Für Mensch & Umwelt

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Use of Nanomaterials in Energy Storage

1 Description of the Application

A sustainable energy supply requires a stepped-up change to renewable sources of energy. By 2050, assuming the demand on the security of supply remains the same, at least 60 percent of the gross final consumption of energy in Germany is to be covered by renewable energy sources. A major challenge is the natural fluctuation in power output, particularly with wind and solar power. In order to guarantee a consistent supply of electrical energy, there are a number of flexibility options available to help balance out the difference between energy supply and demand. In addition to grid expansion, load management and the use of highly flexible conventional power plants, this includes the utilisation of suitable storage methods. Energy storage comprises a wide range of technologies and applications and is classified according to the way in which the energy is stored (see Figure 1):

- Thermal energy: heat accumulator
- Chemical energy: accumulator, battery, redox flow battery, hydrogen, methane
- Mechanical energy: flywheel, spring, pumped-storage power plant
- Electrical energy: capacitor (electrical engineering), superconducting magnetic energy storage (Radgen 2007).

The storage of electricity is relatively complex. It must first be converted into another form of energy, which is associated with loss. Depending on the storage method, even more energy can be lost while the energy is being stored and when it is reconverted into electricity. Nanotechnology innovations are already contributing to improved energy conversion, storage and transmission. In future, nanotechnology solutions (including the targeted use of nanomaterials[1]) could play a prominent role in the energy sector, especially in the development of innovative approaches to energy storage (Seitz et al. 2013). Current research and development is addressed in particular to the development and improvement of rechargeable energy storage devices. Batteries today are of prime importance in many modern technologies and applications such as mobile telephones (mobile phones, smartphones), computers (laptops, tablets) and electric vehicles. In the field of mobile communications technology, there is great interest in producing ever smaller and thus lighter batteries with ever higher energy density. In all mobile energy storage applications, low cost and durability are key factors in technological progress.

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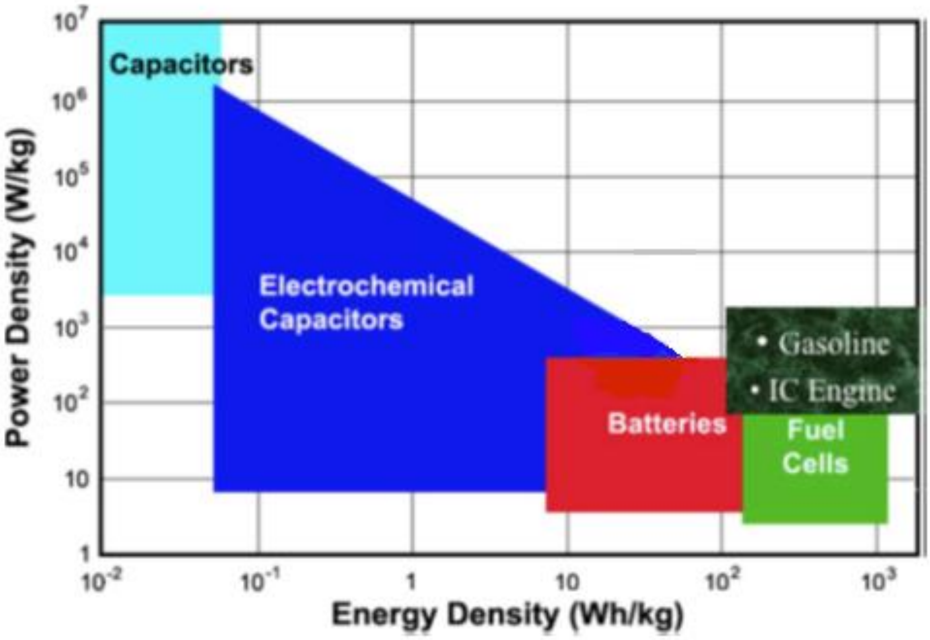
[1] Nanomaterials are composed of structurally definable particles in the size range of 1-100 nanometres (1nm = 10^{-9}m) in at least one dimension (see also the Commission Recommendation of 18 October 2011 on the definition of nanomaterials (2011/696/EU)). Both natural and anthropogenic nanomaterials can be found in the environment. In nanotechnology, engineered nanomaterials are used.

Definitions: battery, accumulator, capacitor

Batteries store electrical energy in the form of chemical energy. All batteries work on the same principle: batteries are made up of two electrodes connected to a circuit. The "*positive electrode*" (cathode) is the electrode that takes up electrons when the battery is connected to a load. The "*negative electrode*" (anode) is the electrode that gives off electrons when in operation. A chemical reaction on the anode creates electrons while the chemical reaction on the cathode uses electrons. The reactions create an electrical current. A battery is recharged by reversing the electrical circuit in which an externally applied charge forces the electrons in the opposite direction. In electrotechnical terms, a battery describes a combination of a number of similar galvanised cells (combination of two electrodes and an electrolyte) that are connected in series or in parallel and thus convert chemical energy into electricity. Originally, the term battery referred only to disposable batteries (primary batteries). Today, this restricted definition is obsolete, both colloquially and legally. Batteries today are understood to be both primary as well as rechargeable secondary cells. A secondary cell is also called an **accumulator** or **accu**. "Rechargeable battery" or "secondary battery" is more frequently used in place of accumulator. Due to the chemical reactions that take place during the charge-discharge cycles, structural changes occur in the electrode materials of the battery, limiting the number of recharge cycles.

A **capacitor**, particularly the electrolytic capacitor, is an electrical component in which the electrolyte serves as the cathode and thus the second electrode. The capacitor stores electrical energy in an electrical field between the capacitor plates. Capacitors can be charged and discharged more than several million times without any significant change in the materials.

Figure 1: Comparison of the specific power versus energy density characteristics of a number of storage media[2].



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[2] Weight-related power/specific power (power denotes the energy converted in an interval); energy density (energy: calculation unit for electricity: 1kWh = $3.6 \cdot 10^6$J).

1.1 Products and purpose of using nanomaterials

Examples of nanotechnology applications and development in the field of energy storage include (BMBF 2011):

- Nanostructured electrode materials and separators for supercapacitors and batteries
    - Optimised lithium-ion batteries for automotive drives and stationary mass storage through nanostructuring and the use of nanocomposites for electrode materials and separator/electrolytic systems, development of new types of batteries (lithium-air, lithium-sulphur)
    - Carbon nanotube (CNT)-based electrode materials with high charge capacities for supercapacitors and batteries
- Nanoporous adsorption storage including metallo-organic cage-like structures for mobile gas storage (hydrogen, natural gas)
    - Hydrogen storage based on nanocristalline metal hydrids.

High market volumes are expected in the energy storage industry in the years to come for products based on nanotechnology (see Table 1):

Table 1: Estimate of market volume of energy storage based on nanotechnology (from Seitz et al. 2013)

Market Segment	Market Volume Worldwide		Annual Growth Rate
Nano-optimised batteries	US$169 million (2009)	US$1.1 billion (2013)	46%
Nano-optimised fuel cells and hydrogen stores (electrodes, catalysators, membranes, nanomaterials for hydrogen production and storage)	US$2 billion (2008)	N/A	N/A
Supercapacitors	US$275 million (2009)	US$713 million (2014)	21%

The areas of use for nanotechnology-based energy storage are seen to be primarily in the storage of decentrally produced energy and in electromobility: thus, the storage of decentrally produced energy (e.g. by a combination of roof-top solar panels and storage in private homes or businesses) will become significantly more important in the near future. Lithium-ion batteries and supercapacitors in particular are regarded as key technologies of the future (Seitz et al. 2013).

Today's batteries for externally chargeable electric cars are still too heavy, too big and relatively expensive for a large-scale changeover of mobile transport. Work is being done to develop a significantly more powerful and lighter power storage system and make it available for mass production. Lithium-ion batteries in vehicles with doubled capacity should be ready to go into production by 2020 (Pander 2014)[3]. All-electric vehicles will first be used only for niche purposes or for short distances until a solution – such as with the aid of nanotechnology – is found for the long charging time of the batteries (several hours as a rule). Once the charging time of an electric car is reduced to an acceptable level (one assumes a charging time of less than 10 minutes), there will be a need for the corresponding infrastructure (Walsh 2007).

In the next sections, the various types of energy storage will be more closely examined:

- Lithium-ion battery
- Lithium-air battery / Sodium-air battery
- Lithium-sulphur battery / Sodium-sulphur battery
- Printed battery
- Supercapacitor
- Nanocapacitor
- Metal hydrid storage.

1.1.1 Lithium-ion battery[4]

Current research and development is particularly dedicated to the rechargeable lithium battery. This type of battery will thus be presented in greater detail in the following. Lithium is suitable for the production of high-performance batteries. Through enlarged electrode surfaces and optimised separators, the energy density and stability of the batteries is increased, thus opening up new potential uses such as in electric and hybrid vehicles or stationary power storage (BMBF 2011).

Lithium in batteries has a number of advantages:

- Its high specific charge
- Its highly negative standard potential (–3.05V)
- Its stability in many organic (and some anorganic) electrolytes.

Lithium-ion batteries are currently the most common (rechargeable) mobile energy storage device: consumers bought five billion lithium-ion batteries in 2013 for use in laptops, cameras, mobile phones and electric vehicles (Van Noorden 2014). For them to be suitable for such purposes, the batteries should have high voltage, high capacity and a long life span while being highly safe and reliable.

Lithium-ion batteries have a relatively high energy density. Owing to the use of new cathode materials (such as the compounds $LiNi_{0,8}Co_{0,15}Al_{0,05}O_2$; NCA), the energy density of lithium-ion batteries could be almost doubled within 10 years. Depending on which subsystem of lithium-ion batteries is considered, energy densities now range from ca. 80Wh/kg (lithium iron phosphate, LFP) up to ca. 250Wh/kg (NCA) (Whittingham 2012). In comparison, lead-acid batteries have energy densities of ca. 40Wh/kg.

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[3] What is meant is that batteries in vehicles of the same size, same weight and same cost (on average) will have double the range in 2025 as compared to 2014.

[4] "Lithium-ion battery" is the collective term for most common terms used in technology such as "*lithium-ion secondary battery*", "*lithium-ion cell*", "*lithium-ion accumulator*". A lithium-ion accumulator generally consists of a series circuit of individual lithium-ion cells.

Despite their higher voltages, lithium-ion batteries have good stability overall. By 2017, energy density could be increased up to 400Wh/kg (van Noorden 2014). They can still have sufficient dimensional stability of the electrodes, high cell voltage values (working voltage: 3.2 to 3.7 volts) and number of cycles (up to more than 5,000 cycles) and an uncomplicated assembly of the cell from compounds that are stable in air and moisture-resistant.

Lithium-ion batteries are made up of an electrolyte, a cathode and anode as well as a separator. The lithium in electrolytes is in an ionised form, which is what makes the charge transport between the electrodes possible.

During the charge process, the lithium ions flow in the direction of the anode. The anode is typically made of graphite with a capacity of 370Ah/kg. Other materials suitable for anodes include carbon black, doped[5] carbon and fullerenes. Beyond that, nanostructured materials (nanowires, nanorods, nanotubes and nanoporous particles) as well as nanocomposites (e.g. carbon matrix with nanoscale silicon or tin) are being used or in development (Seitz et al. 2013). Basically, any material can be used that is capable of storing lithium in its crystal structure. Such electrodes allow for a capacity of 700Ah/kg (Whittingham 2012).

During the discharge process, the lithium ions flow in the direction of the cathode. Lithium cobalt oxide ($LiCoO_2$) is still being used primarily as a cathode material. For economic[6] and ecologic reasons, new materials are being increasingly used. These include nanomaterials made of phosphates from transition metals ($LiXPO_4$ with X = Mn, Fe, Co or Ni; particularly preferable are lithium manganese phosphate, lithium cobalt phosphate or lithium iron phosphate (LFP)[7]). If used in their nanoparticle form, a reduction in the amount of materials used is made possible. Furthermore, by nanostructuring the cathode, its surface can be enlarged, which leads to improved energy storage and stability of the charge cycles.

Separators play a key role in all batteries. They allow the free flow of ions between the electrodes and protect the battery from internal short circuits and overheating. The separator is made of a material of non-woven, non-conductible polymeric fibres[8] that is coated on one or both sides with an ion-conducting anorganic material[9]. The separator materials are preferably made of the nanofibres of the polymers used. These nonwovens have high porosity through the forming of smaller pore diameter. The ion-conducting material is composed of particles whose largest diameters are less than 100nm. High tensile strength and good pliability of the separator furthermore lead to the adapting to the changes occurring in the geometry of the electrodes without being damaged.

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[5] In doping, impurity atoms are introduced into a base material. The amount introduced is very small in comparison to the base material (between 0.1 and 100ppm). This changes the property of the base material, such as its electrical conductivity.

[6] Iron phosphate, for example, is significantly cheaper to manufacture than cobalt oxide. Cobalt is mined in only a few countries which could lead to enormous price fluctuations as a result of commodity speculation. By contrast, raw materials for iron phosphate are more readily available worldwide.

[7] Lithium metal phosphates can have a high redox potential compared to lithium metal. For lithium manganese phosphate, a value of 4.1V and for lithium cobalt phosphate, a value of 5V are known.

[8] The polymeric fibres are made of very different polymers such as polyacrylnitrile, polyolefin or polyesters. The preferred polyesters are polyethylene terephthalates.

[9] The ion-conducting anorganic material is from the group of oxides, phosphates, sulphates, titanates, silicates, aluminosilicates from zircon, aluminium, silicone or lithium.

1.1.2 Lithium-air battery / Sodium-air battery

Lithium-air batteries are still in the research stage, but theoretically have a high specific energy density. Energy densities of lithium-air batteries are conceivable like that of a petrol engine, that is, ten times more than in today's batteries. Lithium-air batteries use atmospheric oxygen: when discharging, lithium is oxidised to lithium oxide whereby energy is released; when charging the battery, oxygen is released back into the atmosphere with the regeneration of the lithium anode. The advantage of this method is that the cathode (in this case oxygen) does not contribute to the weight or volume of the battery. Nanostructured materials in these batteries are important for the structure of the cathode (usually carbon) and the separator membrane to allow the passage of oxygen while preventing that of moisture (Kraytsberg and Ein-Eli 2011). The decisive disadvantage of a lithium-air battery is that a charge in an electric car would be too expensive, so this type of battery would most likely not be considered for this type of use (van Noorden 2014). Experts therefore see greater prospects for the development of sodium-air batteries: the expected energy density is five times higher than in today's lithium-ion batteries; in addition to that, as a key component for batteries, sodium is less expensive than lithium. Up to now though, batteries of this type achieve only 100 charge cycles (van Noorden 2014).

1.1.3 Lithium-sulphur battery / Sodium-sulphur battery

The lithium-sulphur battery is a promising type of battery. In contrast to today's generation of lithium-ion batteries, these can achieve energy densities of two to five times more. Furthermore, the components required for manufacturing the batteries are less expensive. Lithium-sulphur batteries are about to be launched on the market and look set to have an energy density of around 500Wh/kg (van Noorden 2014). In lithium-sulphur batteries, the anode is made of lithium, which serves as both an electrode and the producer of lithium ions. The cathode is made of sulphur. During the discharge process, lithium on the anode dissolves and forms lithium sulphide on the cathode with sulphur. When charging, the resulting lithium sulphide is reduced and lithium is formed on the anode. To prevent premature degradation of the sulphur electrode, this is coated with nanoscale carbon such as graphene[10] (Liu 2014). There are also attempts to optimise these batteries with carbon nanotubes (CNT). Other optimisation variants use different electrolytes and different compositions for the anode: silicon and tin especially have been proposed as materials for the anode that should improve cycling capability. The advantage of the lithium-sulphur battery as opposed to many other lithium-ion batteries is dispensation with scarce and expensive heavy metals such as cobalt or nickel that are hazardous to health and the environment. Sulphur is quite safe for the environment, however, the lithium sulphides resulting from the discharge are toxic; they react with acids to become toxic hydrogen sulphides. For that reason, the cells must be tightly sealed.

Other development work aims to use sodium instead of lithium, since sodium is more highly available. The energy densities of batteries with sodium as the anode material

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[10] Graphene is a two-dimensional network of carbon hexagonals.

are, however, lower. It is conceivable that they could be used in stationary applications, as the decisive factors for these are the cost and cycle stability.

1.1.4 Printed battery

Another relevant technology for energy storage is the printing of electronic components with special inks on various substrates (*printed electronics*). Since these inks consist of a dispersion of metallic nanomaterials, this procedure belongs to nanotechnology. The inks have good conductive properties and are already being widely used as a conductor. MOD inks (metallo-organic decomposition inks) clog the spray nozzles only to a small extent. Metals used are silver, copper, aluminium and nickel. Another type of ink is made of metal oxide, usually zinc oxide. These are transparent and stable with respect to oxidation. Organic conductors and metals can be used as electrodes, thus replacing expensive indium tin oxide (ITO). Printed batteries still have a very low capacity. Experts anticipate that this will be increased in the near future and that this technology will be used for ultra-thin, flexible and rechargeable batteries.

1.1.5 Supercapacitor

A supercapacitor bridges the technological gap between capacitor and battery. As in a battery, the electrolyte serves as the conductive connection between two electrodes. Among capacitors, supercapacitors have the highest capacity value per component (around 10,000 times higher than that of conventional capacitors).

Supercapacitors for the storage of electrical current essentially differ from commonplace batteries (such as lithium-ion batteries) in the following characteristics: they are much more quickly charged and discharged. The storage capacity of supercapacitors is generally still very low. Accordingly, they have high power densities and low energy densities. Because of the low cell voltage of the supercapacitor, a series connection of a greater number of elements is therefore required to achieve the desired voltage (Radgen 2007). Current research is geared particularly to the increase of both performance and energy density. Therefore, production costs should be lower and ecologically-friendly materials be used.

Supercapacitors are already being used in electric vehicles to improve the battery's discharge process or to very quickly store large amounts of energy in regenerative braking systems. Batteries would not be suitable for these usages with the desired rapid power input/output. The service life of a supercapacitor can be up to 80,000 cycles, whereby this depends heavily on the temperature and voltage load.

Nanotechnology solutions should significantly improve the electrical storage capability of high-capacity capacitors as opposed to conventional capacitors, so that they could compete with batteries. Carbon, metal oxides and conductive polymers are being examined for use as main materials, whereby particular progress has been made with carbon nanotubes (SWCNT, MWCNT) (Seitz 2013). Graphene likewise plays a growing role since this material is of significant theoretical and practical importance: relatively low production costs in mass production, a large surface, excellent conductivity and capacity. Developments with graphene have achieved a theoretical specific capacity[11] of $550 Fg^{-1}$, whereby previous values of $200\text{-}300 Fg^{-1}$

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[11] Electrical capacitance is measured in farad. One farad (1F) is the capacitance which, when charged to a potential difference of 1 volt, carries a charge of 1 coulomb (1C = 1As).

were able to be achieved. In comparison, a conventional capacitor with activated carbon achieves a specific capacity of $100Fg^{-1}$ (Liu 2014).

Also, soon to be launched on the market for example are flexible supercapacitors that through the use of nanoporous nickel fluoride layers (NiF_2) on thermoplastics can dispense entirely with lithium. Owing to their large surfaces, they can store large amounts of electricity (maximum capacitance density $66mF/cm^2$, energy density 384Wh/kg, current density 112kW/kg) and display no degradation of the pore structure at more than 10,000 charge/discharge cycles (Yang et al. 2014).

1.1.6 Nanocapacitor

Nanocapacitors are electrical capacitors whose separable individual structures are smaller than 100nm. They are still in the research stage. One of the current developments deals with the manufacturing of an arrangement of nanotubes that are electrically interconnected, so that this results in a high-capacity total capacitor. Other research work includes the examination of a new structuring of electrode surfaces. Thus, with the aid of a nanoporous highly-structured aluminium oxide layer that is coated with conductive titanium nitride (TiN), the power density of a nanocapacitor can be increased more than tenfold that of electrolytic capacitors (Banerjee et al. 2009).

Further studies on the optimisation of the capacity and on practical issues such as encapsulation are currently underway. Above all, expensive production costs still prevent a rapid use of nanocapacitors.

1.1.7 Hydrogen storage for fuel cells

There is great hope placed in hydrogen as a source of energy for automotive drives of the future. Hydrogen is particularly suitable for fuel cell technology[12]: hydrogen is practically infinitely available, has a very high energy density (weight related, for example, it is three times as high as petrol) and burns without harmful emissions. With the support of the government, a number of automobile companies have been conducting research, some for more than 20 years now, on vehicles powered by hydrogen.

As opposed to a battery, a fuel cell has to be constantly refilled with an “energy-rich” substance, such as pure hydrogen in a hydrogen-oxygen fuel cell. In a fuel cell, electrons that are given off during the electrochemical reaction of hydrogen on oxygen, are forced into an external circuit that is then capable of driving an engine and the like. The resulting reaction product in hydrogen fuel cells is just pure water.

Today it seems rather unlikely that hydrogen-powered vehicles will contribute significantly to a reduction in greenhouse gas emissions in the next 10 to 15 years. Costs are high for fuel cells in which hydrogen and oxygen can be converted into electrical current. Energy is required for the production of hydrogen as well as for the removal of hydrogen from the carbon portion of fossil fuel and also for the separation of hydrogen from oxygen in water. Hydrogen can be stored as a highly compressed gas, as a cryogenic gas or bound to solids. To

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[12] The use of hydrogen is relevant not only for fuel cells. Hydrogen (or methane) is a key component of our long-term scenarios, such as Germany in 2050 – a greenhouse gas-neutral country, in which through Power to Gas it is available in all sectors, not just transport.

liquefy hydrogen, it has to be cooled to -253°C, which accounts for 30 to 40 percent of the energy content of hydrogen (Seitz et al. 2013).

Compressed and liquefied hydrogen furthermore present a danger of explosion if there are any undetected leaks. Thus, additional variants for the storage of hydrogen are currently being developed and produced. For this purpose, researchers wish to use nanostructured materials that can store a great amount of hydrogen in the smallest space. Storage substances such as ammonia borane as well as CNTs, metal hydrids or alloys with titanium, iron or nickel are being used, on which the hydrogen is physically or chemically reversibly bound, thus curbing the risk of an explosion. Through the use of nanocubes of metallo-organic compounds that are criss-crossed with a dense network of nanometre-sized pores, a very large surface can be made available for storage. Hydrogen can be released electrically or chemically through the application of heat. Due to the metallic bond, it is a very safe storage technology with low storage loss. Overall, the effectiveness of a hydrogen storage system is, however, still very low at around 29%. It is hoped in the long term that this effectiveness can be increased up to 46% (Radgen 2007). The advantage of metal hybrid hydrogen storage lies in the cost-effective and safe storage of the hydrogen (average working pressure ‹10 bar) and the handling at room temperature. Owing to the alternating charge and discharge cycles, the storage material itself is not used up. There are thus no waste products and such tanks can be operated over a long period of time.

1.2 Release of nanomaterial during use

With normal use of energy storage, no release of nanomaterials is to be expected since these, generally, exist as nanocomposites enclosed in the storage system. Nanomaterials should also make energy storage safer and more sustainable, so that the risk of explosion in current energy storage devices such as lithium-ion batteries would also be reduced. The collection/return of used batteries needs to be ensured by a regulated return system, so that the storage device is handled safely and efficiently and is recycled. If the energy storage device is properly disposed of, no appreciable release of nanomaterials or other components from the product is to be expected. In the case of improper disposal – as a result of ageing processes such as weathering – a release cannot be ruled out.

2 Environmental and Health Aspects

2.1 Potential environmental benefits

The use of nanomaterials in energy storage generally does not have the primary objective of reducing environmental impact. Rather it is the development of an energy-efficient system that is the key objective. Early life cycle assessment shows that the environmental burden, particularly in the manufacturing of nanomaterials, is often greater than with conventional materials (Illuminato and Miller 2010). The power demand and thus the environmental impact of synthetic nanomaterials can be very high: as is generally known, the manufacturing of single-walled carbon nanotubes (SWCNT) is one of the most energy-intensive processes (energy consumption for CNT up to 100,000MJ/kg; graphene, depending on the manufacturing process, of 500 or 1,000MJ/kg, Arvidsson et al. 2014, Kim and Fthenakis 2013). Furthermore, the manufacturing of nanomaterials goes hand-in-hand with high consumption of water and solvents as well as a significant amount of potentially dangerous materials as byproducts (Illuminato and Miller 2010). On the other hand, the increased durability of lithium-ion batteries equipped with ceramic separators as nanoscale components are less of a burden to the environment, thanks to the reduced need to exchange them. Furthermore, because of the greatly reduced probability of explosion, fewer safety measures such as heat dissipation capacity or explosion insulation are needed. The manufacturing of batteries with such ceramic separators, however, can lead to increased power demand in comparison to conventional lithium-ion batteries (Zhang, 2007).

In a case study conducted on behalf of the German Environment Agency (UBA), a comparative analysis was made of conventional drive systems and new systems with hybrid drives in local public transport. In particular, the expected potential for reducing environmental impact of nanotechnology-based lithium-ion batteries was examined (Steinfeldt et al. 2010). The case study compared the use of new hybrid drives in busses using a nickel metal hydrid battery or a nanotechnology-based lithium-ion battery with a conventional system (diesel-powered city bus). The serial hybrid drive with the lithium-ion battery allows exhaust-free driving in pure battery mode over short distances. For the hybrid bus with a lithium-ion battery, depending on the weight (400kg and 240kg) and age (6 and 10 years), a savings in fuel of 15 to 25 percent was realised. This results in a reduced greenhouse effect[13]: the reduced fuel consumption exceeds the extra effort and expense that was entailed in the manufacturing of the hybrid system (Steinfeldt et al. 2010). Here it is to be noted, however, that the results obtained from the study are subject to some uncertainty since at the time the study was conducted (2008/2009) no data was yet available on major industrial production of lithium-ion batteries and the data used was based on estimations. For a life cycle assessment, current reliable data would be required.

The higher the proportion of renewable energies in the production of electricity, the more important the further development of power storage technologies becomes. Important for the environmental friendliness of energy storage systems are the effectiveness and disposal at the end of service life. Especially because of the harmful substances frequently being used in chemical energy storage, special attention needs to be given to the disposal of the system (Radgen 2007). The respective disposal requirements are laid down in the Battery Act (see also section 3).

Due to the increased use of nanomaterials in consumer products, attention should be paid to the effects that may occur which could possibly undermine the expected environmental benefits of such nanoproducts. For example, the use of platinum in nanoparticle form can reduce the material required and the costs of fuel cells. Because of the reduced price, however, there could be increased demand which in turn would lead to more production and thus increased use of resources and high emissions (the so-called rebound effect). It is estimated that in the equipping and operating of 500 million vehicles with such fuel cells, the platinum used would be emitted through the exhaust gases to such an extent that a further use would be lost forever and that supplies of platinum worldwide would be exhausted within 15 years (Illuminato and Miller 2010).

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[13] In comparison to a diesel-powered city bus driven 240,000km in six years (global warming potential: CO_2 equivalent of 279 tonnes), the global warming potential for a hybrid bus (global warming potential: CO_2 equivalent of 213 tonnes) is reduced by up to the CO_2 equivalent of 66 tonnes.

2.2 Environmental impact

Nanomaterials used in new types of energy storage include graphene and CNTs. A release of these nanomaterials could result during the production process or through improper use and/or disposal.

Carbon-based nanomaterials resist degradation under normal environmental conditions (Flores-Cervantes et al. 2014). Some studies have shown that under oxidative conditions, enzymatic degradation of CNTs can result. Non-functionalised CNTs are more resistant to degradation than CNTs with a functionalised surface (Allen et al. 2008 and 2009, Zhao et al. 2011). Due to their complex structure, it is assumed that multi-walled CNTs are more resistant to degradation than single-walled CNTs (Russier et al. 2011).

CNTs can be ingested by invertebrates and vertebrates and for the most part, are excreted – particularly in the presence of food free of CNTs (Jackson et al. 2013). In fish, there is evidence that a significant proportion of CNTs may remain in the organism (Schäffer 2011). Furthermore, CNTs are capable of penetrating plant tissue (Wild and Jones 2009). Graphene, too, can be ingested by invertebrates such as daphnids, but not completely excreted. A transfer of the accumulated graphene to the next generation is being discussed (Guo et al. 2013). CNTs, graphene and also graphene oxide are capable of interacting with organic pollutants, thus influencing their transport in the environment (Farre et al. 2009, Apul et al. 2013, Qi et al. 2014). That could cause organic pollutants in the presence of carbon-based nanomaterials to become increasingly bioavailable.

The data available on potential environmental toxicity of carbon-based nanomaterials is insufficient and difficult to compare. Adverse effects of CNTs have been studied up to now on bacteria, algae, plants, daphnids and fish (Jackson et al 2013). The degree of CNT ecotoxicity depends on the type (single-walled, multi-walled), length, diameter and functionalisation of the carbon lattice as well as any contaminants. The mechanisms of the toxic effect vary (e.g. formation of oxygen radicals, reduced photosynthetic capacity due to shade, influence on feeding behaviour (Long et al. 2012, Schwab et al. 2011, Zhu et al. 2009, Jackson et al. 2013)). Information on the impact of graphene and graphene oxide on the environment is still very limited and up to now has been restricted to algae, bacteria, daphnids and fish embryos. Graphene oxide has a toxic effect on bacteria and for graphene, too, toxic effects on luminescent bacteria and on green algae have been demonstrated (Pretti et al. 2014).

The concentrations of CNTs with ecotoxic effects ascertained up to now in environmental laboratory tests are currently well above the modelled concentrations expected in the environment (Gottschalk et al. 2013). The same is to be expected for graphene. Accordingly, with proper use and disposal no environmental risk from these nanomaterials would be assumed at present. This assessment of the potential environmental risk, however, needs to be updated periodically in view of the increasing amounts and areas of use and in accordance with newly acquired knowledge on environmental exposure and effects.

2.3 Health impact

CNTs are produced as fibres of varying lengths and diameters, single or multi-walled, stretched or entangled and with various surface characteristics. There are indications that long rigid fibres, after being inhaled, could cause asbestos-type effects such as the development of tumours (mesothelioma) (Poland et al. 2008, Takagi et al. 2008 and 2012, Sakamotoet al. 2009, Xu et al. 2012). A comparative overview of the pulmonary toxicity of CNTs and asbestos is found in Donaldson et al. (2013).

The evaluation of inhalation studies and of studies with intra-tracheal administration of single-walled (SWCNTs) and multi-walled (MWCNTs) on rodents carried out on behalf of the UBA proved that the group of CNTs exhibits a broad spectrum of toxicity and that apart from the shape of the fibre, there are other aspects that determine toxicity (Schröder et al. 2014).

A short-term study, also conducted on behalf of the UBA, of inhalation on rats with defined MWCNTs led to an inflammatory reaction one day after exposure; this effect had disappeared after 28 days. Using a high-resolution optical microscope, individual MWCNTs were verified in the liver, kidneys and pleural cavity. This proves that the fibres do not remain locally in the lungs after inhalation but can migrate to the pleura (the lining of the lung) and other tissues/organs (Bellmann et al. 2014). In mice, an extrapulmonary transport of fibres was also shown following one-time inhalation of 30mg/m^3 MWCNTs over a period of 6 hours (Rymann-Rasmussen et al. 2009). Whether certain CNTs have the potential of inducing tumours of the pleura needs to be clarified in individual cases by long-term studies. As part of a BMBF-funded joint project (“CarboTox”), in-vitro screening processes were to be developed which would allow an initial assessment of a possible carcinogenic effect of CNTs. The project has been completed, but the results have yet to be published.

The toxicity of graphene in humans has not been sufficiently studied. The key factors that play a role in toxicity to be discussed are the generation of reactive oxygen species, the adsorption of molecules relevant to metabolism and the interaction of cell membranes with lipids. Overviews of the current state of knowledge can be found in Guo and Mei (2014) as well as Bianco (2013).

In a comparative short-term study on rats on the inhalation toxicity of graphene and MWCNTs, signs of inflammatory reactions were noticed for the selected graphene at exposure concentrations of 10mg/m^3 and for the selected MWCNTs at 0.5mg/m^3. Microgranuloma were observed for the selected graphene at 10mg/m^3 and for the selected MWCNTs at 2.5mg/m^3 (Ma-Hock et al. 2013).

The concentrations of CNTs with toxic effects ascertained up to now in animal testing are currently well above the modelled concentrations expected in the atmosphere (Gottschalk et al. 2013). The same is to be expected for graphene. With proper use and disposal of the above-mentioned energy storage systems, no risk to health from the nanomaterial used in them is currently to be assumed. Analogous to the environmental risk assessment, the assessment of a health risk due to CNTs and graphenes needs to be updated periodically in accordance with newly acquired knowledge of exposure and toxicological effects.

3 Legal Framework

In 2006, the EU issued the battery directive[14]. Its objective is to minimise the negative impact of waste batteries on the environment. In Germany this was implemented into national law in 2009 through the Battery Act (BattG)[15]. The law applies to all types of batteries including car batteries, industrial batteries and batteries used in everyday devices. In the context of product responsibility, the law requires producers of batteries (manufacturers, importers, etc.) to take back any waste batteries. This is done with portable batteries, for example, by establishing a return system for waste batteries. All waste batteries collected and identified as such have to be handled according to the latest technology and recycled, as far as technically possible and economically reasonable. In addition to that, the law limits the use of mercury and cadmium in batteries. The Battery Act does not specifically regulate batteries containing nanomaterials.

Furthermore, producers of batteries have to be registered in the German Batteries Register of the UBA and provide information on the carrying out of their product responsibility. Specific information on nanomaterials is not requested.

Materials used in the manufacturing of energy storage systems within the EU are subject to the provisions of the REACH Regulation (EC) No. 1907/2006[16]. As they are materials, nanomaterials in principle fall under REACH. Specific characteristics of nanomaterials, however, are not taken into account in REACH, so that currently there are no separate obligations for the nano forms of a material. The EU Commission and Member States are thus working on adapting REACH to requirements for nanomaterials (Schwirn et al. 2014). If energy storage systems are imported into the EU, only a comparatively few REACH obligations for products apply.

4 Research and Development Need

In the mid to long term, nano-based energy storage systems will occupy a significant proportion of the market. The advantages and disadvantages of the various materials used in energy storage systems are crucial for future market prospects and areas of application. Work is needed on the technical optimisation of nano-based components whose objective is to replace materials used up to now with materials that are more environmentally friendly, better available and less expensive, taking into consideration the shortage of raw materials and energy consumption. So, from today’s perspective, it is assumed that the availability of electrode materials such as cobalt or rare earths that the EU Commission classifies as critical raw materials[17] will hamper the use of lithium-based energy storage systems in transport, the electrical grid and storage in residential and commercial buildings. Since no storage

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[14] Directive 2006/66/EC of the European Parliament and of the Council of 6 September 2006 on batteries and accumulators and waste batteries and accumulators and repealing Directive 91/157/EEC.

[15] Law on the placing on the market, the return and the environmentally friendly disposal of batteries and accumulators (Battery Act - BattG) of 25 June 2009 (BGBl. I p. 1582) that was most recently amended by Article 4 of the Act dated 24 February 2012 (BGBl. I p. 212).

[16] Regulation (EC) No. 1907/2006 of the European Parliament and of the Council of 18 December 2006 on the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH).

[17] European Commission (2014): Report on critical raw materials for EU. Report of the Ad-hoc Working Group on defining critical raw materials. Brussels.

technology has yet emerged as clearly the most advantageous technology, the funding approach should be as wide as possible and a number of different storage technologies taken into consideration (Radgen 2007). Research is to be systematically directed in particular to the replacement of critical and environmentally hazardous raw materials to guarantee the safeguarding of technological benefits to the environment[18].
In research and development, technology-related issues in the field of power storage technologies are often given priority such as increasing effectiveness of the system, increasing stability (number of cycles), boosting energy storage density, reducing system costs and improving safety. Additionally, with regard to the behaviour in the environment of (nano) materials contained in energy storage systems, their impact on humans and the environment as well as the environmental compatibility of energy storage systems, there is the following need for research and development:

- Examination of the importance of the need for raw materials, in particular those raw materials in short supply and the associated impact on the environment, both negative and positive
- Study of the possible release, behaviour in the environment and the impact on humans and the environment of the materials in energy storage systems throughout the entire life cycle, including disposal
- Examination of recycling possibilities for the recovery of specific loads of technically used metals from energy storage devices. The ramifications of collection and recycling according to the Battery Act (BattG) are to be checked. In particular, the dismantling and recycling of new types of energy storage systems can present a challenge with regard to the materials they contain (e.g. highly reactive lithium in lithium-ion batteries)[19].

5 Summary

The German Environment Agency considers the use of nanomaterials and nanostructures in energy storage systems as a promising future trend. In the successful design of a sustainable energy supply through a stepped-up change to renewable sources of energy, such storage systems could make a significant contribution. The development of these storage systems is still in the initial stages, but the first products are already coming on the market. Because of the dynamic development of the different systems as well as the new types of systems based

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[18] With regard to energy storage, the following projects have been and will be funded within the context of the environmental research plan (Ufoplan): “*Weiterentwicklung der abfallwirtschaftlichen Produktverantwortung unter Ressourcenschutzaspekten am Beispiel von Elektro- und Elektronikgeräten*” – Advancement of product responsibility in waste management with regard to the protection of natural raw materials using the example of electrical and electronic equipment (FKZ 3711 95 318), “*Ableitung von Recycling- und Umweltanforderungen und Strategien zur Vermeidung von Versorgungsrisiken bei innovativen Energiespeichern*” (engl. Formulation of Recycling-Related and Environmental Requirements and Strategies for Preventing Supply Risks in Connection with Innovative Energy Storage Systems”) (FKZ 3713 93 307), “*Substitution als Strategie zur Minderung der Kritikalität von Rohstoffen für Umwelttechnologien – Potentialermittlung für Second-Best-Lösungen*” (engl. Substitution as a strategy for reducing the criticality of raw materials for environmental technologies Determination of potentials for second-best solutions) (FKZ 3714 93 316 0).

[19] The German federal government is currently funding research and development projects for recycling technologies that will be needed for lithium-ion batteries in future.

on nanotechnology, it cannot be foreseen now which of these different technologies will play a key role in future. In addition, the technologies in electrical applications for the consumer change very quickly. It is expected that these energy storage systems will tend to be smaller, cheaper, lighter, more effective, safer and more durable.

For the German Environment Agency, the early examination of the environmental compatibility of new technologies is of prime concern. This applies particularly when new types of materials, such as nanomaterials, come into direct contact with humans or end up in the environment during their life cycle. With normal use and proper disposal of the energy storage system, no release of nanomaterials in the environment is expected since these, as a rule, are enclosed in the storage system. Based on current knowledge, no environmental risk is assumed for nanomaterials in energy storage systems. The assessment of a potential risk to the environment, however, needs to be updated periodically in view of the increasing amounts and areas of use and in accordance with newly acquired knowledge on environmental exposure and effects. There are open issues with regard to the significance of raw material consumption as well as the possibility of recovering the materials used in energy storage. The data for this has been insufficient so far. The German Environment Agency therefore recommends that these topics be studied further.

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Substitution as a strategy for reducing the criticality of raw materials for environmental technologies Determination of potentials for second-best solutions