Battery technology for PV storage and system services

Battery technologies | The development of battery storage is seen as vital in the grid integration of increasing amounts of renewable power, but the various technologies present different advantages and limitations. Stephan Lux of Fraunhofer ISE weighs up the pros and cons of the main battery technologies in a range of applications

The increasing share of renewable energy sources, such as solar and wind, requires storage systems in order to preserve the quality and the power of the grid. On the other hand, for the private user, especially in Germany, the increase in self-consumption is a very important factor. There are certain requirements from an application point of view, as well as some restrictions related to the available technology, that have to be considered. This paper will focus on the question of how to determine the best battery technology for a given application.

Applications and requirements

Home storage systems

The changes to the German Renewable Energy Act (EEG) are resulting in a growing market for home storage systems. End user prices for electricity of up to €0.28/kWh are common, with feed-in tariffs of around €0.12/kWh. With the price for electricity from PV around €0.12/kWh, increasing self-consumption is the more interesting option for private households at the moment. The typical size of a home storage system is 3–6kWh usable energy, with a nominal power of 2–4.6kW (Fig. 1). Depending on the installed PV power and the corresponding load profile, a typical home storage undergoes between 200 and 350 full cycles per year.

Small-business and industrial appliances

For small-business users and industry, the focus lies on the integration of different energy sources, for example solar power, diesel, and combined heat and power technology. These users will benefit not only from cutting down on their maximum power consumption from the grid to reduce the cost of electricity, but also from increasing their self-consumption and keeping production operational during power cut-offs by using the battery system as emergency power.

Source: Fraunhofer ISE.

Figure 1. A 5kWh home storage system offering grid services.

Grid stability

For power distributors and the operators of heavy-usage systems, such as quay cranes and rail lines, grid stabilisation and the recovery of energy are important. For these types of application the storage has to be operated for several seconds at a time, with a high power demand in the megawatt range; in this case the storage might be cycled several thousand times a day. Supercapacitors are favoured for these applications – for example, the Yangshan Deep Water Port, with an energy storage capacity of 17.2kWh, is able to deliver 3MW reserve power for 20 seconds.

Primary reserve

The primary reserve market is of particular interest – here the requirement is a minimum power of 1MW, which is usually only feasible with very large storage units. In Germany some operators, such as Deutsche Energieversorgung (DEV), are coupling a large number (3,500) of home storage systems to act as a virtual battery. For this kind of service almost any type of battery technology is suitable.

Battery technologies

Lead–acid batteries

As compared to other cell technologies, lead–acid batteries are very low cost, with prices in the range €50/kWh to €90/kWh, and hold a market share of approximately 90%. Because of their simple construction and worldwide availability, a variety of designs are currently used in many applications, such as starter batteries in vehicles, non-interruptible power supplies in telecommunication institutions, transaction batteries in fork-lift trucks, and autonomous island systems with regenerative power supplies. Depending on the application, lead–acid batteries are differently optimised with respect to performance density, cycle lifetime and calendar lifetime when being discharged.

Designs

In the case of lead–acid accumulators there are flooded and maintenance-free designs. Flooded batteries contain plugs, which can be opened to control and refill the electrolytes. Maintenance-free batteries are an enhancement, with immobile electrolytes in the form of a glass mat or gel; they also have valves instead of plugs.

Properties

Typical values of the characteristics for lead–acid batteries are shown in Table 1. The specific energy of this type of battery drops to 40Wh/kg in practice. The performance is very dependent on the battery construction and varies from typically 100–200W/kg to 1,000W/kg in high-current batteries. The self-discharge rate at 20°C is approximately 3% per month, but a 10°C temperature increase leads to a doubling of the rate. The cycle lifetime ranges from 200 to 2,000 full cycles, depending on temperature and usage.

Ageing mechanisms

The main ageing processes are acid stratification, grid corrosion and sulphation. The calendar and cycle lifetimes decrease with high depth of discharge (DOD) and high operating temperatures. To enhance the lifetime, the amount of discharge is usually limited to 50% in the cycle application.

Lithium-ion batteries

The term *lithium-ion battery* applies to a number of different lithium-ion cells with very different features. The various lithium-ion technologies are categorised according to the electrodes' materials, which not only yield different characteristics but also affect the price of the cells. On the other hand, the battery quality varies between different suppliers and different production lines (e.g. consumer cells and car batteries for OEMs); this means product quality must be checked thoroughly.

Materials for lithium-ion batteries

Although a wide variety of materials can be used today as the active material for the electrodes of a lithium-ion cell, the fundamental principle – intercalation of lithium atoms into a grid – remains the same. As Fig. 2 shows, these different active materials have different potentials at which they store lithium. Generally speaking, the image illustrates that, for the negative electrode, materials with potentials slightly above the potential of metallic lithium are suitable, whereas for the positive electrode, materials preferably with high potentials are suitable.

The combination of graphite for the negative and LiCoO$_2$ or MNC (manganese nickel cobalt) for the positive electrode is nowadays a common standard solution and is used in mobile phones, electric cars and stationary storage. For stationary storage, LiFePO$_4$ is common for the positive electrode. Titanate might be used to replace graphite on the negative electrode; this leads to a very stable cell with an excellent temperature behaviour and a low energy density.

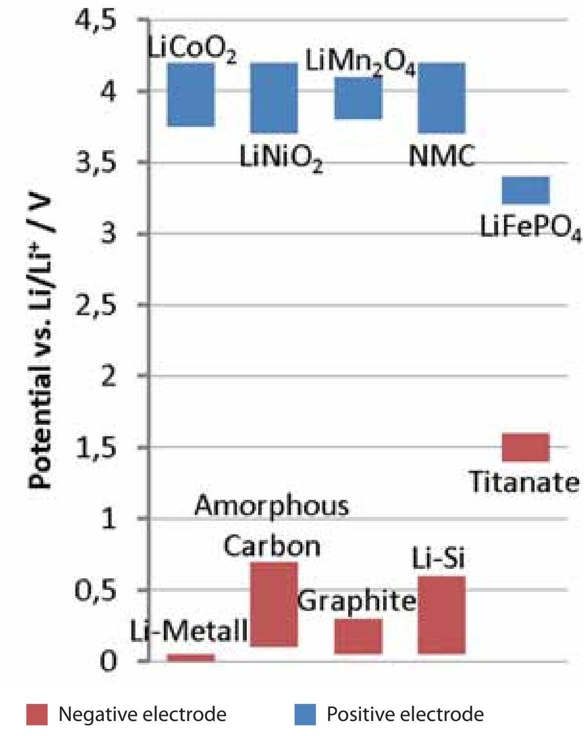
While the electrolytes are usually stable on the cathode side, side reactions between the negative graphite electrode and the electrolyte always occur, forming the solid electrolyte interface (SEI). The formation of the SEI layer takes place in the first charging process and can be influenced by the usage of additives. After its formation, the SEI layer remains quite stable and prevents a fast reaction between the electrolyte and the electrode.

Properties

The development of material for lithium-ion cells is still a work in progress, but the characteristics of some important material combinations for lithium-ion cells are summarised in Table 2. The main advantages of the lithium-ion battery compared with other battery technologies are the high nominal voltage, the high energy density, a long storage ability with low self-discharge, and a wider operating temperature range.

Energy density [Wh/kg]	40
Power density [W/kg]	350
Cycle lifetime	200–2,000
Calendar lifetime [years]	7
Costs [€/kWh]	150
Efficiency [%]	80
Self-discharge [%/month]	3
Operating temperature [°C]	–15 to +50

◂**Table 1. Properties of a high-quality lead–acid battery.**



▴**Figure 2. Potentials of several active materials that can be used for lithium-ion cells. Metallic lithium is chosen as the reference potential.**

Ageing mechanisms

Lithium-ion cells gradually lose capacity, but this can be reversed to some extent by recharging the cell. There is some loss of capacity that is irreversible, however, which limits the maximum calendar lifetime. Ageing is accelerated by frequent cycling of the cell, resulting in a gradual decrease in capacity, energy and power rating; this is mainly a result of the growth of the SEI, which increases the internal resistance of the cell and leads to loss of active material.

> "Lead–acid batteries are very low cost and hold a market share of approximately 90%"

Vanadium redox flow batteries

Vanadium redox flow batteries (VRFB) differ fundamentally from conventional batteries in their design and operation. In this system the energy storage is a solution (electrolyte), which is stored in external tanks (Fig. 3). To charge the battery, the energy storing solution is pumped through the stack; this performs the electrochemical transformation of electrical energy into chemical energy, or vice versa in the case of discharge. Because the tank size and the size of the stack are independent quantities, the

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Cathode/anode	Li (NCM) / graphite	LiMn$_2$O$_4$ / graphite	LiFePO$_4$ / graphite	LiCoO$_2$ / LiTi$_5$O$_{12}$
Energy density [Wh/kg]	160–200	130	110	65
Power density [W/kg]	700	1,500	3,000	3,000
Cycle lifetime [years]	2,500–5,000	3,000	5,000	8,000
Calendar lifetime	8	8	12	15
Costs [€/kWh]	140–400	400	120–400	600
Efficiency [%]	93	94	94	94
Self-discharge [%/month]	3	2	3	2
Operating temperature [°C]	0 to +50	0 to +50	0 to +50	–20 to +70

▲**Table 2. Comparison of the properties of lithium-ion cells with different material combinations.**

Energy density [Wh/kg]	45
Power density [W/kg]	120
Cycle lifetime	12,000
Calendar lifetime [years]	15
Costs [€/kWh]	350
Efficiency [%]	80
Self-discharge [%/month]	5
Operating temperature [°C]	–20 to +80

◀**Table 3. Properties of a vanadium redox flow battery.**

ratio of power to capacity can be chosen independently.

Properties

Table 3 summarises the features of a vanadium redox flow battery. A big advantage of the VRFB is the system’s long lifetime of approximately 15 years. The internal consumption of the electrolyte pump leads to an electrical efficiency of the system of approximately 80%. The possibility of physically separating the tanks from the transformer can be used to avoid internal losses during longer rest phases.

The cost of VRFB does not increase linearly with its capacity and strongly depends on the size of the storage capacity or the corresponding electrolyte tanks. Large systems are proportionally much cheaper than small ones, because the costs of the transformer unit are very high. The determination of the lifetime is more complicated, however, since certain system parts, such as the stack, have to be exchanged after 5–10 years, whereas the electrolyte can be used for up to 25 years.

VRFB differs from conventional systems in its construction, which gives rise to several advantages and disadvantages.

Advantages

- Electrical power rating and capacity are independently scalable.
- Isolation of the unit for electrochemical conversion can be used in order to prevent internal consumption.
- Complete discharge of the solution without capacity loss is possible.
- Electrolyte is easily replaced manually and does not change its aggregate state (fluid).
- Relative costs are low for larger systems with high capacities.
- High level of safety and long lifetime are assured.

Disadvantages

- Capacity is reduced as a result of insufficient mixture of electrolyte in the storage tank.
- Resistant materials must be used for the components because of sulphuric acid in the electrolyte acid.
- Energy density is low.

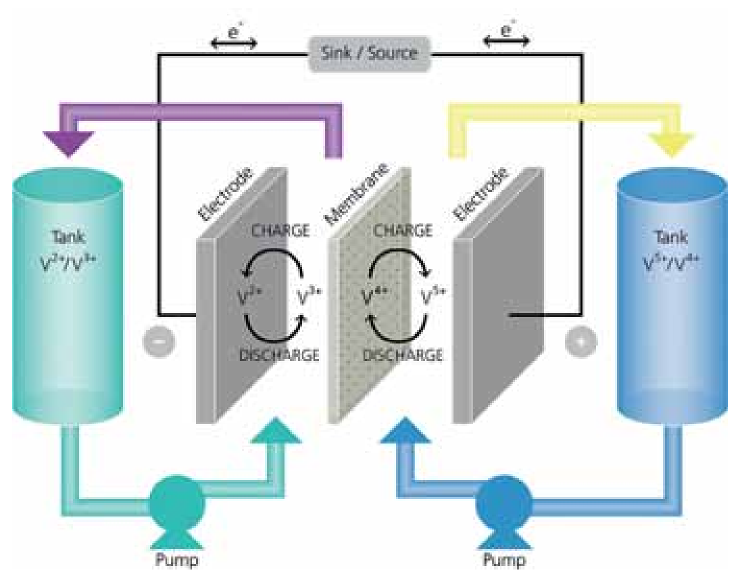
High-temperature batteries

High-temperature batteries (NaNiCl and NaS) are currently used in stationary and mobile systems, but the high operating temperatures of up to 350°C cause significant challenges in relation to thermal isolation and correct tempering. Specially developed covers keep the exchange of heat with the surrounding area as low as possible.

ZEBRA batteries (NaNiCl) differ from most other battery systems because the electrodes are in a fluid aggregation state during operation. The current collector is surrounded by fluid electrodes during operation and is found in the middle of the cell. The positive electrode is surrounded by a ceramic electrolyte, namely β”-aluminium oxide. In the outer area the similarly fluid negative electrode is surrounded by the cell wall, which also operates as the negative pole. In the completely discharged state, the ZEBRA battery consists of sodium chloride (common salt) and nickel. In the charged state, both nickel chloride and sodium emerge. The ceramic electrolyte β”-aluminium oxide is an isomorphic form of aluminium oxide (Al_2O_3) – a solid polycrystalline ceramic – through which only natrium ions (and no electrons) can diffuse.

Sodium sulphur batteries have an anode consisting of melted natrium, and a cathode of a solid graphite material soaked with fluid sulphur. The solid electrolyte β”-aluminium oxide is used as the electrolyte, which

▼**Figure 3. Functional principle of a vanadium redox flow battery.**



becomes Na-ion-conductive at a temperature above 300°C. During discharge, the positive-charged natrium ions split from the natrium polysulphide and diffuse through the electrolyte to the negative electrode, where they receive an electron and form metallic natrium. During the charging phase, this process is reversed.

NaS batteries are as yet only used in stationary systems as temporary storage for grid support and are offered (from Japan only) with system performances ranging from 500kW to several megawatts by the producers NGK Insulators, GS Yuasa and Hitachi. Because of the high internal consumption necessary for maintaining the operational temperature, these batteries are only practical for charge and discharge cycles during the daytime and are not suitable for long-term storage.

Properties

Table 4 summarises the characteristics of a high-temperature batteries; high energy densities and long cycle and calendar lifetimes are demonstrated. The high operational temperature, however, leads to internal consumption, which is why the comparatively small self-discharge is negligible. Natrium strongly reacts exothermically with water, which results in an increased emphasis on ensuring safety. The internal resistance is virtually independent of the charge state, and only towards the end of charge does it increase dramatically. The required operational temperature is obtained by an electrical heater.

The disadvantages of high-temperature batteries are the low power density and the dependence on temperature. If a grid connection, to keep the battery at a constant temperature, is not possible, the energy to heat it must be taken from the battery itself.

Ageing mechanisms

The ageing of the electrodes and the electrolyte in a ZEBRA battery is minimal. Cells and batteries can be used for several thousand cycles, which equates to an operational lifetime of 12 years, but even after that, they are still capable of storing the nominal capacity. The disadvantage of this technology is the operational temperature: repeated cooling and reheating leads to mechanical stress of the ceramic electrolyte, which in turn leads to fracturing of the ceramic layer.

	NaNiCl	NaS
Energy density [Wh/kg]	110	100
Power density [W/kg]	120	100
Cycle lifetime	2,500	4,500
Calendar lifetime [years]	15	15
Costs [€/kWh]	450	300
Efficiency [%]	85	85
Self-discharge [%/day]	10	12
Operating temperature [°C]	270 to 350	310 to 350

▲Table 4. Properties of high-temperature batteries.

Double-layer capacitors

A double-layer capacitor, or more specifically a supercapacitor (also 'ultracapacitor'), is not a battery, but a special type of capacitor that stores energy by shifting charge at the interface of the electrolyte and the electrode. Just as in standard capacitors, the storage is based on the electrostatic principle and not on the electrochemical one. A double-layer capacitor has a performance density comparable to that of high-performance batteries and is therefore mainly suitable for use in applications requiring high performance and low amounts of energy. Basically, the construction of a double-layer capacitor is similar to that of an accumulator; in terms of their characteristics, the gap between capacitors and conventional batteries is closing. Supercapacitors yield a power density of more than 10,000W/kg, with an estimated lifetime of 1,000,000 duty cycles.

Construction and operation

When a voltage is applied, the ions from the electrolyte attach to the interface of the two carbon electrodes and charge them. The storable energy of this system depends on, among other things, the surface of the electrode and the decomposition voltage of the electrolyte.

Energy density [Wh/kg]	15
Power density [W/kg]	10,000
Cycle lifetime	100,000
Calendar lifetime [years]	20
Costs [€/kWh]	2,250
Efficiency [%]	96
Self-discharge [%/month]	60
Operating temperature [°C]	–25 to +80

◀Table 5. Properties of double-layer capacitors.

Properties

Table 5 summarises the characteristics of double-layer capacitors; these types of energy storage system show barely any conversion losses and thus have a very high degree of efficiency, a high power density, and an almost unlimited number of cycles. Since the level of voltage on the accumulator side, in contrast to electrochemical energy accumulators, is linearly dependent on the charge state, an elaborate power controller is necessary. The low energy density of double layer capacitors leads to relatively high specific costs per energy unit.

> "A double-layer capacitor stores energy by shifting charge at the interface of the electrolyte and the electrode"

Sodium-ion batteries

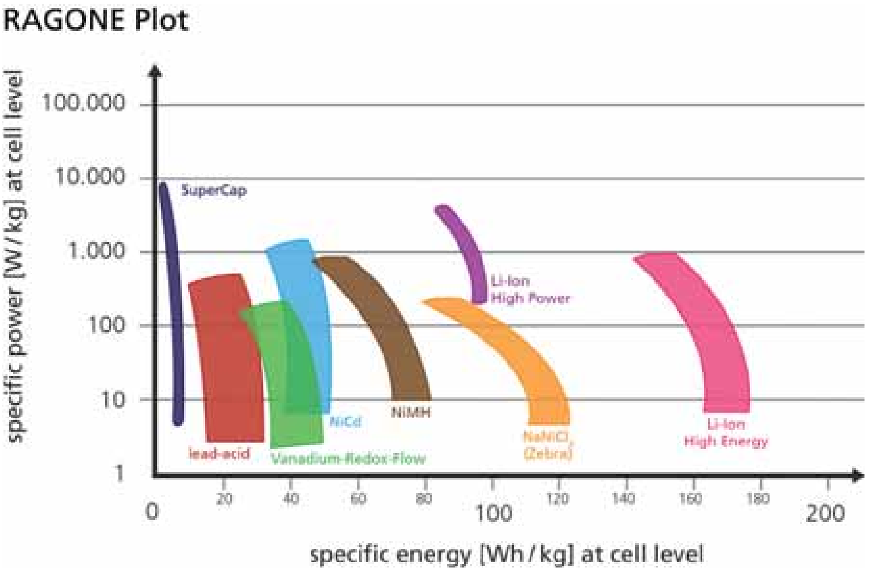
Commercially, sodium-ion technology is very new on the market and production has been driven by Aquion in the USA. The structure of these batteries consists of non-hazardous materials, such as manganese oxide on the cathode, activated carbon on the anode, and a seawater-like electrolyte. Sodium-ion batteries provide a long cycle lifetime, together with a low energy density of 40Wh/kg; in terms of price, they can compete with lithium-ion batteries on a mass-production basis. A drawback, however, might be their low efficiency at high current flows.

Future technologies

Intensive research work is currently under way with the aim of improving electrochemical storage as a result of developments in electric mobility and renewable energies. Alongside the improvements in lithium-ion batteries, there are also many new technologies emerging, such as Li–air, Li-S and Zn–air.

Lithium–air (Li–air)

The most attractive of the new technologies from the point of view of energy density is lithium–air, with a remarkable specific capacity of 3,842mAh/g. The lithium–air system also offers a theoretical potential of 3.72V (in the case of an acidic electrolyte), though in practice only 2.9V is achievable [1]. The approach is still far from being technically usable in any application; moreover, the power density is also much smaller than in commercial lithium-ion cells. If lithium–air batteries are successfully implemented in a working system with reasonable efficiencies and lifetimes, the low power density will be one of the main hurdles to overcome in a real application. Entry into the market for this system is expected in 2030.



▲**Figure 4. Specific energy and power densities at the cell level.**

> “The most attractive of the new technologies from the point of view of energy density is lithium-air”

Lithium–sulphur (Li–S)

Another very promising battery, partly because of both the abundance and the cheapness of raw materials, is the lithium–sulphur system, with a theoretical specific capacity as high as 1,600mAh/g. In a best-case scenario, in which the complete formation of Li_2S from lithium and sulphur is assumed, a specific energy of 500Wh/kg might be achieved [2]. The low charge and discharge efficiency at the end of charge and discharge, respectively, are still making it difficult to obtain a good cycling behaviour of Li–S cells, and only about 50% of the maximum capacity potential, equating to ~800mAh/g, can be achieved so far.

Two companies – Sion Power Corporation and Oxis Energy – are just entering the market with Li–S products, but in the literature it is not expected that marketable, mass-produced Li–S batteries with long lifetimes will be seen in the next five years.

Zinc–air

Zinc–air batteries are commercially used today as primary batteries. Electrically rechargeable zinc–air batteries include a bifunctional oxygen electrode, so that the charge and discharge processes take place within the battery. The negative electrode consists of zinc particles, and the bifunctional air electrode comprises a plastic membrane and carbon with suitable catalysts. The NaOH electrolyte contains gel-forming additives and fibrous absorbent materials.

With such a structure, specific energy densities of 180–200Wh/kg are possible at an operating voltage of 1.2V. Additionally, zinc–air batteries not only achieve low costs, but also have another advantage over lithium batteries, namely improved safety properties. It remains unclear, however, whether this technology can become established on the market, particularly since the cycle lifetime and energy efficiency are poor at high power [3].

Conclusion

Each battery technology has its pros and cons; for special applications, therefore, it is always useful to have a look at what the technologies offer in terms of energy and power densities (Fig. 4).

The market for home storage options is currently dominated by lithium-ion systems: compared with lead–acid systems, they are small, lightweight and maintenance free, with a higher efficiency and longer lifetime, but suffer the drawback of higher cost. If Tesla delivers its systems with a price of $350/kWh and 10 years' warranty, then lithium-ion will be the winner.

As regards small-business and industrial appliances, all the above-mentioned technologies might be appropriate. For smaller appliances, lithium-ion and lead–acid batteries are mostly employed, whereas for large installations and longer storage times, high-temperature batteries and redox flow batteries are used, as they deliver a high energy content at a reasonable price.

For grid stabilisation, most technologies are suitable; however, high currents are needed, and it is useful to pick a technology with a high energy density, such as supercapacitors or high-power lithium-ion cells. If other technologies are used, for example lead–acid batteries, it is necessary to upsize the energy content of the storage system, even in the case of advanced technologies. ■

Author

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