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Chapter 4

Materials for Electrochemical Energy Storage Devices

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The global quest for intermittent renewable energy sources (wind, solar), consumer goods (mobile phones, notebooks), and electrification of the transport sector (electric vehicles), requires a strong increase in the use of rechargeable energy storages devices, such as batteries. Hence, novel types of rechargeable batteries are to be found that are cost-effective, consist of environmentally friendly materials and non-critical materials, and deliver a high performance in terms of energy density and power, during a long cycle and service life, taking current legislation laws into account. Here we concentrate on various types of batteries and their materials, their typical sectors of application, and their forecast, including potential market share. It turns out that metals will still remain the predominant type of battery material, irrespective of the choice of battery system. From the required materials that are important for future rechargeable batteries, a number are critical in terms of scarcity, geopolitics, supply risk, competition with the food industry, carbon footprint, and/or ethical mining. With respect to the critical elements, particularly once those concern scarcity and supply risks, recycling is of utmost relevance, and needs to be regarded as an industrial sector of paramount importance.

4.1 Introduction

Cheap, reliable, safe and high energy density electricity storage systems have always been of paramount importance for large-scale introduction of portable consumer electronics and of (hybrid) electric vehicles (EVs) today. From an economical point of view, companies in the battery and battery materials market are investing time and money to develop systems to fulfil the above goals. In addition, because of current legislation which emphasizes environmental protection and recycling, companies are coming up with

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less polluting materials, which may be easier to obtain and worthwhile to recycle. Obviously this often increases the cost of the materials. Hence, it is necessary to find adequate trade-offs. According to a report by Transparency Market Research,[1] the battery materials market is expected to rise by 13.6% Compound Annual Growth Rate (CAGR) from 2017 to 2025.

Today, consumer goods such as mobile phones and notebooks dominate the end-use market for battery materials. However, the transportation sector, e.g. cars, trains, boats and aircrafts, is rapidly catching up.

Storage systems can be divided into primary (non-rechargeable) and secondary (rechargeable) batteries. Primary systems are found mainly in consumer goods, whereas secondary systems find use in both the transportation and consumer goods sector. A third sector, medical appliances, is becoming more and more important because of the increasing amount of advanced implants, such as pacemakers, defibrillators, and neurostimulators. A last sector is the industrial one, which is increasingly knocking on the door. An example of activity in the industrial sector is when utility companies search for systems required for large-scale electricity storage to permit peak shaving and load levelling. These four sectors of consumer goods, medical, transportation and industry require different types of batteries all with their own particular specifications and priorities. These are briefly presented in Table 4.1.

In this chapter, we concentrate on various types of batteries and their materials requirements. Other electrochemical devices, such as (super)capacitors and/or fuel cells are not considered here. The chapter

Table 4.1: Relevance of a Rechargeable Battery Issue for the Specific Sector.

	Issue							
Sector	Costs	Energy density	Power density	Life time	Cycle life	Safety	Reliability	Recycle-ability
Consumer Goods	☺[1]	☹	😐	😐	☹	😐	☹	☹
Medical	☺	😐[1]	😐	☹	☹	☹	☹	☺
Transportation	☹	☹	☹	☹	☹	☹	☹	☹
Industry	☹	☺	☺	☹		☹	☹	☺

☹: very critical 😐: critical ☺: less critical

[1] It becomes ☹ once a primary cell is considered.

thus includes battery chemistry and electrochemistry, typical applications by sector, and the forecast of use, including potential market share.

4.2 Electrochemistry in Brief

A battery typically is composed of one or more electrochemical cells placed in series or in parallel. The cell in turn is an electrochemical device that produces an electric current by spontaneous redox reactions at the negative and positive electrode. These conductive electrodes are the anode and the cathode respectively, where the oxidation and reduction occur. The anode donates the electrons, whereas the cathode accepts them. This means that the anode and cathode change sides as the battery is charged and discharged. However, in the battery world, the anode is often erroneously referred to as the negative electrode, and the cathode as the positive electrode.

In the simple case of the Daniell cell (see Fig. 4.1), the galvanic cell uses two different metal electrodes, zinc and copper, immersed in a sulfate salt, referred to as the electrolyte. Both compartments are then connected

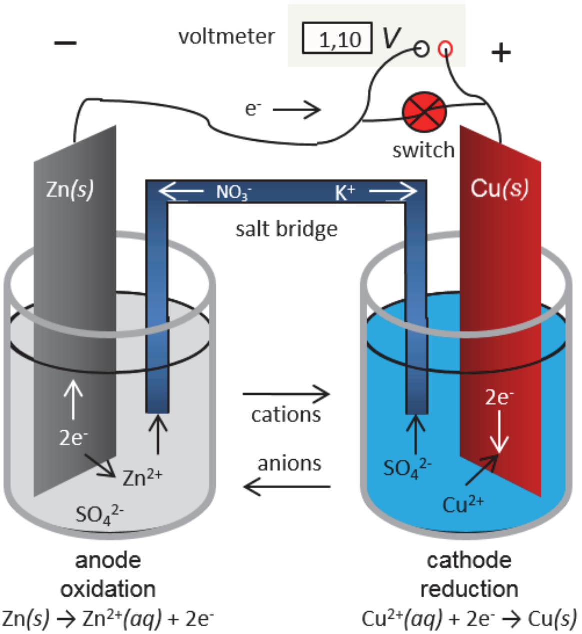

Fig. 4.1. Schematics of a Daniell cell.

via a so-called salt bridge that allows ion transport, so as to electrically balance the compartments once electrons start to flow from the anode to the cathode via an external electrical circuit doing work.

The actual redox reactions — **red**uction and **ox**idation — usually referred to as half reactions, are given below for the Daniell cell:

Zinc electrode (anode, negative electrode): $\mathrm{Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-}$
Copper electrode (cathode, positive electrode): $\mathrm{Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}}$

In order to simplify the cell notation, a cell diagram is constructed where the electrons spontaneously flow from left to right, meaning that the anode is on the left side, when the cell is discharging, i.e. doing work. This order is shown below:

$$\mathrm{Zn_{(s)}|Zn^{2+}(1M)||Cu^{2+}(1M)|Cu_{(s)}}$$

where a vertical line represents the phase boundaries between the solid and the liquid phase and the double vertical line represents the salt bridge of the cell.

The measured electrochemical cell voltage is often referred to as electromotive force (emf) or cell potential.

In the case, this cell would be rechargeable, the spontaneous reaction is reversed when electrons are forced to flow from the positive to the negative electrode of the cell.

4.3 History

When Luigi Galvani in 1780 was studying a dead frog which was lying on a copper alloyed bench, he touched it with his iron scalpel and suddenly its leg twitched. Although Galvani ascribed the effect to "animal electricity", it was Alessandro Volta who disagreed with this idea and he discovered a few years later that placing two different metals against each other separated by a wetted intermediate layer provides a voltage. In 1800, he then constructed his famous voltaic pile based on zinc and copper that provided continuous electricity and a stable current. Unfortunately, the battery was subject to severe electrolyte loss and parasitic reactions, leading to failure of the system after about one hour's use. After a few decades the British chemist Frederic Daniell figured out to solve those problems and in 1836 he presented the Daniell cell, which uses two compartments of the metal, each soaked in its metal sulfate. Both compartments were separated by a earthenware container, which was thus porous for ions to move through, but prevented mixing of both solutions. Soon it became the industry standard, important for the new telegraph networks. The system became even more popular after the Frenchman, Monsieur Callaud, improved the system by reducing the internal resistance. Hence "the gravity" battery was born and survived till the 1950s. In 1842, the German scientist Johann Christian Poggendorff had already further improved the system in terms of voltage up to 1.9V by modifying the electrolyte composition and changing the positive electrode material to a carbon plate. Clearly the chemistry was different from the actual Daniell cell, and therefore it became later known as the "chromic acid cell" or "bichromate cell". Similarly, in 1839 the Welshman, William Robert Grove, replaced the copper electrode with platinum soaked in nitric acid. The "Grove cell" provided a high current and almost doubled the voltage compared to the Daniell cell. Unfortunately, platinum was and is expensive and the cell produces poisonous nitric oxides. Already the importance of materials plays a role as well as safety issues. Therefore, rechargeable systems would have been of definite interest. In 1859, it was Gaston Planté who invented the first rechargeable system, namely the lead acid battery. It consists of lead as the negative electrode and lead dioxide as the positive electrode both immersed in sulfuric acid. Today, this cell is still used in the transport industry as the Start, Lighting and Ignition (SLI) battery as well in stationary storage systems. Nevertheless, at that time, the weight of this rechargeable battery was enormous and was not acceptable for consumer goods. In 1866, Georges Leclanché showed a battery — the Leclanché cell or the zinc-carbon cell — that consisted still of a zinc negative electrode, but now with a manganese dioxide positive electrode, where both electrodes were immersed in the same ammonium chloride solution. In a later stage, the ammonium chloride solution was "solidified" or immobilized so as to make a dry cell, by e.g. plaster of Paris by Carl Gassner in 1886. This most famous primary battery is still manufactured in huge quantities today, mainly in the alkaline form. However, this battery was not the first cell using an alkaline based electrolyte. In 1899, the Swedish scientist, Waldemar Jungner, invented the nickel–cadmium battery. This rechargeable battery uses nickel and cadmium electrodes in a concentrated potassium hydroxide solution. Commercialization started in Sweden in 1910, and was adopted in the U.S. in 1946. The cells were superior to the lead-acid cells, but much more expensive. In order to reduce the cost, Jungner replaced nickel with iron, but it was Thomas Edison who further developed it to certain success, e.g. in rail transport. Another attempt to replace the toxic cadmium was achieved via the nickel metal hydride

(NiMH) battery. Here cadmium was substituted by an alloy of various metals, including rare earth ones. The NiMH batteries were introduced in 1989 for the consumer, although it had already been shown to work back in 1970. Still the quest was to find an improved energy density rechargeable battery to assure its use, e.g. in electric vehicles. Lithium, being the lightest metallic element, therefore was always of interest, also because it produces a high voltage. Finally in the 1970s, the first lithium batteries were introduced on the market, with a 3V primary lithium coin cell, a device still on the market. In 1980, a boost in rechargeable lithium batteries arose when the American chemist John B. Goodenough and the Moroccan research scientist Rachid Yazami proved that lithium cobalt oxide as the positive electrode and graphite as the negative electrode can both reversibly accept lithium. In 1991, Sony introduced the first commercialized rechargeable Li-ion battery.

Missing from the list are the primary batteries zinc-air, silver oxide, mercury oxide, nickel oxyhydroxide, and lithium-thionyl chloride batteries. The first four still use zinc as the negative electrode, whereas the lithium-thionyl chloride cell uses lithium. This last battery has not been generally released to the public for safety reasons, but found its use, e.g. in medical applications such as automatic external defibrillators (AEDs). The most important missing secondary batteries are the sodium-sulfur batteries — used in stationary electricity storage systems, (redox) flow batteries, lithium sulfur — developed by Sion Power in 1994[2] — and lithium air batteries. These will however be discussed in the following sections with respect to their chemistry.

4.4 Battery Composition and its Chemistry

In this section, the chemistry of the various batteries will be briefly touched upon. This is important to show which materials are relevant for the system under study. However, it does not immediately say something about the non-active components, i.e. the casing, binders, current collectors etc. These materials will be discussed in section 4.5. Furthermore, this section has been split up into primary (non-rechargeables) and secondary cells (rechargeables).

4.4.1 *Primary batteries*

Primary cells today find their place mainly in consumer goods, but also in medical devices such as implants. A striking observation is that these two sectors are both important, both for reasons of cost and recyclability. This immediately reflects the importance of the materials used.

4.4.1.1 *Alkaline batteries*

The alkaline battery has a zinc negative electrode and a manganese dioxide positive electrode. Potassium hydroxide is used as the alkaline salt in the cell, and is relevant for the two half reactions, but is not consumed in the end.

Hence, the two half-reactions at the negative and positive electrodes are:

$$\mathrm{Zn_{(s)} + 2OH^-_{(aq)} \rightarrow ZnO_{(s)} + H_2O_{(l)} + 2e^-}$$

$$\mathrm{2MnO_{2(s)} + H_2O_{(l)} + 2e^- \rightarrow Mn_2O_{3(s)} + 2OH^-_{(aq)}}$$

With the overall reaction:

$$\mathrm{Zn_{(s)} + 2MnO_{2(s)} \rightarrow ZnO_{(s)} + Mn_2O_{3(s)}}$$

4.4.1.2 *Mercury batteries*

Mercury batteries have mercury(II) oxide as the positive electrode and zinc as the negative electrode. Potassium hydroxide or sodium hydroxide is used as the alkaline salt in the cell, and like in the alkaline cells it is used at the electrodes but overall is not consumed. The two half-reactions at the negative (two steps) and positive electrodes are:

$$\mathrm{Zn + 2OH^- \rightarrow ZnO + H_2O + 2e^-}$$

$$\text{Step 1: } \mathrm{Zn + 4OH^- \rightarrow Zn(OH)_4^{-2} + 2e^-}$$

$$\text{Step 2: } \mathrm{Zn(OH)_4^{-2} \rightarrow ZnO + 2OH^- + H_2O}$$

$$\mathrm{HgO + H_2O + 2e^- \rightarrow Hg + 2OH^-}$$

With the overall reaction:

$$\mathrm{Zn + HgO \rightarrow ZnO + Hg}$$

4.4.1.3 *Silver oxide batteries*

Silver-oxide batteries are quite similar to the earlier mentioned mercury batteries, but have silver oxide as the positive electrode and also zinc as the negative electrode. For the electrolyte, aqueous solutions of sodium hydroxide or potassium hydroxide are used. The half reactions at the negative electrode (two steps) were shown earlier; the half reaction at the positive electrodes occurs also in two steps according to:

$$\mathrm{AgO_{(s)} + H_2O_{(l)} + 2e^- \rightarrow Ag_{(s)} + 2OH^-_{(aq)}}$$

$$\text{Step 1}:\ \mathrm{2AgO_{(s)} + H_2O_{(l)} + 2e^- \rightarrow Ag_2O_{(s)} + 2OH^-_{(aq)}}$$

$$\text{Step 2}:\ \mathrm{Ag_2O_{(s)} + H_2O_{(l)} + 2e^- \rightarrow 2Ag_{(s)} + 2OH^-_{(aq)}}$$

With the overall reaction:

$$\mathrm{Zn + AgO \rightarrow ZnO + Ag}$$

4.4.1.4 *Zinc-air batteries*

Zinc-air batteries use a zinc negative electrode and a positive electrode where air can penetrate the cell. These cells are typically used for hearing aids, where you have to remove a sticker before use, so the positive electrode can be exposed to air. The electrolyte used is similar to that used for the alkaline cell, and the half reaction of the zinc electrode as well. The positive electrode (air) half reaction then is:

$$\frac{1}{2}\mathrm{O_2 + H_2O + 2e^- \rightarrow 2OH^-}$$

With the overall reaction:

$$\mathrm{2Zn + O_2 \rightarrow 2ZnO}$$

4.4.1.5 *Lithium batteries*

There exist many variations of lithium batteries, but all of them have a lithium negative electrode. The positive electrodes, however, vary from system to system. A brief overview is given in Table 4.2. The table includes the material and the electrolyte composition used. The half reaction at the positive electrode is somewhat complex for certain systems and will not be given here., However, the half reaction at the negative (lithium) electrode is given by:

$$\mathrm{Li_{(s)} \rightarrow Li^+_{(aq)} + e^-}$$

Table 4.2: Composition of Commercial Primary Lithium Batteries.

Material	Typical electrolyte composition[1]
Metal oxides[2]	Lithium perchlorate in PC/DME
Metal sulfides[3]	PC, dioxolane, DME
iodine	Lithium iodide
Silver chromate	Lithium perchlorate solution
Carbon monofluorde	Lithium tetrafluoroborate in PC, DME, or ϒ-BL
Copper chloride	Lithium tetrachloroaluminate in inorganic liquid SO_2
Thionyl chloride[4]	Lithium tetrachloroaluminate in thionyl chloride
Sulfur dioxide	Lithium bromide in SO_2

[1] PC = propylene carbonate, SO_2 = sulfur dioxide, ϒ-BL = gamma-butyrolactone, DME = dimethoxyethane.

[2] manganese dioxide, silver oxide, vanadium pentoxide, bismuth trioxide, cobalt oxide, copper(II) oxide.

[3] iron sulfide, iron disulfide (Pyrite), copper sulfide, lead sulphide.

[4] sulfuryl chloride systems do exists as well.

4.4.2 *Secondary batteries*

4.4.2.1 *Lead-acid batteries*

Lead-acid batteries use lead, lead oxide and lead sulfate for their electrodes. The positive and negative electrodes are both immersed in concentrated sulfuric acid, which plays a crucial role in the working of the cell. The electrode reactions on discharging are:

$$Pb_{(s)} + HSO^-_{4\,(aq)} \rightarrow PbSO_{4(s)} + H^+_{(aq)} + 2e^-$$

$$PbO_{2(s)} + HSO^-_{4\,(aq)} + 3H^+_{(aq)} + 2e^- \rightarrow PbSO_{4(s)} + 2H_2O_{(l)}$$

With the overall reaction:

$$Pb_{(s)} + PbO_{2(s)} + 2H_2SO_{4(aq)} \rightarrow 2PbSO_{4(s)} + 2H_2O_{(l)}$$

Since the system is rechargeable, on charging, the above reaction will be reversed.

4.4.2.2 *Nickel-cadmium batteries*

Once the nickel-cadmium cell has been charged, the negative electrode is cadmium and the positive electrode is nickel(II) oxide hydroxide. The electrodes are separated by a porous membrane, referred to as the separator, which is soaked in an alkaline solution of potassium hydroxide.

The electrode reactions on discharging are:

$$Cd_{(s)} + 2OH^-_{(aq)} \rightarrow Cd(OH)_{2(s)} + 2e^-$$

$$2NiO(OH) + 2H_2O_{(l)} + 2e^- \rightarrow 2Ni(OH)_{2(s)} + 2OH^-_{(aq)}$$

With the overall reaction:

$$2NiO(OH) + Cd_{(s)} + 2H_2O_{(l)} \rightarrow 2Ni(OH)_{2(s)} + Cd(OH)_{2(s)}$$

4.4.2.3 *Nickel-metal hydride batteries*

The nickel metal hydride (NiMH) cell has a metallic-like material (M) as the negative electrode and nickel(II) oxide hydroxide as the positive electrode. The electrodes are separated by a porous membrane, referred to as the separator, which is soaked in an alkaline solution of potassium hydroxide. During discharging the electrode reactions are:

$$MH_{(s)} + OH^-_{(aq)} \rightarrow M_{(s)} + H_2O_{(l)} + e^-$$

$$NiO(OH) + H_2O_{(l)} + e^- \rightarrow Ni(OH)_{2(s)} + OH^-_{(aq)}$$

With the overall reaction:

$$MH_{(s)} + NiO(OH)_{(s)} \rightarrow M_{(s)} + Ni(OH)_{2(s)}$$

The metallic-like material at the negative electrode is a so-called intermetallic compound, a crystalline metallic structure of various metals with regular order and distinct composition, hence it is not an alloy, because an alloy typically allows all compositions of metal mixtures. Several compounds have been identified for this NiMH battery according to the following composition, AB_5, with A being a mixture of various rare-earth metals (lanthanum, cerium, neodymium, praseodymium) and B a transition metal (cobalt, nickel, manganese, cerium, neodymium, praseodymium,) or aluminum. Besides, AB_2 compounds have been used as well, where A is either vanadium or titanium and B is nickel or zirconium. It is further stressed that modifications of these materials was done with several other elements and added to the compounds as impurities.

4.4.2.4 *Lithium ion batteries*

Typically the lithium ion (Li-ion) battery uses a carbonaceous material (graphite, hard carbons, etc) at the negative electrode and a transition metal oxide, phosphate or silicate at the positive electrode (see Table 4.3).

Table 4.3: Various Positive Electrode Materials Used for Li-ion Batteries.

Material	Composition	Crystal structure
Lithium cobalt oxide, LCO	$LiCoO_2$	Layered, $LiCoO_2$
Lithium nickel manganese cobalt oxide, NCM	$LiNi_aCo_bMn_cO_2$	Layered, $LiCoO_2$
Lithium nickel cobalt aluminum oxide, NCA	$LiNiCoAlO_2$	Layered, $LiCoO_2$
Lithium manganese oxide, LMO	$LiMn_2O_4$	Cubic, spinel
Lithium nickel manganese oxide, LNMO	$LiNi_{0.5}Mn_{1.5}O_4$	Cubic, spinel
Lithium iron phosphate, LFP	$LiFePO_4$	Olivine
Lithium iron silicate, LFS	Li_2FeSiO_4	β-Li_3PO_4

The electrode half reactions during discharge are simplified to the following reactions:

$$\mathrm{LiC_{6(s)}} \rightarrow \mathrm{Li^+_{(aq)}} + 6\mathrm{C_{(s)}} + \mathrm{e^-}$$

$$2\mathrm{Li_{0.5}CoO_{2(s)}} + \mathrm{e^-} + \mathrm{Li^+_{(aq)}} \rightarrow 2\mathrm{LiCoO_{2(s)}}$$

With the overall reaction:

$$\mathrm{LiC_{6(s)}} + 2\mathrm{Li_{0.5}CoO_{2(s)}} \rightarrow 6\mathrm{C_{(s)}} + 2\mathrm{LiCoO_{2(s)}}$$

Besides the standard carbonaceous materials, novel types of Li-ion cells may use titanium oxides, tin compounds or silicon.

4.4.2.5 *Lithium air batteries*

The lithium air (Li-air) battery is not yet commercially available. Still this system is regarded as the holy grail. The material used for this system is lithium metal or similar negative electrodes as used for Li-ion batteries. For the positive electrode, usually carbon mats are used together with typically a transition metal oxide catalyst. The reactions at the negative and positive electrodes are respectively:

$$\mathrm{Li_{(s)}} \rightarrow \mathrm{Li^+_{(aq)}} + \mathrm{e^-}$$

$$\mathrm{O_{2(g)}} + 2\mathrm{e^-} \rightarrow 2\mathrm{O^-}$$

$$\mathrm{O_2(g)} + \mathrm{e^-} \rightarrow \mathrm{O_2^-}$$

$$\mathrm{O_2^-} + \mathrm{e^-} \rightarrow 2\mathrm{O^-}$$

With the overall reaction:

$$2\mathrm{Li_{(s)}} + \mathrm{O_{2(g)}} \rightarrow \mathrm{Li_2O_{2(s)}}$$

It must be stressed that the steps and final overall reaction is still under debate.

4.4.2.6 *Lithium sulfur batteries*

The lithium sulfur (LiS) battery is on the verge of full commercialization. It offers a high capacity and is cheap, but safety might still be an issue. The materials that are used in a Li-S cell are sulfur at the positive electrode and similar materials as mentioned in the section about the Li-air battery for the negative electrode. The half reactions at the negative electrode therefore are similar as mentioned earlier, but the half reactions occurring at the positive electrode are complex via various polysulfides:

$$\mathrm{S_{8(g)}} + 16\mathrm{e^-} \rightarrow 8\mathrm{S^{2-}}$$

$$\mathrm{S_8} \rightarrow \mathrm{Li_2S_8} \rightarrow \mathrm{Li_2S_6} \rightarrow \mathrm{Li_2S_4} \rightarrow \mathrm{Li_2S_3} \rightarrow \mathrm{Li_2S_2} \rightarrow \mathrm{Li_2S}$$

These polysulfides tend to dissolve in the liquid electrolyte and thus short the cell. Besides, the sulfur compounds have an extremely low electronic conductivity. For this reason various carbon cages are being constructed to contain the sulfur compounds and to achieve an adequate electronic conductivity for this positive electrode.

4.4.2.7 *(Redox) flow batteries*

Redox flow batteries (RFB), initially developed by NASA in the 70's for its space programm, use two liquid electrolytes containing dissolved metal ions as active species, which are thus pumped across each other along an ion exchange membrane. These electrolytes at the negative and positive electrodes are referred to as an anolyte and a catholyte, respectively, and are an important part of the cell, with respect to materials. In Fig. 4.2 an example of a vanadium redox flow battery is shown, where all chemicals remain in the solutions of either the anolyte or catholyte. Besides the vanadium redox flow batteries, a number of other flow systems exist, of which only a few are commercially feasible at the moment, see Table 4.4. These include hybrid flow batteries, where typically solid species are formed or are present as a precipitate (e.g. zinc bromine, hydrogen bromine, lithium polysulfide, iron-iron), or where solid active components are dispersed in the electrolyte solvent as a kind of viscous ink (e.g. lead-acid, Li-ion systems). This however requires a smart design of the flow battery. A new trend in flow batteries is the use of an all-organic system. However, these are still under development and in a premature phase.

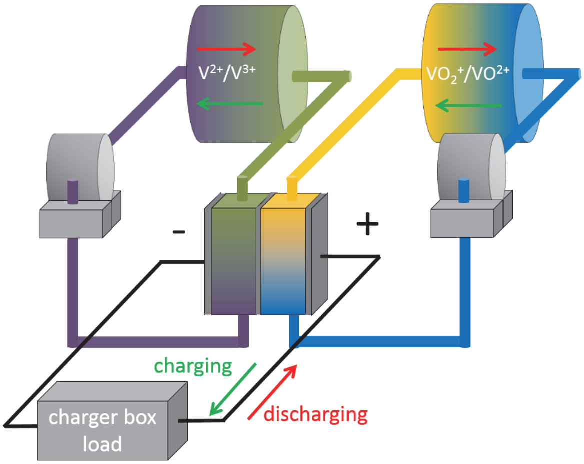

Fig. 4.2. Vanadium redox flow battery scheme.

Table 4.4: Material for Various Flow Batteries.[3]

Flow battery	Materials used	Reactions
Redox flow battery		
Vanadium	Vanadium, nafion	$V^{2+} \rightarrow V^{3+} + e^-$ $VO_2^+ + e^- + H^+ \rightarrow VO^+ + OH^-$
Polysulfide bromide	Sulfur, sodium, bromine	$2Na_2S_2 \rightarrow Na_2S_4 + 2Na^+ + 2e^-$ $NaBr_3 + 2Na^+ + 2e^- \rightarrow 3NaBr$
Aqueous redox flow	Alkalimetal, water, nafion, iron, iodine[1,2]	$Fe^{2+} \rightarrow Fe^{3+} + e^-$ $NaI_3 + 2Na^+ + 2e^- \rightarrow 3NaI$
Non-aqueous redox flow	Organic redox coulple, organic solvent[3]	Too many to present
Hybrid flow battery		
Lithium polysulfide	Lithium, sulfur	See lithium sulfur batteries
Zinc bromine	Zinc, sodium, bromine	$Zn \rightarrow Zn^{2+} + 2e^-$ $NaBr_3 + 2Na^+ + 2e^- \rightarrow 3NaBr$
Zinc cerium	Zinc, cerium	$Zn \rightarrow Zn^{2+} + 2e^-$ $Ce^{4+} + e^- \rightarrow Ce^{3+}$
Iron iron	Iron, graphite	$Fe^{2+} \rightarrow Fe^{3+} + e^-$ $Fe^{2+} + 2e^- \rightarrow Fe$
Dispersed systems		
Lead-acid	See Lead-acid battery	See Lead-acid battery
Li-ion	See Li-ion battery	See Li-ion battery

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[1] Only one possible example is shown.

[2] N,N,N,2,2,6,6-heptamethylpiperidinyloxy-4-ammonium chloride (TEMPTMA) is also used.

[3] This is a new class of materials, but are mainly based or organic materials.

4.5 Battery and Battery Materials Market

The global materials demand for electricity storage systems will be increasing in the next few decades. This obviously has to do with the increasing costumer interest in cellular consumer goods such as smart phones, laptops, etc, as well as (hybrid) electric vehicles. Besides, there is a trend in the market towards renewable energy systems, such as solar, wind, and hydro, that requires electricity storage devices as they are intermittent in nature. Hence, these renewable energy sources either separately or in combination require a storage system to supply continuous, reliable power, e.g. in remote areas.[1] Besides, electricity storage may well be used in parallel systems next to the power plant. The above systems thus require mainly rechargeable (secondary) batteries. Hence, the focus will be on these systems, but the primary battery market will not disappear in the next decade, and thus will be addressed as well with respect to materials demand. In this section the following key questions will be addressed:

- Which are the key end-user applications that use batteries extensively?
- Who are key players deciding on the implementation?
- How will the market for end-users grow in the next decade?
- How does the demand pattern for different battery chemistries vary?
- What are the main materials supporting the coming demand?
- What further chemistries are beyond the horizon?

Depending on their application, batteries are divided into *energy batteries* and *power batteries*, reflecting a high *specific energy* for long run-times and high *specific power* for high-current loads, respectively. Figure 4.3 shows the relationship between specific energy in and specific power for various existing energy storage systems.

4.5.1 *Key end-users and systems*

The battery market for end-users can be split into the following sectors[4]:

- Consumer goods: mobile phones, laptops/notebooks
- Transportation: automotive, locomotive, marine, and aerospace
- Utility: power plants - fossil fuels and renewables
- Industry: power tools, energy savings (*note that compared to Table 4.1, the medical part falls under Industry here, and the industry part has been split up into industry and utilities.*)

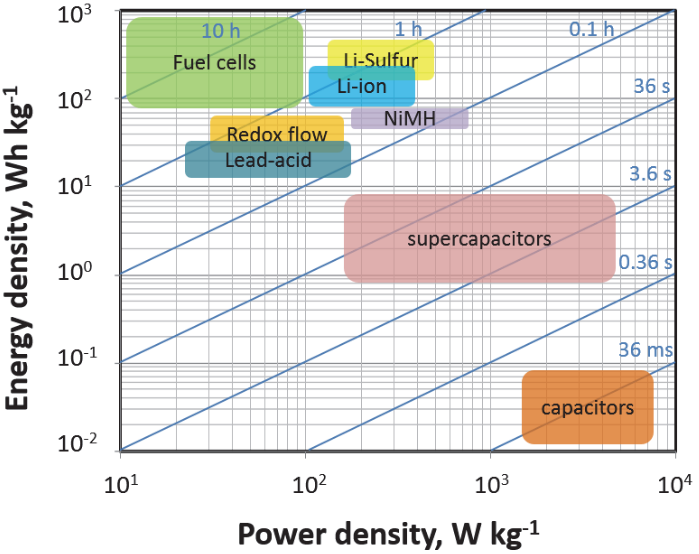

Fig. 4.3. Specific energy *vs* specific power of rechargeable batteries. Note that the specific energy is the capacity a battery can store and is measured in watt-hours per kilogram (Wh/kg), whereas specific power is the ability to deliver the energy per time, i.e. the power, which as such is measured in watts per kilogram (W/kg).

Table 4.5: Comparison of Various Distributed Energy Storage Technologies for Utility Storage Applications (Selected Characteristics).[5,6]

	Lead-acid	Li-ion	Flow[1]
Cost	☺	😐	😐
Energy density	☹	☺	☹
Capacity	☹	😐	☺
Power density	😐	☺	☹
Installation	☹	😐	😐
Cycle life	☹	☹	☺
Depth of Discharge (DoD)	☹	☺	☺
Environment (recycleability)	☹	☹	😐

[1] Redox flow and hybrids
☹: poor 😐: average ☺: good

Since Li-ion batteries have higher energy densities compared to lead-acid or NiMH batteries, this makes the Li-ion batteries ideal for use in consumer goods, electric vehicles, energy storage for electricity utilities, and industrial applications, but at a certain cost as shown in Table 4.5. Lead acid batteries are subject to improper battery disposal in landfills, which may result in the contamination of groundwater by lead and sulfuric acid. Hence, the large scale introduction of lead acid batteries for utility services is less interesting.[1] The energy density makes these cells unattractive for consumer goods and electric vehicles. Nevertheless, due to the cost, lead-acid batteries may find their way to domestic energy storage,[5] as well as to advanced military electronic systems. Flow batteries, being huge in size, are becoming the preferred chemistry for utility-based storage, e.g. in grid energy storage or in power storage for solar and wind power. This includes load levelling, peak shaving and uninterrupted power supply (UPS) applications. The use of nickel-based rechargeable systems is expected to decline in the next few decades, and they are thus not discussed in detail.

New markets that may further boost battery growth are electric bicycles and scooters, as well as domestic/residential electricity storage.

Primary batteries will be mainly used for consumer goods, such as watches, electronic keys, remote controls, toys, flashlights, beacons, and military devices in combat, etc.[4]

4.5.2 *Key decision makers*

The four sectors addressed in the previous section (consumer goods, transportation, utility, and industry), particularly the transportation and utility sectors, are strongly dependent on political decisions. Legislation and regulation promoting the electrification of vehicles is expected to create a significant boost to (hybrid) electric vehicles sales, strongly catalyzed by the rapid development of advanced high energy density Li-ion batteries. Since renewable technology is becoming more and more mature, with the gap between conventional and renewable fuels closing, thus renewables are becoming competitive with fossil fuel power plants. Various governments encourage the use of renewable power via specific subsidies or regulations.[5,6]

The legislation, regulation promoting, and subsidies are important activities for the growth of the battery market as we will see in the following sections.

4.5.3 *Market growth by sector*

Market growth by sector — consumer goods, transportation, utilities, and industry — are discussed in several reports, for example: Fredonia,[7] Frost&Sullivan,[4] MIMB,[8] Markets and Markets,[9–11] Grand View Research.[12] It should be stressed that the focus here is not on cost, but on sales figures and market volume, so as to understand the future materials demand, rather than cost. Obviously, cost is a major driver for specific materials and is therefore the underlying reason for the selection of specific materials, and deciding the sales and volumes. Hence, market growth in cost goes hand in hand with market share in volume, and thus with materials demand. The percentage distribution of the battery market share by

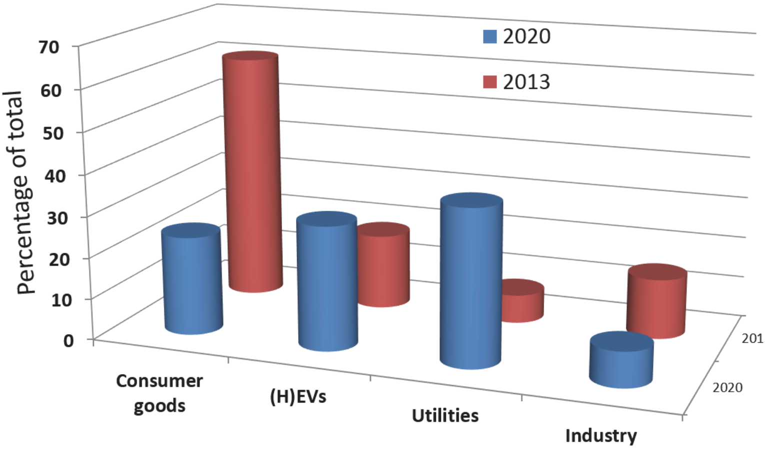

Fig. 4.4. Distribution of the battery market sales by sector.[4]

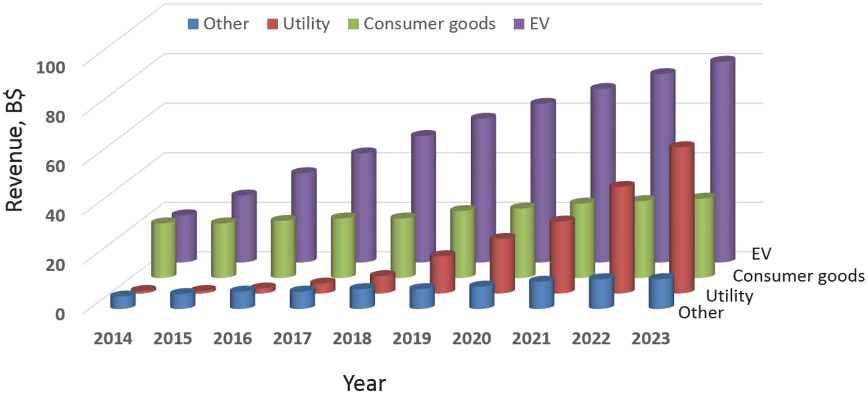

Fig. 4.5. Growth of the battery market sales by sector.[13] Note that here cost is used, but these can be just as easily seen as volume or power installed.

sector is shown in Fig. 4.4, whereas in Fig. 4.5 the annual growth is shown by sector.[9,10]

4.5.4 *Market growth by battery chemistry*

The various applications as identified by the four sectors require different battery specifications. Here we will distinguish between flow batteries and other rechargeable batteries, such as Li-ion, lead-acid, and NiMH batteries. Despite the fact that the global primary battery market is forecast to grow at a Compound Annual Growth Rate (CARG) of 4.06% during the period 2016–2020,[14] the major battery volumes will come from the secondary battery market. This growth of the battery market will thus have an immediate consequence on the materials demand as will be shown in section 4.5.5.

4.5.4.1 *Lead-acid, NiMH, and Li-ion batteries*

The year 2009 has been taken as a base for the distribution of the battery market (excluding flow batteries)[4] — see Fig. 4.6. This year has been chosen because it is foreseen that NiCad batteries and to a lesser extent NiMH batteries will decline completely in the next decade, otherwise the market for these battery types would not show up at all.

The growth of the primary battery market is 4.06% CAGR,[14] whereas the growth of rechargeable batteries is about 10% CARG. The actual data per battery chemistry are shown in Table 4.6.

Lead-acid batteries remain of interest because they are robust and find their place in starter batteries for Start, Lighting and Ignition (SLI) and Uninterrupted Power Supply (UPS), and deep-cycle batteries for wheeled mobility (golf cars, wheelchairs, scissor lifts, etc.).

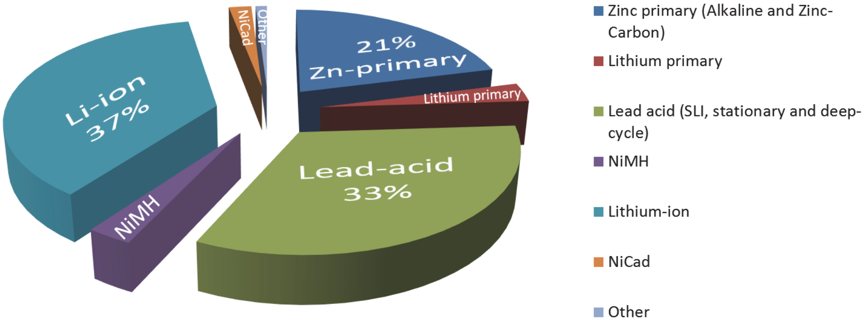

Fig. 4.6. Battery market distribution in 2009 after Frost&Sullivan.[1]

Table 4.6: Annual Market Growth of Various Battery Chemistries, Measured in CAGR.

	CAGR	Ref.
Primary batteries	4.06	14
NiCad	−4%	15
NiMH	−4%	15
Lead-acid	+4%	15
Li-ion	16% (3% for power tools)	15

Despite the forecasted decline in the NiCad and NiMH in total energy (Wh), on a pack level there still will be batteries available, but in the total volume of materials, this will be of minor importance. On the other hand, new systems are appearing on the horizon, such as lithium-sulfur, sodium-aqueous, magnesium-ion, and organic batteries, etc. A revival of the iron battery is also expected. These systems are still under development and will be discussed in section 4.5.6 in more detail.

4.5.4.2 *Flow batteries*

Flow batteries are often regarded as a semi-battery, a system that is a mixture of a fuel cell and a battery. However, since the waste materials after use are still stored in a container, and not disposed of to the environment, they will be considered as a battery system here.

From around 2006, Redox flow batteries (RFB) were used mainly for large scale electricity storage, e.g. for stationary applications, such as renewable energy utilization, and at the residential, industrial, and (micro-) grid level. The volume is expected to grow to a $4bn market by 2027.[16] Although, RFBs do not deliver the same power as a Li-ion battery, they compete in terms of cycle life, safety, 25-year service life without maintenance, and thus reliability for the above mentioned application.[5] In Fig. 4.7, the expected growth of the RFB is shown. Obviously, the vanadium RFB are the ones that are most mature and have significant potential in the near future. Nevertheless, in terms of cost and environmental issues, novel systems based on less polluting materials are required. Many demonstration projects have been initiated, and several showed that RFBs are mature enough for further exploitation in China, Japan, Canada and the U.S. One example is the 15MW (60MWh) Minami Hayakita Substation in Japan for integrating photovoltaics into the grid.[17] It has further been forecasted that RFBs will compete with Li-ion and sodium-sulfur systems, which are now the two leading chemistries in this market sector.[16] Other chemistries, such

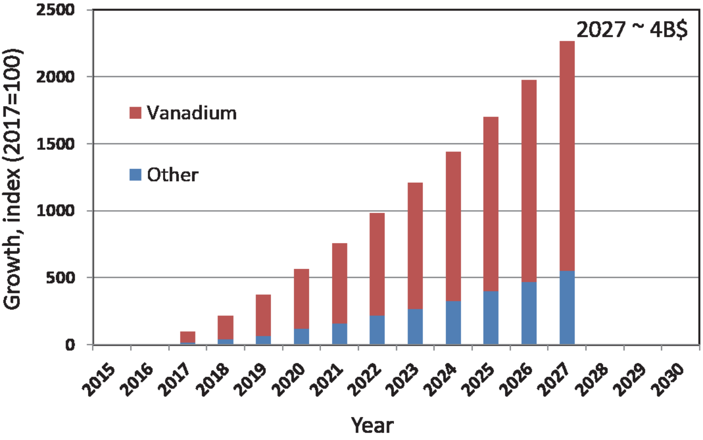

Fig. 4.7. Market forecast for redox flow batteries.[16] Other chemistries include zinc/bromine and hydrogen/bromine.

as zinc/bromine and hydrogen/bromine, may also have the potential to gain a significant market share as shown in Fig. 4.7. Besides these mature and commercial RFBs, a number of alternatives exist as nicely described by Su *et al.*,[18] and briefly discussed in section 4.4.2.7. Several studies have appeared on the growth of flow batteries for the stationary battery storage market.[5,16,17,19,20] It was reported that approximately 72% of the stationary battery market share originated from the redox battery segment.[20] This figure will further increase, giving rise to a global flow battery market at a CAGR of 3.38% during the period 2017–2021.[20] This however, is in contrast to another study where it is believed that Li-ion batteries are going to dominate the market, i.e. 80% of the global installations by 2025.[21] Nevertheless, an increase in the use of flow batteries is expected for stationary energy storage from 145 MW in 2016 to 5,770 MW in 2025, i.e. an increase by a factor of 40. In contrast, the use of Li-ion batteries will grow only from 10,600 MW in 2016, to 19,280 MW in 2025, hence by a factor of 20.[13]

4.5.5 *Future material demand pattern by battery*

The variety of existing systems requires different battery materials, each offering their own characteristics. The demand is for low cost systems with high performance. Hence, materials and battery producers, as well as research institutions, are working to create batteries with high power density, long life cycle, low cost, and high performance that are environmentally friendly to satisfy the needs of the battery and end-user industry.[9–11] Hence, price and availability have a strong influence on battery materials use, and thus demand. The global battery materials market grew at a CAGR of 13% from 2013 to 2018 (from U$5.1 billion to U$11.3 billion),[9–11] and according to Transparency Market Research,[1] the market for battery materials will further increase at a 13.6% CAGR during the period between 2017 and 2025 (US$13.70 billion). An even more optimistic prediction was made by Fredonia,[7] where a forecast was made of 8.3% increase per year to $46.8 billion in 2019.[7]

The battery market will be dominated by secondary systems. Hence, the materials market will be dominated likewise. The relatively small primary systems market will mainly use manganese oxides, zinc, sodium or potassium hydroxide, and graphites (carbons).

The remaining usage of lead-acid batteries in the automotive sector is responsible for the growth of the materials for them. These will mainly be lead, lead oxide, graphite, arsine and other impurities, and polymers. Other rechargeable batteries, based on nickel chemistry currently on the market, will almost completely vanish in the next decade, and thus will the need for these materials, including the rare earth elements.[7] This means that for the coming decade, the Li-ion battery and its materials will dominate the materials demand. However, with increasing stationary electricity storage, the RFBs are becoming important. Since, these systems will cover enormous storage capacities, they therefore require a significant amount of materials, particularly taking the increase in renewable energy into account. The materials that are of interest are vanadium for the vanadium RFB, and zinc and bromine for the zinc-bromine RFB. Both systems require membranes which are typically of polymeric origin, and stainless steel tanks.

4.5.5.1 *Li-ion rechargeable batteries*

Li-ion batteries are more efficient as compared to others today, having a high performance with outstanding properties like high energy and power density, and a long discharge cycle. The Li-ion battery is on the market as a pouch cell — typically in mobile phones — and as a cylindrical cell — the so-called 18650 cells. These cylindrical cells are becoming more and more standard and are being used, for example, in the Tesla cars. Figure 4.8 shows the structure of such a cylindrical cell. It is constructed by coating a metal current collector with a wound laminate of positive and negative electrode materials. The positive and negative electrode materials are separated by

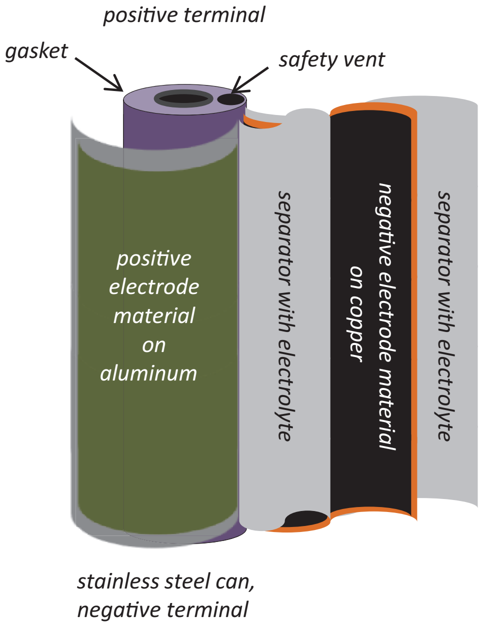

Fig. 4.8. Cylindrical (18650) Li-ion battery showing the various coatings and foils.

a porous plastic foil soaked with the liquid electrolyte to prevent internal shorts. The electrolyte further contains a specific lithium salt.

The materials to be used in Li-ion batteries are:

- Negative electrode: lithium, carbon, graphite, silicon, lithium titanium oxide, etc.
- Negative current collector: copper
- Positive electrode: lithium cobalt oxide (LCO), lithium nickel manganese cobalt oxide (NMC), lithium nickel cobalt aluminium oxide (NCA), lithium ferrophosphate (LFP), etc.
- Positive current collector: aluminium
- Electrolyte: lithium hexafluorophosphate, ethylene carbonate, propylene carbonate, etc.
- Separator: polyethylene, polypropylene,
- Binder: PVdF, carboxy methyl cellulose (CMC)
- Casing and binder materials: stainless steel and polymers/plastics.

In Figs. 4.9 and 4.10, the forecasted amount of positive and negative electrode material are presented, respectively.[22–24] These forecasts show

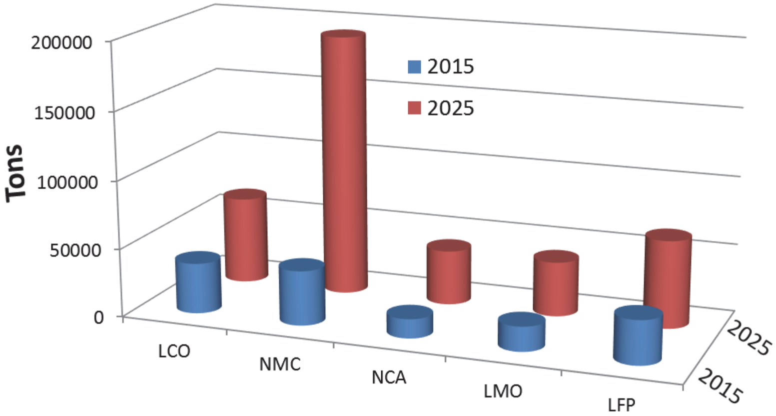

Fig. 4.9. Forecasted market demand for selected positive electrode materials.[22–24]

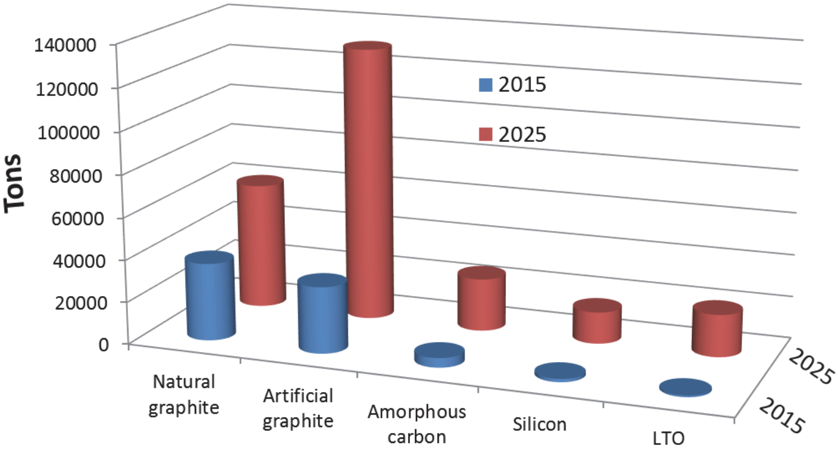

Fig. 4.10. Forecasted market demand for selected negative electrode materials.[22–24]

that NMC and LFP and artificial graphite will be the major components for this generation of Li-ion batteries. With respect to the electrolyte (Fig. 4.11), separator (Fig. 4.12) and binder material, the demand goes linearly with the demand for the total electrode materials.[22–24] With respect to the NMC and LFP batteries, the amount of components percentage-wise per cell are presented in Fig. 4.13.[22–24] The projected electrolyte salt, binder material, and separator material are lithium hexafluorophosphate, PVdF, and polyethylene/polypropylene, respectively. This means

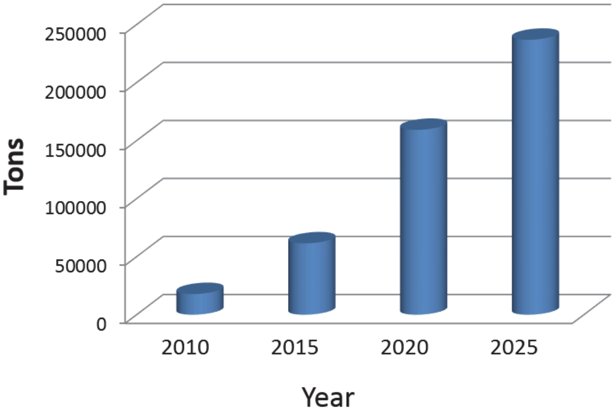

Fig. 4.11. Forecasted market demand for electrolytes.[22–24]

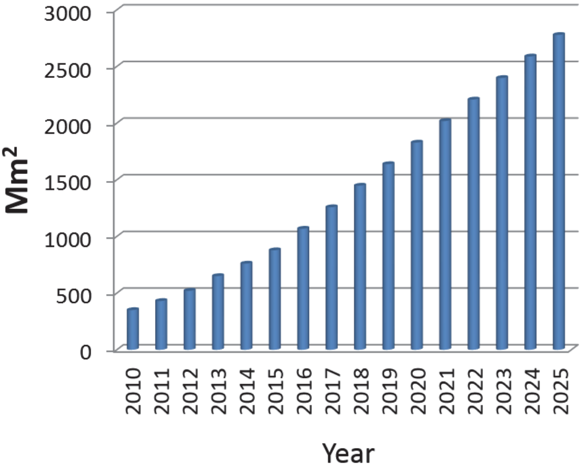

Fig. 4.12. Forecasted market demand for separator materials in surface area (Mm^2).[22–24]

that beside metal-containing and carbonaceous materials, a significant percentage of fluorine- and phosphorus-containing components are present in the battery.

4.6 Future Systems

The future systems that are of interest in terms of high power density, long life cycle, low cost, and high performance, and that are environmentally

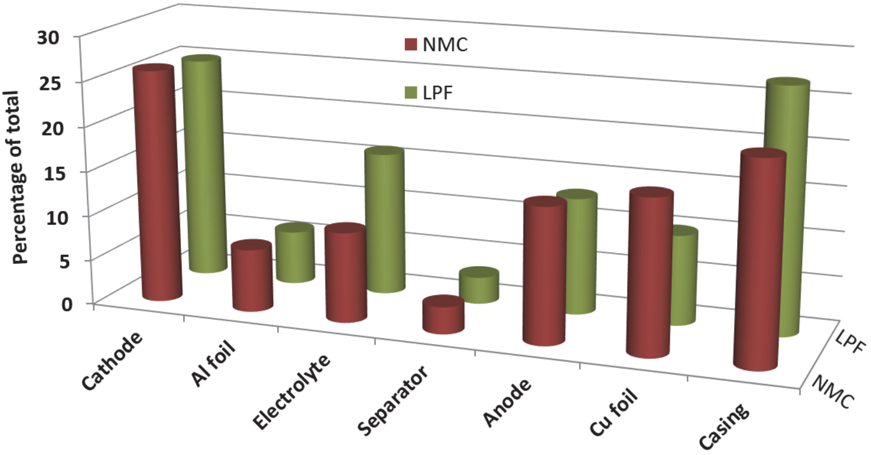

Fig. 4.13. Distribution of the various battery components in percentage for a cell made with LPF and NMC.[25]

Table 4.7: Future Rechargeable Batteries.

	Voltage V	Energy density Wh/kg	Ref.	Remark
Lithium-sulfur	2.1	500	26	Operates similarly to Li-ion
Lithium-air	1.7–3.2	13000	26	Theoretical capacity
Lithium-metal	3.6	300	26	
Solid state lithium	3.6	300	26	
Lithium aqueous	1.2–2.4	75	27	Often the positive electrode material is of the same origin as that in Li-ion batteries
Sodium aqueous	1.2–2.4	50–60	27	Often the positive electrode material is of the same origin as that in Li-ion batteries
Magnesium-ion	1.8–3.0		28, 29	Often the positive electrode material is of the same origin as that in Li-ion batteries, including sulfides

friendly to comply with the battery and end-user industry are listed in Table 4.7.

The materials that are being used in the above potentially rechargeable batteries comprise lithium, sodium, sulfur, magnesium, manganese, and eventually other transition metals such as nickel, iron and titanium.

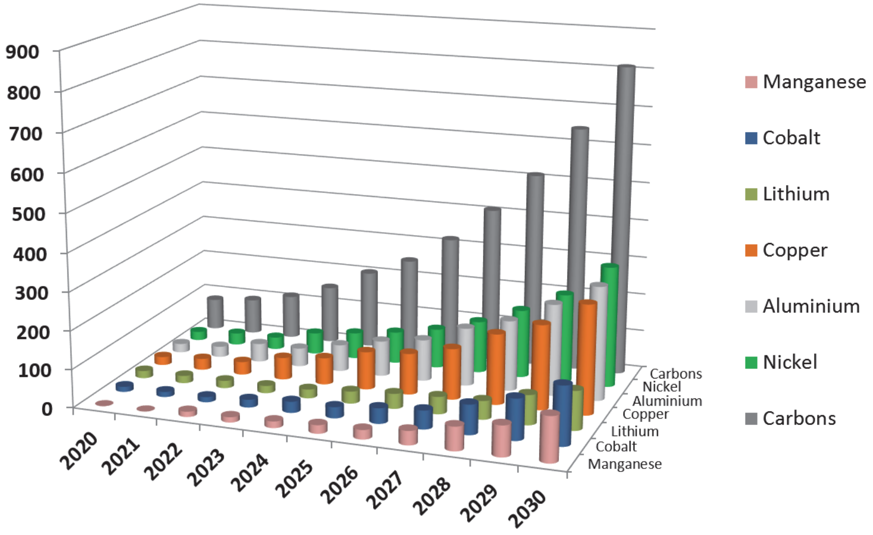

Fig. 4.14. Forecasted market demand for metals for EVs.[30]

4.7 Discussions and Conclusions in Brief

The goal for novel types of rechargeable batteries is to find cost-effective, environmentally friendly materials delivering high performance in terms of energy density and power during a long cycle and service life. Metals will still remain the predominant type of battery material, irrespective of the choice of battery system, see Fig. 4.14 as an example for components for electric vehicles, which will be more than 50% of the total Li-ion battery demand. In summary, the materials that are expected to be needed in bulk in future batteries are:

- Negative electrode: lithium, cobalt, lead, carbon, graphite, magnesium, sodium, vanadium, antimony, etc.
- Positive electrode: (lithium/sodium) manganese oxide, lead dioxide, lithium cobalt/nickel/manganese/aluminum oxide, lithium ferrophosphate, sulfur, vanadium, etc.
- Electrolyte: ammonium chloride, sodium/potassium hydroxide, sulfuric acid, lithium hexafluorophosphate, organic solvents
- Separator: polyethylene, polypropylene,
- Casing and binder materials: stainless steel and polymers/plastics.

In order to improve the performance of the batteries, certain additives are projected, such as rare earth materials and e.g. niobium. From the

Table 4.8: Evaluation of critical elements in selected future battery materials.

	Supply risk[1]	Geopolitics[2]	Competition with food industry[3]	Ethical mining[4]
Antimony	☹	☹	o	o
Cobalt	☹	☹	o	☹
Lithium	😐	☹	o	o
Magnesium	☹	😐	o	o
Niobium	☹	☹	o	o
Vanadium	☹	😐	o	o
Natural graphite	☹	o	o	o
Silicon	😐	😐	o	o
Phosphorus	☹	o	☹	o
Fluor	😐	😐	o	o

[1] The supply risk is measured according to the 3rd list of critical raw materials for the EU of 2017.[31]

[2] Geoplitics issues are evaluated from the same document as "Supply risks".

[3] See: .Phosphorus, Food and Our Future.[32]

[4] Ethical mining is a particular issue with respect to cobalt mining in the Democratic republic of Congo (DRC) according to many reports, particularly those from UNICEF and Amnesty International — references are not further specified.

☹: very critical; 😐: medium critical; o: not analysed

abovementioned bulk materials and trace elements that are important for future rechargeable batteries, a number are critical in terms of supply risk — including scarcity and geopolitics, competition with the food industry, ethical mining, and carbon footprint. In Table 4.8 these materials, or actually their component elements, are thus summarised with respect to these critical aspects. In this evaluation, geopolitics is taken as an individual aspect, whereas the materials scarcity is included in the supply risk. The evaluation regarding carbon footprint has not been presented here, as it requires much more information and/or explanation to justify the qualification.

With respect to the critical elements, particularly for the ones that concern scarcity and supply risk, recycling is of utmost relevance, and needs to be regarded as an industrial sector of paramount importance.

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