 1986
- [26] Advanced Batteries Technology, March 2010, including announcement of IBM project launch
- [27] Polyplus Company data, 2009
- [28] Li-air battery, US patent 2005/0095506, 5 May 2005
- [29] Matsushita, EP 0569 037, 7 July 1993
- [30] Sion Power paper, Electrochemical Society Meeting, 2010, High Energy Rechargeable Li-S Cells for EV Application. Status, Challenges and Solutions
- [31] Advanced materials and devices for stationary electrical energy storage applications: Sandia December 2010
- [32] Sony: EP1058330 and JP2001076720); Toyota (JP2002025555)

General References that can be of use (apart from those specifically mentioned in the text, some of them are more recent than others).

- http://www.er.doe.gov/bes/reports/files/EES_rpt.pdf
(Report on a DOE workshop, it targets both fundamental research and technology applier R&D needs for energy storage. For the latter both transportation and stationary energy storage are discussed)
- M.R. Palacín “Recent advances in rechargeable battery materials: a chemist’s perspective”. *Chemical Society Reviews*, 2009, **38**, 2565-2575.
(A short introductory review with the state of the art of battery materials, tough an important part is devoted to lithium, others technologies are also discussed)
- F. Fusalba & S. Martinet “Energy Storage” Edited by Yves Brunet, John Wiley& Sons, Inc., ISTE LTd 2011Chapter 8, pp. 11175-214.

ANNEX II: Figures and Tables



Sandia National Laboratories (2002)

Figure 1: Supply Side Storage Technologies

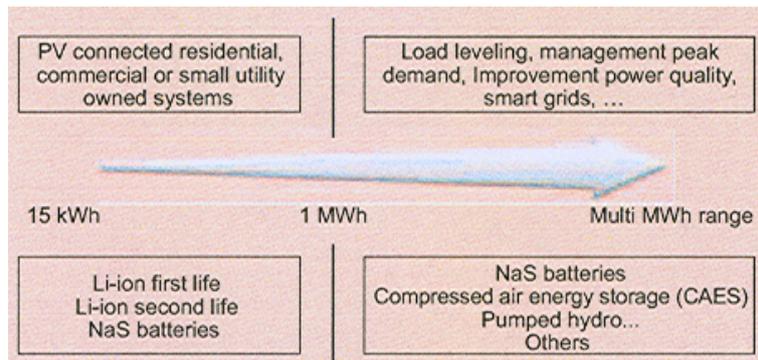


Figure 2: Overview stationary energy storage: partial fit for Li Ion battery technology

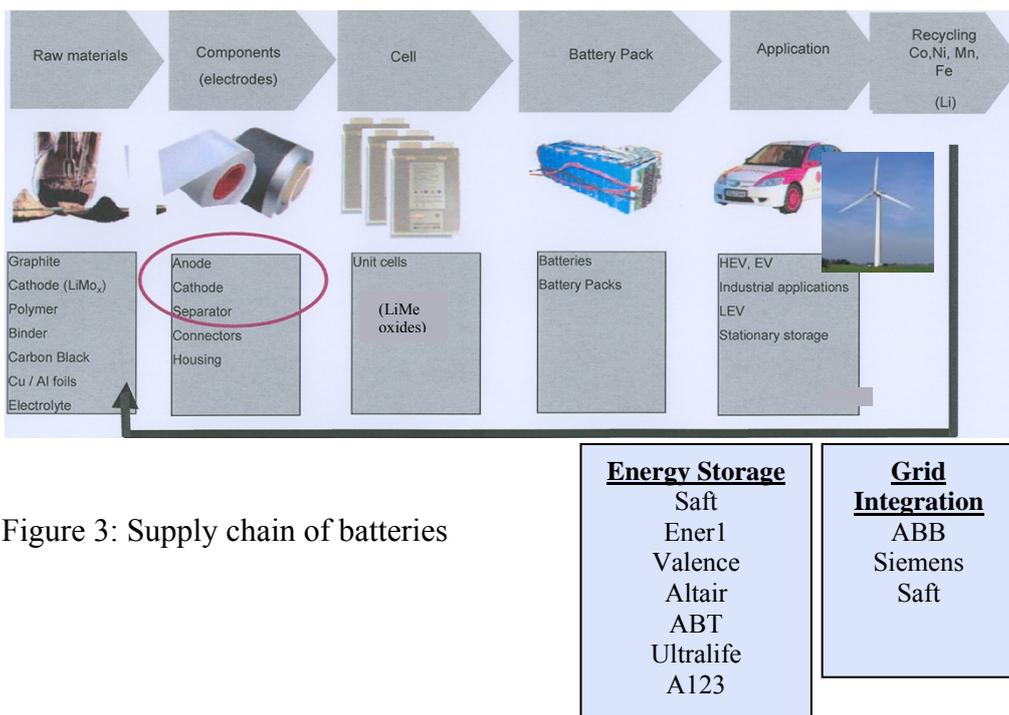


Figure 3: Supply chain of batteries

Energy Storage

Saft
Ener1
Valence
Altair
ABT
Ultralife
A123

Grid Integration

ABB
Siemens
Saft

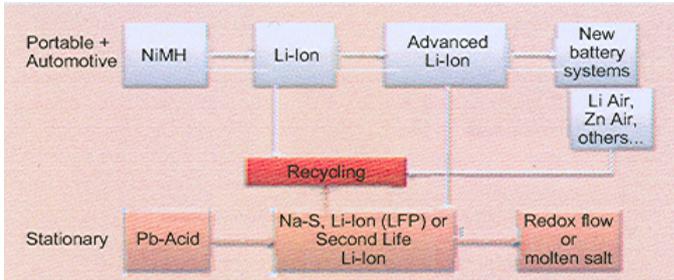


Figure 4: Closed loop system covering technology development application

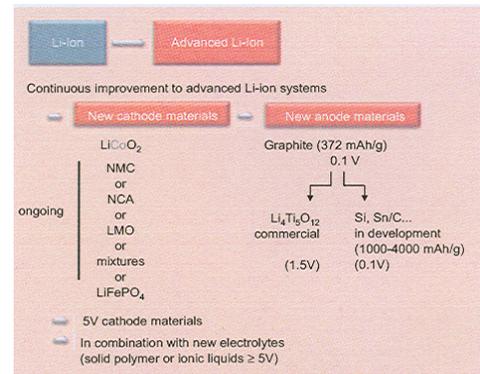


Figure 5: Current cathode and anode research. Aiming the introduction of advanced Li-Ion systems

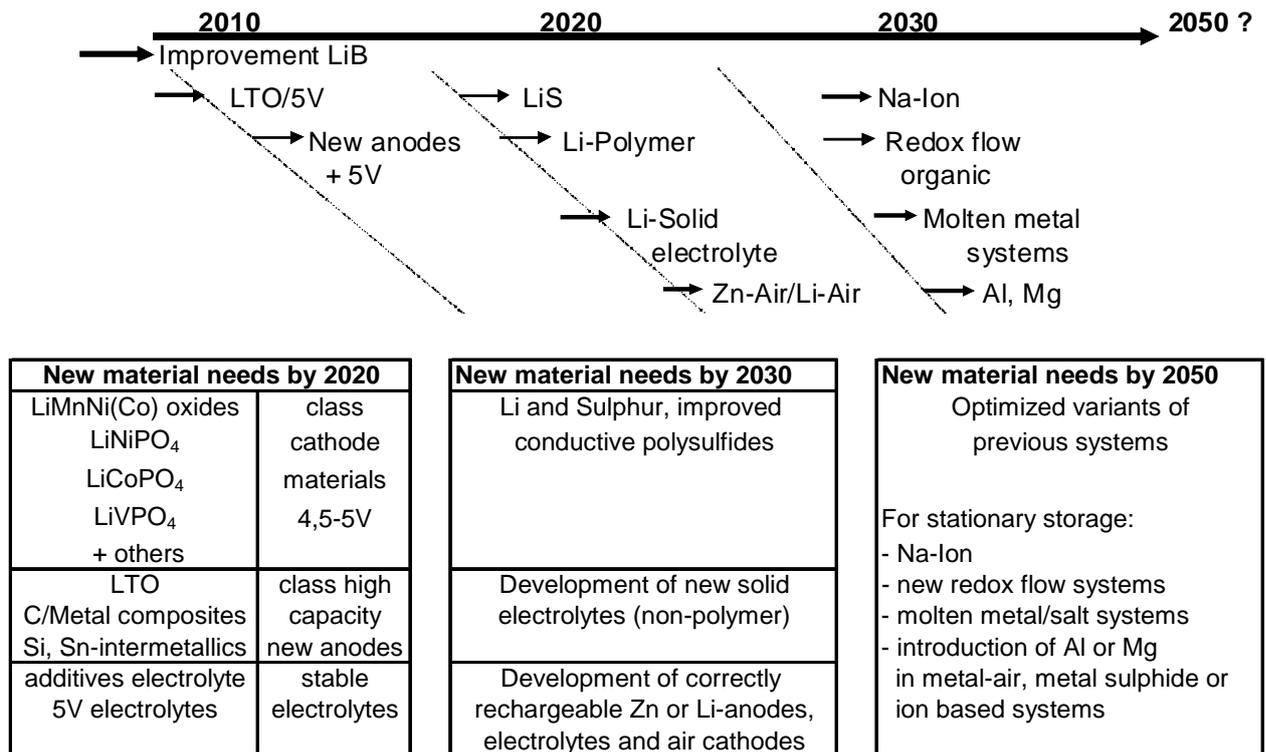


Figure 6: Technology penetration scenario for the Batteries materials roadmap

Technology Penetration scenarios for the Materials Roadmap

Low Scenario (low penetration of SET-Plan technologies)

The Low Scenario, which represents a low uptake of SET-Plan technologies, stems from the European energy outlook “EU energy trends to 2030 — Update 2009, DG-Energy (2010)”

Table 1: Technology penetration for Low Scenario

Energy Source	Capacity			Installed per year	
	2010	2020	2030	2010-2020	2020-2030
Nuclear (GW) ⁺	127	123	124	1.4	2.1
Wind (GW) ⁺	86	222	280	13.6	5.8
Solar PV (GW) ⁺	15	84	150	6.9	7.0
CSP (GW) ⁺	0.5	1.2	3.6	0.1	0.2
CCS (GW) ⁺	0	5	6	0.5	0.1
Biofuels (Mtoe)	15	26.2	34.5	1	1
Fuel cells non-automotive (GW _e)*	0	14	38	Max 3	2.4
Hydrogen (Mcars)	0	1	5	Max 0.4	0.4
Efficient buildings (energy consumption reduction %)	0	20	40		

⁺ expressed in terms of net generation capacity

* incl. fuel cells using other fuels than hydrogen

High Scenario (high penetration of SET-Plan technologies)

The High Scenario represents industry estimates for the uptake of SET-Plan technologies.

Table 2: Technology penetration for high scenario

Energy Source	Capacity			Installed per year	
	2010	2020	2030	2010-2020	2020-2030
Nuclear (GW) ⁺	127	198	297	8.9	11.9
Wind (GW) ⁺	86	230	400	14.4	17.0
Solar PV (GW) ⁺	15	360	630	35	27
CSP (GW) ⁺	0.5	30	60	3.0	3.0
CCS (GW) ⁺	0	20	80	2.0	6.0
Biofuels (Mtoe)	15	48.9	72.7	3.5	2.5
Fuel cells non-automotive (GW _e)*	0	22	75	Max 6	5.3
Hydrogen (Mcars)	0	5	25	Max 1.8	2.0
Efficient buildings (energy consumption reduction %)	0	30	80		

⁺ expressed in terms of electricity production capacity

* incl. fuel cells using other fuels than hydrogen

Figure 7: Technology penetration scenarios for the Materials Roadmap (High scenario: Moved it in the text to be further discussed)

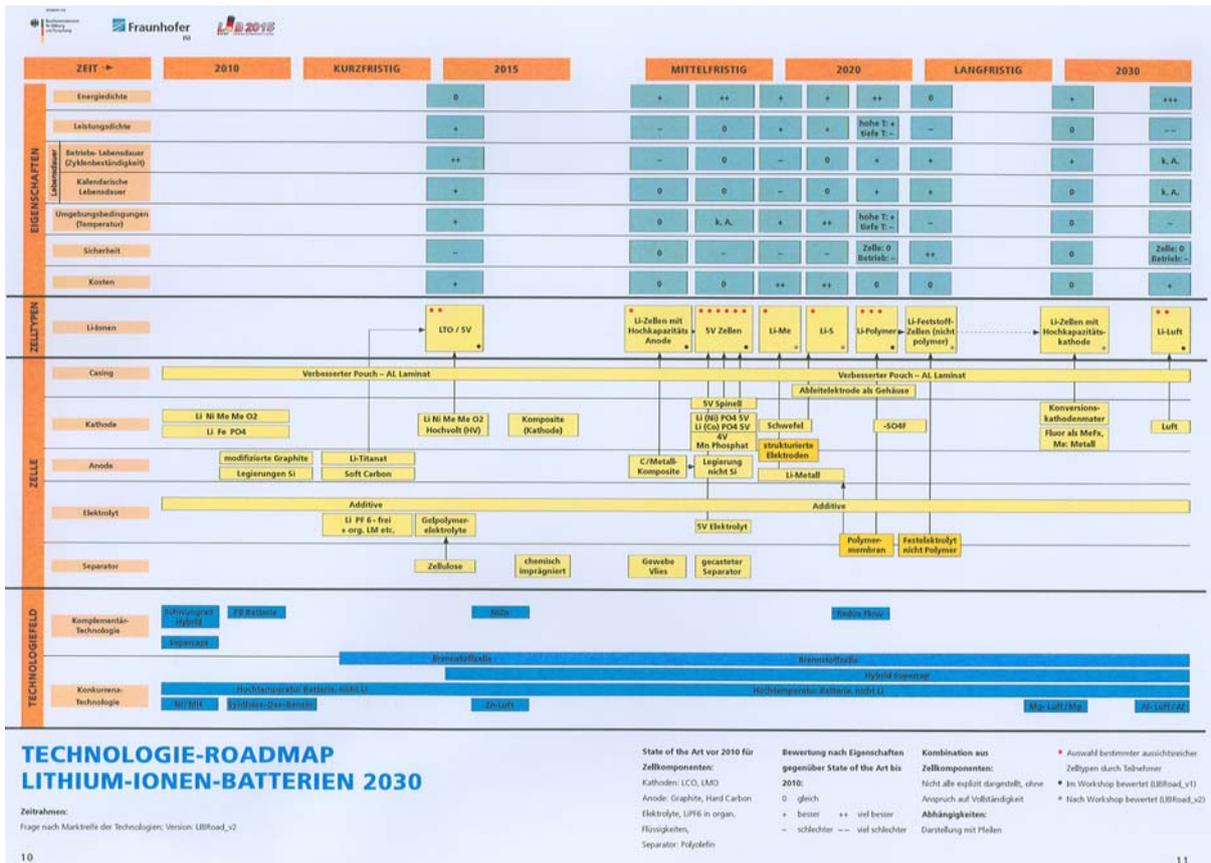


Figure 8: “Technology-Roadmap Lithium-Ion Batteries 2030”, funded by the German Ministry of Research and Education (BMBF), Fraunhofer ISI 2010

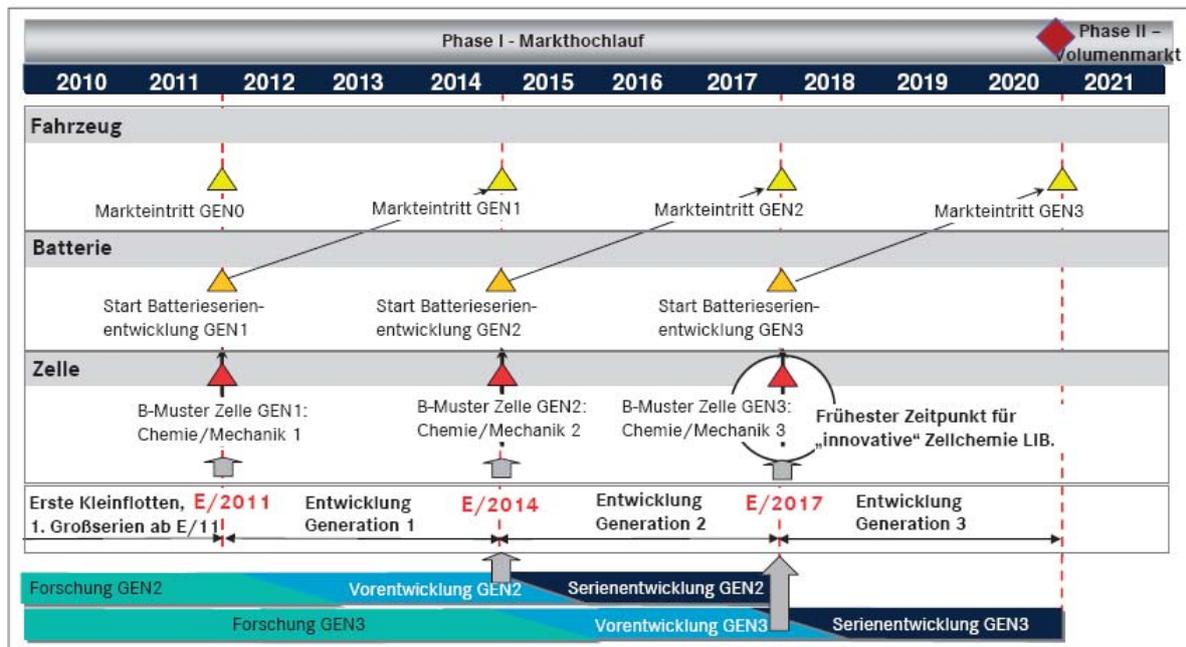


Figure 9: Battery Roadmap, Working Group 2-Batterytechnology, NPE 2010

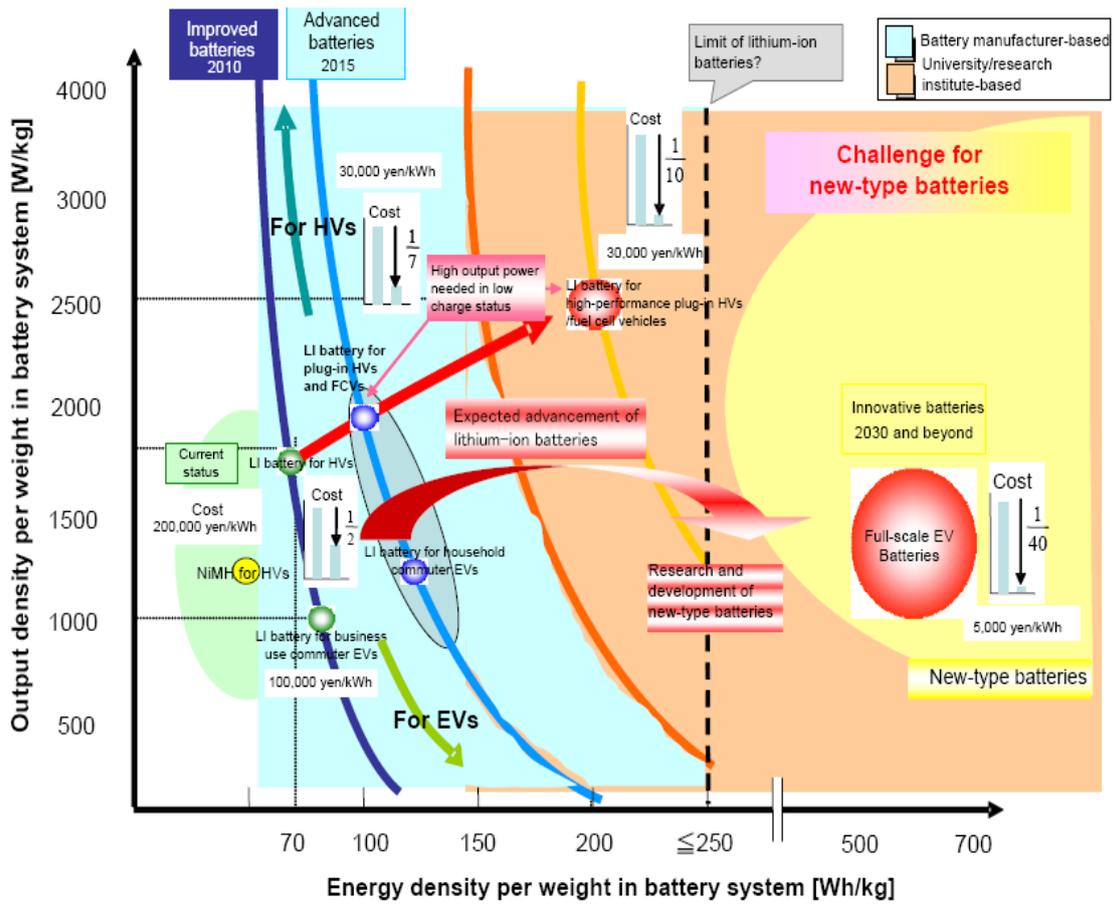


Figure 10: METI-Report on Target Values of Rechargeable Batteries for Vehicle Use, Japan 2006

Table 1: Major characteristics of energy storage systems

Storage system	Service period n_{ss} (years)	DoD (%)	Power efficiency η_p (%)	Energy efficiency η_{en} (%)	Specific energy cost c_e (€/kWh)	Specific power cost c_p (€/kW)	M&O m (%)
P.H.S.	30 ÷ 50	95	85	65 ÷ 75	10 ÷ 20	500 ÷ 1500	0.25 ÷ 0.5
C.A.E.S.	20 ÷ 40	55 ÷ 70	80 ÷ 85	70 ÷ 80	3 ÷ 5	300 ÷ 600	0.3 ÷ 1
Regenesys	10 ÷ 15	100	75 ÷ 85	60 ÷ 70	125 ÷ 150	250 ÷ 300	0.7 ÷ 1.3
F.C.	10 ÷ 20	90	40 ÷ 70	35 ÷ 45	2 ÷ 15	300 ÷ 1000	0.5 ÷ 1
Lead Acid	5 ÷ 8	60 ÷ 70	85	75 ÷ 80	210 ÷ 270	140 ÷ 200	0.5 ÷ 1
Na-S	10 ÷ 15	60 ÷ 80	86 ÷ 90	75 ÷ 85	210 ÷ 250	125 ÷ 150	0.5 ÷ 1

Table 2: Various electricity storage contributions at different locations

	Central Storage	Grid Storage	End-user Storage
Balancing Demand & Supply	<ul style="list-style-type: none"> - Seasonal / weekly fluctuations, - large geographical unbalances 	<ul style="list-style-type: none"> - Daily / hourly variations, - Peak shaving 	<ul style="list-style-type: none"> - Daily variations - Auto Consumption
		Virtual storage plants	
Grid Management	<ul style="list-style-type: none"> - Voltage & frequency regulation - Complement to classic power plants for Peak generation. - participate in balancing markets 	<ul style="list-style-type: none"> - Voltage & frequency regulation - substitute existing ancillary services (at lower CO₂) - participate in balancing markets 	<ul style="list-style-type: none"> Aggregation of small storage systems providing grid services
			EV integration
Energy Efficiency	<ul style="list-style-type: none"> - Better efficiency of the global mix - Time-shift of Off-Peak into Peak energy. 	Demand Side Management Interaction Grid – end user	Local production and consumption, Behaviour change Increase value of PV Efficient buildings
		Smart grids	

Table 3: Description of the Key Technologies for Energy Storage / Challenges to Technology, Materials and Processes

System	Characteristics	Key Materials	Key Processes	Main Challenges	Status
<ul style="list-style-type: none"> • V scarcity • stability and durability of membranes • influence impurities • improve membranes to enable min. cross-over • develop non aqueous systems to widen cell voltage 	<ul style="list-style-type: none"> - 20 Wh/kg (low), - 25 Wh/l (low), - 80% efficiency, - cycle durability: 10 – 20 yrs - calendar durability: >10.000 - V: 1,15 – 1,55 V 	<ul style="list-style-type: none"> • positive electrolyte $\text{VO}_2^+ \quad \text{VO}^{2+}$ • negative electrolyte $\text{V}^{+2} \quad \text{V}^{3+}$ • proton exchange membrane 	Electrolyte production.		Large scale demonstration plants
<ul style="list-style-type: none"> • focus on increasing manufacturing yield and reducing cost • decrease operating temp. <p>Challenge: dependency on one major Japanese system producer</p>	<ul style="list-style-type: none"> 300°C, 15 years, efficiency 90%, 100 Wh/kg, 1000 cycles, 100 MW installed in Japan 	<ul style="list-style-type: none"> • molten electrodes of sodium and sulphur • solid electrolyte of β-alumina 	see NGK technology		Commercialized (Japan)
<ul style="list-style-type: none"> • high temperature operation 	<ul style="list-style-type: none"> 300°C, 100 Wh/kg, 100 W/kg, 100 V 	<ul style="list-style-type: none"> • molten NaAlCl_4 as electrolyte, molten Na • Ni/NiCl₂ • β-alumina 	in existence for more than 30 years		Under development (Commercialized at small scale for EV applications)
<ul style="list-style-type: none"> • improve cycle life (>5000 cycles) and cost • design and manufacture novel electrode architectures (3D) • develop a conductive inorganic solid state 	<ul style="list-style-type: none"> 100 Wh/kg, 100 Wh/l, 3,7 V, 100 P 3,1 V), cycle life ~ chemistry 	<ul style="list-style-type: none"> • cathodes: LCO, NMC, LFP, LMO, 5V in development • anodes: graphite, Si/Sn, LTO • electrolyte/salts: EC/DMC/LiPF₆ 	batteries for use in EV's and HEV's are currently being developed		Large scale demonstration plants

<ul style="list-style-type: none"> • still in development phase for rechargeability anode (Zn, Li) and cathode • reversibility air cathode • electrolyte choice (Li-Air) • nano catalyst 	<p>main systems: Zn-Air and Li-Air (1,6 V) (3 V)</p>	<ul style="list-style-type: none"> • Li-metal • Zn powders/ZnO • corrosion inhibitors • nanocatalysts (MnO₂ ...) • electrolytes (aqueous for Zn, organic for Li) 	both systems have a long history as primary battery		Basic research
<p>ZnBr₂ batteries study and improvement at interface, membranes and electrodes</p>	<p>low temperature, low pressure operation, low maintenance, but low energy density and medium powder, (50 – 60 Wh/kg), >2.000 cycles (1,6 V)</p>	<ul style="list-style-type: none"> • aqueous ZnBr₂ solution (plates Zn on the negative with Br₂ stored on the positive) 	again a flow type battery realized in a kind of electro-plating device		Under development
<ul style="list-style-type: none"> • focus on reducing maintenance and extending operating life • more advanced carbon materials 	<p>30 – 40 Wh/kg, 60 – 80 Wh/l, 2,10 V, 500 – 800 cycles</p>	<p>PbO₂, Pb electrodes, H₂SO₄, grids</p>	well established, but lead-carbon battery still in development		Commercialized
<p>Cd environmental issues</p>	<p>40 Wh/kg, 150 Wh/l, 1,2 V, 1500 cycles</p>	<p>Ni(OH)₂, CdO, Cd metal, KOH</p>	well established		Commercialized
<p>no further specific research needed unless RE critical material availability</p>	<p>80 Wh/kg, 300 Wh/l, 1,2 V, 500 cycles</p>	<p>Ni(OH)₂, MH containing rare earths, KOH</p>	well established		Commercialized (For HEV)

<ul style="list-style-type: none"> improvement of EDLC supercaps by increasing energy while maintaining high power (Ragone plot) development of new carbon electrodes (CNT, ...) 	<p>extremely long cycle life, high power density but low energy density</p>	<ul style="list-style-type: none"> supercaps: carbons CNT pseudocaps: metal oxides nitrides polymers 	<ul style="list-style-type: none"> non-Faradaic (EDLC) Faradaic (pseudo caps) 		Under development
<p>high storage reservoir that can be used for hydro-electricity during peak hours, often requiring high capital cost</p>	<p>MW storage capability, low cycle cost but high capital cost</p>	<p>hydraulic turbines</p>	<p>development underground facilities</p>	<p>capital cost</p>	<p>Commercialized (Mature technology, generalized in use)</p>
<p>advanced adiabatic CAES are currently being developed Liquefied gas systems Capital cost / demonstration of Thermal</p>	<p>compression and expansion of air can be: adiabatic diabatic isothermic also storage as liquefied gas</p>	<p>High temperature and pressure thermal Energy Storage / High temperature and pressure compressor</p>	<p>air-tight underground storage caverns Liquefied gas systems can be compact and use standard chemical engineering plant,</p>		<p>Large scale demonstration plants (Two in Germany and US)</p>
<ul style="list-style-type: none"> continuous improvement of magnetic bearing and development of composite materials for large systems magnets with higher strength 	<p>low maintenance, long life, environmentally inert, high cycle life (>100.000 cycles), electricity being stored as the kinetic energy of the disc, FW farms being planned for MW's</p>	<ul style="list-style-type: none"> magnetic bearing to reduce friction large systems requiring strong materials like composites to resist the centrifugal forces 			Commercialized

<ul style="list-style-type: none"> • overall efficiency of hydrogen storage 50 – 60%, lower than pumped hydro and batteries • FC without precious metals, new thin film catalysts 	hydrogen produced e.g. by electrolysis, compressed or liquefied and then reconverted back to electrical energy (fuel cells) and/or heat	<ul style="list-style-type: none"> • catalysts in the water electrolysis • fuel cell catalysts and substrates • MEA's 	preferred by electrolysis and fuel cell technologies (alternative production of H ₂ by reforming natural gas with steam produces CO ₂ as a by product)	overall efficiency of hydrogen storage 50 – 60%, lower than pumped hydro and batteries	Under development
<ul style="list-style-type: none"> • improvement of cost and critical temperature of the superconductors 	<ul style="list-style-type: none"> • store electricity in magnetic field of a superconducting foil cryogenically cooled below its critical temperature • highly efficient (> 95%) • currently used for short duration energy storage, mostly focused on power quality 	superconductors			Under development
<ul style="list-style-type: none"> • technology still in improvement phase (2 tanks, 1 tank, types of salt, nitrates, solid materials, concrete,...) 	uses molten salt to store heat collected by a solar power tower	<ul style="list-style-type: none"> • molten salt • heat transfer media (oil, H₂O or steam) 			Under development
study impact of V2G on battery durability and life time					Under development

Table 4: Public systems foster the gathering of private actors

EU	Member States	Others
<ul style="list-style-type: none"> • EU climate and energy targets “20-20-20”. • SET-Plan 2010-2018. • SAFT (Fr): project SOL-ION. • ABB: supplier of power grid systems. 	<ul style="list-style-type: none"> •Germany: LESSY LIB2015-project, a 1MW Li ion storage device at Fenne power plant. • UK 150 MW Na-S batteries agreed to be provided by NGK to EDF Energy in UK • ADEME: Agence de l’Environnement et de la Maîtrise de l’Energie (France) • CSTB: Centre Scientifique et Technique du Bâtiment (France) • Saft Li-Ion Guadeloupe Project • Cellstrom GmbH (8) • Solvicore (Solvay-Umicore) Lillo project: cooperation with Nedstack (FC) for large scale power generation from waste hydrogen • Air-Liquide Axane: FC division for small stationary applications 	<ul style="list-style-type: none"> • DOE (Jan 2010): 12 mio \$ in early stage smart grid technologies. • DOE Recovery Act smart grid funds: \$ 4.5 billion. • Main Li-Ion stationary US projects: <ul style="list-style-type: none"> - AES energy storage and A123 Systems 12 MW frequency regulation and spinning research project in Chile; - Southern California Edison (SCE): a 25 \$ million grant to build Li-Ion grid storage battery (A123 technology); - Altair technologies: 1 MW, 250 KWh battery storage system at the PJM Regional Transmission Organization (RTO) as part of a joint development with AES; - American Electric Power (AEP): plans for community LiB energy storage; - SEEO: \$ 6,2 mio grant for a 25 KWh prototype LiB for the power grid; - Valence: LFP solutions for UPS. • China: <ul style="list-style-type: none"> - BYD (LFP Systems): regulations in China are expected to direct 15% of utilities investments to battery storage. • Japan: <ul style="list-style-type: none"> - Panasonic 1,5 KWh Li-Ion for home use PV systems; - SANYO LFP based Li-Ion. • Korea: MKE project (Ministry of Knowledge Economy) - Development of cathode materials for high efficiency rechargeable batteries for energy storage system <ul style="list-style-type: none"> - SDI energy storage projects with LiB. • Worldwide: 300MW Na-S battery systems installed capacity

ANNEX III: Safety, cost, feasibility and environmental aspects additional parameters to be considered when selecting a system for a given application

Potential applications for storage are described in brief below. This does not represent a comprehensive list, but does provide a worthwhile summary to facilitate an analysis of applications and to place the technologies in context.

- Peak shaving is possibly the most straightforward application for electric utility companies to understand and to extract. This application derives revenue by charging a storage medium when the grid-wide electricity price is low, and discharging when the price reaches its highest daily projected level. Daily price fluctuation is typical of electricity grids (including the UK grid) and is indicative of the challenges associated with matching supply against normal fluctuations in demand. This matching (called ‘balancing’) also entails a CO₂ cost because of the significant demands that it places on generating equipment.

- Protection systems are installations where energy storage (usually on a small or medium scale) is used to ensure an uninterruptible supply of power to priority equipment at a user’s site. For example, vital equipment in a hospital could be supported by an energy storage installation. Protection systems commonly incorporate an alternative power source, such as a stand-by generator. In this case, energy storage serves to allow a run-up time for the stand-by equipment, reducing the cost associated with maintaining instantaneous availability.

- Power quality differs from protection in that the goal is to ensure consistent characteristics of the delivered power, not its continuous availability. In power quality applications, a storage medium acts as a buffer to facilitate power factor correction or to dampen fluctuations in line voltage. This is often required where sensitive equipment, such as electronics, is grid-connected near to large equipment subject to on-off cycling.

- Ancillary services are provided by large generators to the grid operator. A typical ancillary service is the ability to start without an external power source (‘black start’).

However, here the term is intended to refer more broadly to the range of control which a large generator must be capable of exerting on its output. At a wind farm site, energy storage could provide a degree of short-term accountability for generated output.

- Balancing mechanism support is a short-term energy trading application for storage.

The balancing mechanism is the special energy trading market for ensuring a match between demand and supply on a 30 minute time horizon. This market is very volatile.

Arguably, the widespread application of storage could remove the need for the balancing mechanism, allowing a more natural model of an open commodity market.

- Deferred grid upgrades may be possible by placing storage at strategic physical locations on the grid. Where the grid is stressed at times of peak or peak supply (for example, near an expanding town or a recently upgraded wind farm), a storage device could reduce the risk of a fault or defer an increase in capacity. This kind of local demand management requires daily cyclic operation, but managing a variable supply, such as wind farm output, may force a charge/discharge cycle of one week or more.

- Various supplier support and flexibility services can be provided by energy storage.

Essentially, generators can often operate more efficiently if not subjected to arbitrary changes in demand. Large generators comprise discrete units with minimum stable generation quantities and generation efficiency figures which are a function of gross output and the operators’ appraisal of the risk of volatility on the network. There is significant and complex scope for adjusting the dispatch and control philosophies within a large generator if reliable, large-scale energy storage is available.

Multiple Applications

A number of potential applications have been cited here and it is worth noting that an energy store technology can find its place in several of them.. For example a battery installed to smooth output from a wind farm on a weak grid could provide frequency response if not working close to the limitations of the local network. It is appreciated that these multiple benefits are not always financially additive, but clearly a battery can offer different services at different times depending on which are offering the most value.

Climate change is increasing the need to use renewable energy sources, like wind, tidal and solar for both centralised and de-centralised sources of power. Generation from renewable sources is intermittent and cannot be controlled to follow the electrical load at all times, both at a local distribution level and at a national transmission level. Maintaining the required power frequency, voltage stability, security of supply and quality of power supply is becoming an increasingly difficult challenge for the electrical power industry with more use of renewable energy. As a result, there is a growing need for rapid release energy storage systems with a significant capacity. The lack of energy storage capacity has been identified in the European Strategic Energy Technology Plan² as a critical barrier to large scale wind deployment. The two main applications for storage in electrical power grids with a large penetration of intermittent generation are (i) the provision of reserve power or peak-shaving on electrical networks typically over a few hours (ii) to facilitate power balancing and frequency control at the transmission level¹. In addition, there may also be opportunities for bulk electrical energy storage to alleviate congestion in distribution or transmission systems, for improving user power quality or for smoothing the output from wind farms making it more predictable.

There is a strong perception of a high future worldwide demand for energy storage, but as yet there has been little investment in the EU. The reasons for this are complex but broadly relate to technical performance, the availability of alternative technologies, actual demand and cost. Most current short term storage requirements are met by the combination of a high interconnectivity of European energy grids and the use of a spinning reserve of fossil fuel plants (gas turbine and coal). However with more renewable generation there is an increased requirement for short term reserve and less opportunity to use the spinning reserve of fossil-fired plant which will become more expensive in the future due to the cost of emitting or capturing the CO₂. Fossil fired plant is thus likely to become less efficient at balancing the networks as the percentages of renewable and distributed generation increases.

Traditional storage technologies like pumped hydro and CAES are geographically dependent: Pump hydro are more or less set up on mountain area that can be far away from the electricity demand and CAES are, today, linked to salt underground (as natural gas storage but without competition) but a depleted gas field will be used for an industrial demonstration in the USA. Those two technologies are not suited for medium scale application (10s kW to MW).. Batteries are, however, an attractive approach to energy storage. From the viewpoint of an electrical power grid system with a large penetration of intermittent generation, they are able (i) to facilitate power balancing and frequency control at the transmission level and (ii) to overcome local distribution network constraints to keep currents and voltages within acceptable limits and to enhance security and quality of supply¹. Furthermore, a battery unit is able to fulfil other needs within this storage system, such as peak-shaving in electrical networks, quality of service, avoidance of network reinforcement, efficient operation of distributed generation and transport applications such as stationary regenerative transportation systems. Current battery technologies are not ideal for energy storage in the 100 kW - MWs range due to problems with poor cyclability (especially lead acid), low efficiency (Ni-MH),

high cost per kW & kWh (all except Pb acid), low energy density (Pb acid), lack of robustness (Li-ion) and complexity of assembly large multi-cell packages with many small batteries (all).

Flow batteries have many of the characteristics essential for a successful electricity storage technology at grid scale and they have the advantages of separating the power and energy components (large storage capacities), a quick response time, a long cycle life and, with appropriate choice of chemistries, no harmful emissions in use. Still, pumping systems or maintenance are some of the potential drawbacks to further investigate.

APPENDIX: More detailed data on electrochemical storage technologies and their evolution

Electrochemical storage technologies: batteries, redox flow and super capacitors

Since the invention of the lead accumulator by Gaston Planté in 1859, batteries have continued to improve. Until the end of the 1980s, the two main technologies available on the market were lead accumulators (for starting-up vehicles, supplying secure telephone networks, etc.) and nickel-cadmium (Ni-Cd) accumulators (for mobile tools, toys, security lighting, etc.). Lithium accumulators entered the market early in the 1990s, thanks to Japanese companies. At the time, these accumulators offered a specific energy density (100 Wh/kg), which was greater by a factor of two than that offered by Ni-Cd technology and greater by a factor of three than that offered by lead-acid accumulators. Since then, the performance of lithium accumulators has greatly improved, and in 2008 they attained 200 Wh/kg, 220-240 Wh/kg more recently (best energy value for low power cells used in portable computers).

Present systems:

Lead-Acid batteries

Lead/acid technology first patents were granted during the second half of the 19th century. It uses lead redox couples in both electrodes and the electrolyte takes active part in the reactions through the formation of lead sulfate during the discharge. Even if the theoretical specific energy has not been reached because the utilization of active material is far from 100%, lead/acid are still the most commonly used secondary batteries, especially for Starting Lightning and Ignition (SLI) in cars, forklifts, and standby applications. They consume more than 70% world lead production. Secondary lead is dominant.

Lead-acid battery materials status:

Lead content is around 60 % of the weight of the batteries.

Lead grids are alloys which, in addition to lead can content small amounts of Sn, Ca, Sb, or in a lower amount Ag, Se or other metals as traces. Negative oxide paste can also contain a small amount of barium. Tin begins to be considered as a critical material in terms of supply [3].

In addition to lead alloy and paste, lead-acid battery uses sulfuric acid as electrolyte and organic additives. No critical issues in other components:

- Plastic case (PP, ABS)
- Separator: polyethylene for flooded batteries, glass fibers or silica for valve regulated

Ni-MH Batteries

The first patents on nickel batteries were also granted around the turn of the 19th century for prototypes using either cadmium or iron as the negative electrode and nickel hydroxide as the positive electrode. Batteries using hydrogen gas as the negative electrode were specifically developed for spacecraft applications during the 1970s and 1980s and this triggered the later advent of the nickel/metal hydride technology that found widespread application in portable electronics, and is currently present in commercially available hybrid electric vehicles. The main current bottlenecks within nickel based technologies are the low temperature performance of the hydride anode and the tendency to form dendritic and mossy deposits for the Zn anode, which severely hampers its cyclability. The energy efficiency of the nickel

oxyhydroxide electrode is limited by the oxygen evolution reaction concomitant to the oxidation of the active material in the last part of the charge, but can be largely improved through the use of additives. Finally, the limited availability and high cost of rare earth elements is a factor that could potentially limit the generalized use of Ni/MH for large scale applications.

Nickel-metal hydride (Ni-MH) battery materials status:

NiMH is presently the most widely used technology with more than one million Toyota Prius already sold. Ni-MH uses the following materials:

Ni-MH batteries operate in aqueous alkaline media ensuring a good safety at the cell level.

Component	Composition	Critical materials
Negative active material	Rare earth alloys AB ₅ , RMgNi _x	Nd, Pr
Positive active material	Ni(OH) ₂ , Co(OH) ₂ additive, Zn, Y, Yb, Nb also used	Y, Yb, Nb
Other	Polymer separator, steel case	

The critical supply of rare earths materials or cobalt will be discussed in the next chapter

Lithium-ion batteries

Contrary to the above mentioned technologies, where progress has been application driven and entailed a relative small number of combinations of compounds, lithium based batteries rely on much more varied chemistries. Indeed, even if only a small number of them is actually in use, the spectrum of potential electrode materials is rather large. Electrolytes range from the mostly used solutions of lithium salts in organic liquids to ionic conducting polymers or ceramics additions to polymers.

The key engineering parts of a lithium ion battery cell are a cathode and an anode with an electrolyte in between. The electrolyte also contains a separator, which has good ion conductivity and prevents short circuits. Further important components are current collectors, binders and the cell casing including safety devices.

The lithium-ion concept uses two materials that allow the reversible electrochemical insertion of lithium ions into two materials, with different potential values. The negative electrode is usually a thin layer of carbon (graphite), in which atoms of lithium have been inserted (LiC₆). For the positive electrode, a mixed lithium transition metal oxide with lamellar structure (generally LiCoO₂, LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ or LiNi_xMn_yCo_zO₂), spinel structure (e.g. LiMn₂O₄), olivine structure (e.g. LiFePO₄) or a Nasicon type structure. Important cathode materials from the industrial point of view are lithium cobalt oxide, lithium nickel oxide, lithium manganese oxide and lithium iron phosphate.

The liquid electrolyte is usually an organic/aprotic solvent like a mixture of alkyl carbonates (propylene carbonate, ethylene carbonate, dimethylcarbonate, etc.) with a dissolved lithium salt like hexafluorophosphate of lithium (LiPF₆). It can also be solid: an organic compound based on polyethylene oxide or an inorganic compound based on amorphous lithium borate, for example. The most typical operating voltage of a lithium-ion cell is 3.7 V. A membrane is used as separator and tank for liquid electrolytes. The separator is a key component for the safety of the lithium ion battery.

In the lithium-ion polymer battery technology the lithium-salt electrolyte is hosted in a solid polymer. These are complexes between a polymer, such as the oldest one poly(ethylene) oxide(PEO), and a salt of lithium. There are several different materials systems of polymer

electrolytes. The disadvantage of this system is that the ion conductivity is not high enough at room temperature. Therefore gel-type electrolytes have been developed, which consists of a lithium salt in a solvent and a polymer ensuring mechanical stability.

In gel polymers, the lithium salt is dissolved in an organic solvent, such as ethylene carbonate, while being immobilized in a polymer such as polyacetonitrile (PAN) or copolymers PVdF-HFP. These materials have significant ionic conductivities, of the order of 10^{-5} S/cm to 10^{-3} S/cm, even if their performances are generally below those of liquid electrolytes.

In 2008, Sony proposed a lithium-ion polymer technology, produced in Singapore, with a high specific energy (Apelion, 241 Wh/kg, 535 Wh/liter) based on LiCoO_2 and graphite, using a gel electrolyte. According to Sony, the technological limit seemed to have been reached.

The electrode/ electrolyte interface is not stable forms a passive layer to protect the electrolyte and the electrode against further degradation. This protective coating is called solid electrolyte interface (SEI).

A critical point for the life time of the battery is the quality (purity) of the materials components in the production process.

The lithium-ion gel system has some advantages regarding the freedom for design, the chance to produce a light weight casing (it must not be metal alloys) and low production costs. The disadvantage is a questionable security of the gel-type polymer electrolyte, when it comes to sensitive applications like transport. This is due to the presence of volatile components, which are flammable, since solvent-free types do not have the needed conductivity. A solution might be to use room temperature ionic liquids as electrolytes, which are not flammable.

Lithium ion batteries materials status:

The advent of this technology played a key role in the enormous development of portable electronics. Given this success in the, scaling up of the current technology would, at first sight, seem to enable rapid and successful penetration in other domains of energy storage applications. Nonetheless, there are still some technological issues related to scaling-up, since priorities change when going to larger size applications (e.g. cost and safety become crucial) and on the other, the scalability of individual cells is limited. As a result of this moderate voltage electrode materials (e.g. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and LiFePO_4) or polymer electrolytes are postulated to ensure safety against thermal runaway for HEV and EV applications, while the difficulty to scale-up cell sizes results in elaborate and costly multi-cell pack solutions that need complex battery management. Thus, the advantage of high energy density of Li-ion batteries is somewhat compromised for large scale applications both at the fundamental electrode material level and also in the technological battery packaging strategy concept.

As above mentioned, lithium-ion has already several sub-systems according to the choice of electrode materials.

a) Positive active materials:

Historical material LiCoO_2 is still partly used for portable applications, but not considered in the SET-Plan due to high cost, average life and limited availability. The presently used materials with their characteristics are given in the following table:

	LiCoO ₂	NCA (LiNi _{1-x-y} Co _x Al _y O ₂)	NMC (LiNi _x Mn _y Co _z O ₂) with x+y+z=1	LiMn ₂ O ₄	LiFePO ₄
Energy Wh/kg or L	Good	Good	Good	Average	Poor
Power	Good	Good	Good	Good	Good
Low T	Good	Good	Good	Good	Average
Calendar life	Average	Very Good (if charge at 4.0 V)	Good	Poor	Average
Cycle life	Average	Good	Very good	Average	Average
Safety *	Poor	Poor	Poor	Average	Good
Cost/ kWh	Higher	High	High	Average/High	Average/High
Maturity	High	High	High	High	Average

- Safety assessment of this table refers to cathode material only. **In any case the safety must be ensured at battery level:** the same graphite negative can react with electrolyte and the same solvent can burn whatever the cathode.

b) Negative active materials

The most commonly used materials are artificial graphites which have higher degree of purity than natural graphite. Cheap natural graphite is also used.

More sophisticated mixes of carbon materials are also used:

- mixes with sloppy discharge carbons to facilitate SOC knowledge or for capacity increase
- coated carbons for high rate or low temperature applications

Besides the graphite family, lithium titanate (Li₄Ti₅O₁₂) is also introduced in some cells for high power applications. One example is Toshiba Scib for power tools.

c) Separator is a fast moving topic to improve thermal stability for safety issues and wettability. Microporous thin films of PE and PP are the most used presently. New materials with higher melting temperature, mineral additives or surface treatment are now being introduced in industrial applications.

The science needed for advanced separators is high skill in processing to get the right properties.

High temperature Sodium-beta alumina batteries

The first prototypes, developed at Ford Motor Company at the end of the sixties contained sulfur as the positive electrode and the so-called sodium β"-alumina as solid electrolyte. This material is an electronic insulator and exhibits sodium ion conductivity as high as 20 S/m around 300°C, a value comparable to that of many aqueous electrolytes. To achieve enough electrochemical activity today Na-S battery operates between 300 and 350°C. Ford's objective was electric vehicle market. After the oil crisis, in the 80ies a lot of effort has been invested by European Industry (like ABB) to develop sodium-beta alumina battery for automotive applications. Safety problems later caused the shut down of these activities in Germany Surprising as it may initially seem, a technology operating at such a high

temperature and involving the handling liquid sodium and sulfur has been in development for over 40 years.

A derivative of this technology based on the use of NiCl_2 instead of sulfur, termed ZEBRA battery [16], was later evaluated toward automotive applications, having the advantage of being assembled in the discharged state and hence without the need of handling liquid sodium. The main current technical bottlenecks associated to materials deal with corrosion of containers and seals.

Since the coulombic efficiency of this system is very close to 100%, attempts were made to extend its domain of application to storage. Large size (8 MW / 40MWh) batteries have been produced and installed in Japan and are successfully operating in large scale stationary storage applications.

High temperature Sodium-beta alumina batteries materials status

Sodium sulfur (NaS) and sodium nickel chloride batteries (the so called Zebra) have the common points and following differences:

Comparison of characteristics	NaS	NaNiCl ₂
Operation temperature	330 °C	295°C
Separator	Solid beta alumina	Solid beta alumina
Specific energy (Wh/kg)	100	90
Most common mode of failure	Open circuit	Closed circuit
Material cost	Low	Higher (Ni)
Life duration	15 years	Lower

The advantages of Na/MCl₂ (ZEBRA) over Na/S are increased safety as the sulphur electrode is replaced by a benign low vapour pressure metal chloride cathode and cell assembly is conducted in the discharged state thus avoiding handling liquid sodium. Present cells use nickel chloride as positive electrodes as they yield higher power. Iron chloride cells have been developed which are more suitable for lower power, lower rate applications due to its lower voltage and more limited temperature range. The drawback is higher cost.

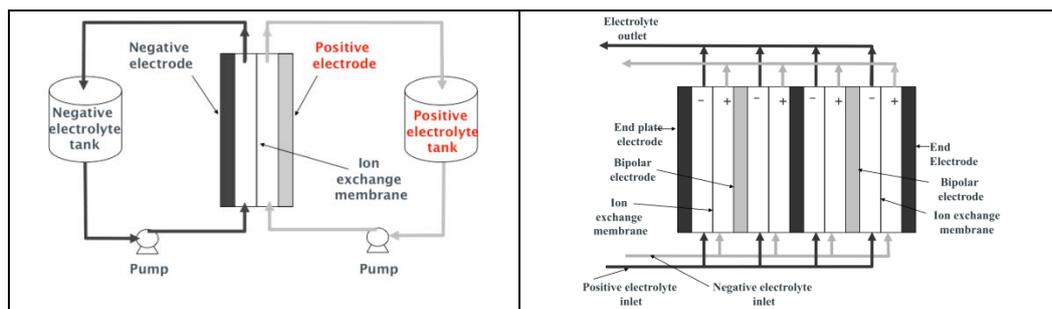
Those systems can be very interesting for large standby batteries. Both systems suffer of having only one major supplier: NGK in Japan for NaS, and MES-DEA in Europe for Zebra. However, GE is now developing US project.

NGK has already implanted a significant number of systems in Japan and has successfully begun exportation in the United States. Demonstration test is running in Europe.

Flow Batteries

For grid storage applications, specific power and energy density are secondary considerations and the critical parameters cost driven. More specifically: cost per kWh, cost per kW, capital cost, operating cost and lifetime cost.

Flow batteries store and release electricity by the valence change of the species in the electrolyte that circulates past the anode and cathode which may be separated by an ion exchange membrane or porous separator. An example unit cell and a series of unit cells assembled into a stack to give higher voltages are shown below.



Categories of flow battery:

1. Classical redox flow battery, where both anode and cathode reactions do not involve a phase change e.g. all vanadium RFB.
2. One phase change reaction (typically metal deposition) and one solution reaction e.g. Zn-Ce.
3. Two phase change reactions such as metal deposition and metal oxide deposition e.g. soluble lead.
4. Metal air batteries with a flowing liquid electrolyte e.g. Zn - air
5. Slurry type systems where a solid phase in suspension e.g. a pumped Li compound system being developed by A123.

Advantages of Flow batteries are:

- Power and energy are separable
- Modules are capable of mass production
- Flowing electrolyte allows thermal and chemical management of the system.
- State of charge is the same for all cells on the same fluid circuit (classic redox flow only) making cell management relatively easy.
- Low cost & easy maintenance.
- High efficiency (60 to 90% depending upon battery type and duty).
- Excellent response time.
- Perfect deep discharge capacity.
- Very little self-discharge.
- Long cycle life.
- No special site requirement.
- Proven scalability up to very large systems.

The cost of the system is split between: electrolyte, cell stack and balance of plant (tanks, pumps etc). Generally the stack cost is dominant. Even for systems with expensive electrolytes like all vanadium FB, the biggest cost reductions can be achieved by increasing the power of the stack.

This can be done by increase practical current density that the system can operate at for a tolerable efficiency and by using a redox couple with a higher potential difference but this is fixed for each chemistry. Unfortunately energy efficiency tends to drop with increasing current density and is the prime reason for the relatively high cost of flow batteries. Typical energy efficiency at a current density of 50 mA/cm² is probably around 70% and drops off rapidly above this value. For comparison fuel cells operate around 1000 mA/cm², metal deposition at >>100 mA/cm² and general electrochemical synthesis reactors at over 1000 mA.cm².

The main factors which affect the overall system energy efficiency are:

1. Current efficiency – reduced by transport of active species across the membrane, side reactions, shunt currents and self discharge
 2. Voltage efficiency – reduced by overpotentials, ohmic losses (electrolyte, membranes and electrodes)
 3. Balance of plant energy consumption - pumping energy and system balancing
- Anything that can improve these efficiencies at higher current densities (over 100 mA/cm²) would substantially reduce the stack costs and increase overall system efficiency.

Flow batteries materials status

Zn-Br

Status - Robust technology with commercial systems being sold by a number of manufacturers: Premium Power (US), Redflow (Aus) and ZBB (US & Aus).

Advantages - Mass manufactured cost CLAIMED to be about 50% of equivalent lead acid for small (10 kW) batteries. Other estimates are quite high at >\$200/kWh.

Disadvantages – Zn dendrites, bromine costly, high self discharge and management of the bromine sludge (complexant, extra tank and pump).

All Vanadium (Generation 1)

Status – Commercially available. RedT (UK), Cellstrom (A), Proven (China) and Golden Fuel Cell (China). Previously sold at MW scale by Sumitomo (Japan).

Advantages – no solid deposits, membrane transport is not an problem, reliable and robust system.

Disadvantages – high cost of vanadium, only 1 electron reactions, electrolyte stability limits operation to between 10 and 40°C, requires ion exchange membrane, relatively aggressive electrolyte, low current density therefore relatively high stack costs.

Vanadium (Generation 2) – Vanadium Bromide

Status – Pilot scale. Patented by V-Fuel (Aus).

Advantages – double energy density of Gen 1, wider operating temperature range

Disadvantages – Membrane development still required.

Zn-Ce

Status - Patented technology. Developed by Plurion in the UK to pilot scale..

Advantages – high cell voltage, 2 electron reactions, Zn is cheap, good electrolyte energy density.

Disadvantages – Zn dendrites, expensive acid used (MSA), Ce solution is very aggressive leading to material selection problems and Ce is not cheap.

Soluble lead

Status – lab / pilot scale.

Advantages – no membrane, only one fluid system is required, 2 electron reactions and reasonable cell voltage.

Disadvantages – Pb dendrites and poor adhesion of the PbO₂ deposits.

Zn-air

Status – lab scale

Advantages – High current density coupled with reasonable voltage. Potentially the cheapest kWh cost and the high energy /power density could be suitable for some mobile applications,

Disadvantages – Dendrites, high over-potentials of the air electrode reducing voltage efficiency.

Supercapacitors

The correct term for this group of devices is 'Electrochemical Capacitors'. However, they are often referred to as 'ultra capacitors' or 'supercapacitors' but these latter are commercial names with associated copyright.

Electrochemical Double Layer Capacitors refer to devices that store electrical energy in the electric double layer (EDL), which is formed at the interface between an electron conducting surface and an electrolyte. One side of the EDL is formed by the surface of electron conductor while its other side is formed by ions in the electrolyte. The EDL may be considered as a capacitor with two electrodes; the capacitance is proportional to the area of the plates and is inversely proportional to the distance between them. Capacitance is very large because the distance between the plates is very small (several angstroms), and because the area of conductor surface (for instance of the activated carbon) reaches 1500-2000 m²/g (16000-21500 ft²/g). Thus, the energy stored by such capacitors may reach 5 Wh per Kg (about 50-60 J/g). They are thus over systems that can deliver their energy within few seconds (typically up to 5s). They are intermediates between batteries (high energy, low power density) and conventional capacitors (high power low energy densities). ECs are thus complementary to batteries and are not in competition with them.

Typical electrochemical capacitor contains two chemically inert electrodes immersed in an electrolyte. The electric double layer on the surface of each electrode represents a separate capacitor. These are connected in series through the electrolyte having ion conductivity.

The most common design of electrochemical capacitors is the so-called 'symmetric' design, wherein positive and negative electrodes are made of similar material (in most cases a high surface area carbon referred as activated carbon) each with the same capacitance. Another important class of ECs are pseudocapacitors, which undergo electron transfer reactions but behave like capacitors. These materials store energy through highly reversible surface redox reaction in addition to the double layer storage. Ruthenium dioxide (RuO₂) pseudocapacitor was firstly studied and could reach 10 times more capacitance than a conventional activated carbon. Huge efforts are today directed towards the synthesis of low cost, high pseudocapacitance materials. Cycle life of these systems might be a concern because of the presence of the redox function in slower time constant for reacting to a pulse demand.

A third type of electrochemical capacitors combines a battery or redox electrode with a carbon electrode, such as nickel hydroxide or manganese oxide cathode with a carbon anode. These super capacitor or hybrid capacitors will be referred to as an asymmetric electrochemical capacitor. This makes it possible to substantially increase the capacitance and the energy stored. As a result, specific energy is increased 4-5 times as compared with a conventional symmetric system using similar (KOH aqueous electrolyte for nickel hydroxide) electrolyte. An important advantage of asymmetric capacitors vs. conventional symmetric electrochemical capacitors is their lower self-discharge rate, which is of critical importance in some applications. However, power performance is 2-3 times lower for these asymmetric devices compared to conventional symmetric electrochemical capacitors.

Both aqueous and organic electrolytes are used to manufacture electrochemical capacitors. Aqueous electrolytes are cheaper and easier to use, and they do not pollute the environment. Organic electrolytes allow increased capacitor operating voltage and, correspondingly, higher specific energy. At the same time, they are more expensive, require more complicated capacitor packaging and manufacture, (water contamination must be prevented) and are often ecologically unfriendly (some organic electrolytes are flammable and/or toxic).

Operating characteristics of asymmetric capacitors depend on the combination of positive and negative electrodes.

Supercapacitor materials status

In the last two decades, interest in electrochemical capacitors as power sources has increased sharply. A great number of publications have appeared describing developments electrochemical capacitors and materials thereof. High-surface-area carbon is the material of

choice, as it combines a large surface area wetted by the electrolyte, high electronic conductivity, and chemical and electrochemical stabilities with low cost. Improving capacitance for EDLC capacitors deals with tuning pore size for each electrode to be compatible with corresponding ions size and controlling pore size distribution. Another approach to achieve higher surface areas needed for higher capacitance, proposes to make electrodes with nano-structured materials-particles, facing the challenge of demonstrating that nano materials can be made with good electrochemical and physical properties in a working super capacitor device. However, introducing nanotubes for instance, exhibits low specific energy (gravimetric and volumetric).

Supercapacitors are already used in transportation applications. They have been announced last Nov 2010 to be used in the starter/alternator of the next generation of C4 and C5 micro-hybrid Citroën cars by Peugeot (early 2012) and are under study by many car manufacturers (Toyota, BMW, Renault). Together with their outstanding cycle life, another key feature of EDLC systems () is that, unlike Li-ion batteries, they can be recharged as fast as discharged. This is why they are used today in large-size applications for energy recovery in trams in Madrid, Paris, Manheim, Koln (...). While today's super capacitors offer the high burst-power performance important to next-generation mobile electronics, they still suffer from low energy density when compared to batteries that limits the use of EDLCs systems in embedded applications (mobile). Thus "hybrid" capacitors were proposed and are still under investigation. In some cases, the kinetics of the redox charge discharge reactions can proceed almost as quickly and reversibly as EDLC charging. Thin film redox electrodes, based on the lithium intercalation/insertion principle such as $\text{Li}_4\text{Ti}_5\text{O}_{12}$, exhibit high reversibility and fast kinetics. Also, polymeric materials such as polyaniline, polypyrrole, and polydiaminoanthraquinone (DAAQ) show "pseudo-capacitive" charge-discharge behavior. These have facile kinetics and have shown high capacitance but suffer today from the cycle life especially at high Depth of Discharge (DOD). The insertion of anions and cations into their structure can yield capacitances of up to $200 \mu\text{F}/\text{cm}^2$ and, moreover, they can be easily fabricated as thin films.

Today several super capacitor projects have the scope to develop green, safe, and higher energy and power densities. EDLCs and Hybrid Supercapacitors for application as peak power device in hybrid and electric vehicles as well as for energy recovery (braking). They are also studied for power grid applications (peak power smoothing) in combination with other systems (batteries, fuel cells), in delocalized energy production (e.g., CHP = Combined Heat and Power Production) plants using PEMFC. Electrolyte is a key material to succeed in this search. Typically, supercapacitors use organic liquid electrolytes like acetonitrile, which is toxic and flammable, or aqueous electrolytes, which offer a limited voltage window (and hence limited power and energy). Novel electrolytes such as Ionic Liquids are investigated both for use in super capacitors and batteries. These electrolytes are usually quaternary ammonium salts that contain organo silicon groups. Unlike electrolytes currently in use, these are stable at high voltages and not highly flammable or toxic. However, so far, they cannot replace known liquid electrolytes in conventional super capacitors or batteries, because of lower ionic conductivities in addition to low temperature issue. Some trends consist in mixing ionic liquids (IL) and molecular liquids (ML).

Potential future systems

Lithium sulphur cells

Another potential battery system is the lithium sulfur battery. In comparison to lithium ion cells they are rechargeable galvanic cells with a very low specific weight and an extremely high energy density. The theoretical specific energy density is 2 to 5 times higher than in Li

ion batteries [12]. Key engineering components are the electrodes, the liquid electrolyte (polysulfide) and a separator. Lithium-sulfur batteries have one electrode made of lithium and another made of sulfur that is typically paired with electronic conductors like carbon or metal powders and binders [13]. Sulfur is usually loaded into a porous structure of carbon materials, similar to the one used in Na-S batteries. Recently carbon nanotubes and mesoporous carbon have been used to improve the conductivity of the sulfur electrode. Like in lithium-ion batteries, charging and discharging the battery involves the movement of lithium ions between the two electrodes. Between the two electrodes there is an organic electrolyte containing a polysulfide shuttle substance. Also a separator is part of the system. The lithium ions are stripped from the lithium metal electrode by polysulfides during discharge. These ions react at the sulfur electrode to lithium polysulfides.

Lithium sulfur batteries might replace lithium-ion cells because of their higher energy density and the low cost of sulfur. The lithium metal electrode is a risk for the safety of the battery. Technical challenges are the insulating nature of sulfur as well as the solubility of long chain polysulfide ions.

The major problems preventing up to now their commercialization are high self-discharge, poor life and safety.

Metal(Li)-air batteries

The Lithium-air battery is of great interest, since the oxidation of 1 kg of lithium releases 11680Wh/kg and is therefore in the same range as gasoline. The practical energy density of the lithium-air battery will be much less (1700 Wh/kg) but is exactly at the same level as gasoline. Another advantage of Li-air batteries is due to their high energy capacity a cyclability of 300 would already meet requirements of automotive industry [14].

Metal-air batteries are unique power sources because the cathode active material, oxygen, does not have to be stored in the battery but can be accessed from the environment [15]. Of the various metal-air battery chemical couples, the Li-air battery is the most attractive since the cell discharge reaction has an open circuit voltage of 2.91 V and a theoretical specific energy of 11680 Wh/kg. Other metal air battery systems are Na/air, Mg/air, Ca/ Air and Zn/air. Not all metal air batteries are electrically rechargeable.

The key engineering elements of a lithium-air battery are a lithium anode, an air cathode (porous carbon containing atmospheric oxygen) and an electrolyte. The electrolyte could be a lithium ion conducting polymer electrolyte (PAN, PVdF) or a conductive ceramic (Lisicon). During discharge, lithium ions flow from the anode through the electrolyte and combine with oxygen at the air cathode to form lithium oxide (Li_2O) or lithium peroxide (Li_2O_2). Li/oxygen batteries can be rechargeable, if the carbon/air cathode contains a catalyst (like complexes of cobalt). Due to the electrolyte that is used different architectures of Li-air batteries can be distinguished. There are three different liquid electrolytes that can be used (fully aprotic, aqueous, mixed) as well as the all solid state battery.

There are many challenges and technical problems that have to be overcome in the development of metal (Li)-air batteries. A weakness of the Lithium-air battery is today's low power density (W/kg), which could be overcome by a hybrid with a super capacitor. A technical challenge is that very high internal surface areas in the cathode are needed (for 100 W/ kg power output, a 2,5V cell voltage and a current density of 25 mA/cm² a surface of 160 m² is needed!). The electrical energy efficiency of Li-Air is today only at 60% and therefore poor. This is because the charging voltage is considerably higher than the discharging voltage. The cause for this is under scientific investigation. Furthermore there are two safety concerns: The use of a lithium-metal electrode is a risk, since lithium-metal tends to form dendrites that could cause shortcuts.

Aqueous lithium-air cells

Aqueous lithium-air cells have also been demonstrated using a Lipon protected Lisicon ceramic electrolyte to isolate the negative lithium electrode from the aqueous electrolyte. This configuration has the advantage of being able to use fuel cell air electrodes and air, but it also has important limitations. The product of discharge of the cell is lithium hydroxide which has a limited solubility (5.3 M) and the reaction of LiOH with CO₂ from the air produces insoluble lithium carbonate which destroys the air electrode within a few hours of operation. It was however demonstrated the feasibility of such aqueous lithium-air concept in which the product of the reaction is stored in the aqueous electrolyte as a precipitate and not in the porosity of the air electrode as is done in the anhydrous Li-air concept. Following, the objective aims to increase the current density, to increase the number of cycles and the capacity of electrode. In addition, one targets to develop new Li⁺ conducting ceramics which are stable in contact with Li metal, in order to have a barrier to air and water, and sufficiently thin to not enable high current densities. These thin electrolytes have to be reinforced with a mechanical support. In parallel, more stable anionic polymer membranes have to be developed to protect the air electrode from CO₂ and LiOH precipitation inside the electrode. Novel reversible air electrode stable to oxygen evolution is also of interest.

Room temperature Sodium batteries

There are several challenges that have to be solved before the sodium-beta alumina battery can be part of a broad market penetration. The operating temperature has to be reduced (solutions under investigation: thinner electrolyte or alternative ion conductors like NASICON, use of ionic liquids in the cathode). Recently Wang et al. reported results with a room temperature Na/S-system [17]. The cost has to be reduced, which is closely connected to the development of new materials and progress in manufacturing technologies (development of robust seals)/ cell design.

The sodium-ion concept, analogous to lithium ion, has deserved less attention due to the intrinsic lower energy density with respect to the lithium ion. Nonetheless, the advantages in terms of lower cost and higher abundance of the raw materials for sodium when compared to lithium (*US Geological Survey 2007*) may bring this technology competitive for large scale applications provided high performance electrode and electrolyte materials can be developed.

Recognizing that none of the technologies being developed can make a sufficient difference on their own and that their commercialization will take place over differing time horizons, Europe should adopt a broad technology portfolio approach in order to ensure its competitiveness at the global scale and reduce the risk and potentially the costs, if one or more technologies fail to make the expected progress.

On-going Research in the Field of Material Research for Energy Technology

Li ion Applied Research

Development of positive electrode materials

1. Current situation

Compounds with poly-anionic structures have great potential to replace lithium oxides such as LiCoO₂. Among these compounds, the most accomplished material is LiFePO₄, which has already been commercialized by Phostech and integrated in an accumulator by several companies such as Valence Technology, A123 Systems and several Chinese companies. This compound, intrinsically an insulator, has been the subject of numerous research studies to change this property. It has a theoretical specific capacity of 170 mAh/g linked to a voltage of 3.45 V versus Li⁺/Li. Composite LiFePO₄/C systems have been developed that can reach a

reversible specific capacity of 160 mAh/g. The principal interest of these poly-anionic structure compounds resides in their stability, even at high temperature, which makes them suitable for lithium-ion accumulators with large capacity and with reinforced security.

2. In the medium term

Among the positive electrode compounds that could replace the cobalt oxide, LiCoO_2 , and its derivatives, which are currently used in almost all lithium-ion accumulators, high potential insertion materials such as spinel structured oxides (for example: $\text{LiNi}_{0.4}\text{Mn}_{1.6}\text{O}_4$) and olivine structured materials (for example, LiCoPO_4) could allow stored energy densities to be improved. New lamellar oxides of the $\text{Li}_{1+x}(\text{Mn},\text{M})_{1-x}\text{O}_2$ ($\text{M} = \text{Ni}, \text{Co}, \text{etc.}$) type can also give higher capacities when the voltages for a charge cut are sufficiently high (4.5-5 V versus Li^+/Li).

In practice, the use of these positive electrode materials leads to the problem of the reactivity of the electrolyte, which is in contact with an electrode operating at high voltages. This leads to a significant self-discharge effect (up to 80% per month). Yet, the solvents used in the electrolytes for lithium-ion accumulators have intrinsically high oxidation stability [25] (up to 5.5 V versus Li^+/Li or more for EC = ethylene carbonate, PC = propylene carbonate, DMC = dimethyl carbonate). Nevertheless, the potential limit values measured in practice vary a great deal, and are always lower when the electrodes employed for measuring are electrodes based on active materials [26, 27]. Following the example of the works on the negative electrode materials, especially graphite, it would seem of interest to undo this phenomenon, by looking to create a stable solid electrolyte interface (SEI) on the positive electrode by the introduction of additives in the electrolyte or creating a deposit of inorganic compounds that are electrochemically inactive ($\text{Al}_2\text{O}_3, \dots$). The film formed on the surface of the electrode should have a sufficient conductivity of Li^+ ions so that the electrochemical performance (for example speed of charge and discharge, internal resistance) of the accumulator is not limited. The presence of additives should not induce electrochemical instability at the level of the negative electrode, by perturbing, for example, the formation of the passive film. This passive film could avoid the loss of oxygen from an insertion material for high states of charge (a problem that is usually encountered with lamellar oxides), but would not protect the positive electrode as a whole, i.e. the oxidation of the electrolyte. In other words, the protection of electrodes at high potential, using *ex situ* methods cannot alone be an efficient solution.

Development of anode materials

Current work on active materials for the negative electrode for a lithium battery are centred on synthesis of compounds using nano-metric insertion (reduction of the diffusion pathway of Li^+) while staying in the right region of size/specific surface which is compatible with a practical maximum electrode density.

1. In the short term

The properties of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as an active negative material for the lithium power battery are very interesting, especially the redox potential for $\text{Ti}^{4+}/\text{Ti}^{3+}$ which is greater than that for Li^+/Li , namely around 1.55 V/ Li^+/Li . This criteria is linked to the weak chemical reactivity of electrolytes, to weak dimensional variations between the reduced/oxidized phases and to the great reversibility of electrochemical phenomena, and allows favourable charge and discharge regimes to be attained. As $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is considered to be a “zero strain” material, an excellent cohesion at the heart of the electrode and between the electrodes, separators and current collectors is, therefore, maintained throughout the cycling. This avoids the appearance of fissures and avoids damage to the matrix that could lead to a loss of capacity and performance. In practice, the recovered capacity is close to this value for slow cycling regimes. The power performances are more or less high, according to the material synthesis mode and the morphology of the grains. The potential for lithium ion insertion is above the

potential for reduction of the electrolyte, which means that almost no passive layer is formed at the electrode/electrolyte interface, as the electrolyte is not degraded. Moreover, this material has great thermal and chemical stability. It can be used for cycling in high power regimes, and/or at low temperature. In addition, due to its high insertion potential compared to the potential for lithium deposition, there is no risk of internal short-circuits under strong charge currents [28]. Finally, working at this potential, it is possible to use an aluminium current collector, which is lighter than a copper collector (used for graphite electrodes). Conversely, this relatively high potential (negative electrode) does not allow energy densities to be as high as graphite permits. Currently, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is a commercialized, low-volume material for lithium-ion accumulators that have high power or rapid charging. Applications such as portable tools, intelligent smart cards, or electric traction are envisaged for this material.

However, the practical capacity obtained with $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is already near the theoretical value (175 mAh/g), which is relatively low compared with that of graphite (330 mAh/g). The margin of progression is therefore limited. Some structural forms of TiO_2 (B notably) [29-31], which are less compact than anatase TiO_2 possess the same advantages as $\text{Li}_4\text{Ti}_5\text{O}_{12}$ compared with the graphite carbon that is currently used. Moreover, they have a theoretical capacity that is clearly superior to the lithium titanium oxide (338 mAh/g for TiO_2 (B) versus 175 mAh/g for $\text{Li}_4\text{Ti}_5\text{O}_{12}$). Thus, for electrodes with low surface capacity ($<0.5 \text{ mAh/cm}^2$), the maximum capacity obtained at a very slow regime (C/100) is 260 mAh/g [32]. Recent studies have in practice reached around 60% of this slow regime capacity (C/10) and very recently some authors have obtained 75% of the theoretical capacity using nano-wires of TiO_2 in regimes of up to 10 C. Granulometry, morphology, specific surface and microstructure seem to be the key parameters for improvement of performances [33- 38].

Moreover, for these materials there is the chance to improve by playing on the morphology and the nano-structure via the original synthesis conditions in order to approach capacities close to that of graphite. Depending on their morphological characteristics (nano-materials, large specific surface, etc.), the capacity of these materials ($\text{Li}_4\text{Ti}_5\text{O}_{12}$ [39] or TiO_2 (B) [40]) to attain the higher charge and discharge regimes makes them between the battery and the super capacitor. In addition, optimization of the active environment at the heart of the electrode composite will play a major role in highlighting the remarkable intrinsic performances of these compounds and reproducing them for thicker electrodes (which have a superior surface capacity or one that is equal 1 mAh/cm^2) and could therefore lead to high energy and power densities.

2. In the medium term

Numerous studies exist concerning, for example, silicon, tin, or metal alloy nano-particles which could replace the graphite that is currently used. It is foreseeable that the 350 mAh/g stored by graphite used in lithium-ion accumulators can be exceeded, reaching more than 1,000 mAh/g (3,800 mAh/g theoretically).

Different materials integrating nanometric silicon in the form of a film or particles, deposited or integrated in a conducting carbon matrix, are well on the way to realizing such performances. Yet, the complete optimization of the electrodes, and of the overall system of an accumulator with these components integrated, will still need a couple of years of research. Indeed, the expansion of the volume of the Si-Li alloy and the isolation of particles (passivation) are problems that still need to be resolved. Finally, their potential for functioning at around $0.5 \text{ V/Li}^+/\text{Li}$ remains close to that of graphite, and risks limiting the capacity during rapid charge, despite significant energy densities (problems with an increase in lithium dendrites leading to important safety issues).

Li ion Basic research

Regarding Li ion technology, as a longer & riskier approach, polyanion-based structures have been then (since the discovery of possible extraction of lithium from LiFePO_4) the object of very intense research activities, both at academic and industrial levels. An immense variety of structural types can accommodate reversibly Li^+ and/ or Na^+ insertion / extraction. The operating voltages vs. Li (or Na) are generally high, thanks to the inductive effect of the polyanion groups (in particular for SO_4 and PO_4) and also of fluor in fluoro-phosphates and fluoro-sulfates. However, these materials suffer intrinsically from their lower theoretical gravimetric capacity due to presence of three “heavy” XO_4 ($\text{X} = \text{P}, \text{S}, \text{Si}, \text{Mo}, \text{W}$) groups besides transition metals. Most of them offer a particularly stable open 3-D frameworks (especially for $\text{X} = \text{P}$) ideal for long term cycling and fast ion motion. These materials could be considered for the development of Na-based batteries or used both as solid electrolytes and electrodes (see solid state ceramic batteries).

Work is currently carried out on alternative technologies to Li ion such as Li-organic, Li-air, Li-S technologies... Significant efforts remain to be devoted to these topics before the practical application can be granted. The Li/S system has an intrinsic protection mechanism from overcharge, providing safety wide temperature range of operation and the possibility of long cycling. This is a closed system where chemistry is controlled, compared with the open Li/air. However, despite several works under progress the self discharge remains an issue. In addition despite this system exhibits high mass energy density, its volumetric energy is rather low that makes this technology less interesting for embedded applications.

In a more advanced approach, Hiroyuki Nishide [41], working with NEC, reported a battery designed with an electrode made from an Organic Radical film with a thickness of 200 nm. The polymer has nitroxide radical groups which act as charge carriers. This battery (ORB) is reported to take only one minute to be fully charged and it has a long cycle life, often exceeding 1000 cycles. The battery has a high charge/discharge capacity because of its high radical density (two radicals for each repeat unit). The thin polymer film is applicable by liquid coating techniques: A soluble polymer, polynorborene with pendant nitroxide radical groups, is spin coated onto a surface. On UV irradiation, the polymer becomes cross-linked with the help of a bis(azide) cross-linking agent. Peter Skabara, an expert in electro active materials at the University of Strathclyde, UK, praised the high stability and fabrication strategy of the polymer-based battery. The plastic battery plays a part in ensuring that organic device technologies can function in thin film, flexible form as a complete package. However, these materials can not give slow energy release, which limits them to capacitor applications. The polymers can undergo rapid charging/discharging which will be useful in delivering burst power. This technology is printable and environmentally benign. In a long term manner, it could be envisaged for EVs application.

European Commission

EUR 25143 EN – Joint Research Centre – Institute for Energy and Transport

Title: **STRATEGIC ENERGY TECHNOLOGY PLAN. Scientific Assessment in support of the Materials Roadmap enabling Low Carbon Energy Technologies - Electricity storage**

Author(s): M. Rosa Palacin, Anne de Guibert, John Collins, Marcel Meeus, Gerd Schumacher and Florence Fusalba - **JRC Coordination:** A. Perujo, E. Tzimas

Luxembourg: Publications Office of the European Union

2011 – 82 pp. – 21 x 29.7 cm

EUR – Scientific and Technical Research series – ISSN 1831-9424 (online), ISSN 1018-5593 (print)

ISBN 978-92-79-22606-9 (pdf)

ISBN 978-92-79-22605-2 (print)

doi:10.2788/401

Abstract

This report has been produced by independent and renowned European materials scientists and energy technology experts, drawn from academia, research institutes and industry, under the coordination the SET-Plan Information System (SETIS), which is managed by the Joint Research Centre (JRC) of the European Commission. It provides an in-depth analysis of the state-of-the-art, future challenges and the needs for material research activities to support the development of Electricity Storage technology in Europe both for the 2020 and the 2050 market horizons. Before being published the report has been presented and discussed with a wide pool of stakeholders.

How to obtain EU publications

Our priced publications are available from EU Bookshop (<http://bookshop.europa.eu>), where you can place an order with the sales agent of your choice.

The Publications Office has a worldwide network of sales agents. You can obtain their contact details by sending a fax to (352) 29 29-42758.

The mission of the JRC is to provide customer-driven scientific and technical support for the conception, development, implementation and monitoring of EU policies. As a service of the European Commission, the JRC functions as a reference centre of science and technology for the Union. Close to the policy-making process, it serves the common interest of the Member States, while being independent of special interests, whether private or national.

