

Electrochemical Storage for Photovoltaics

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18.1 INTRODUCTION

The availability of solar energy is not only different with respect to the annual yield but varies within the seasons of the year, during day and night and from day to day due to the weather conditions. So do the electrical loads. To balance the differing time patterns of loads and solar energy production, energy storage must be included in almost all autonomous power supply systems. Thirty percent or even more of the lifetime costs of autonomous power supply systems based on solar energy may be attributed to the storage. Only very few autonomous photovoltaic (PV) power supply systems have no battery storage system. These are PV or wind-pumping systems where the difference between water demand and energy supply (solar radiation) is levelled out by means of a water storage tank.

PV-powered autonomous power supplies power the complete range of appliances from very small appliances (watches, calculators) with a few milliwatt power requirements to large village power supply systems with about 10 kW power requirements. This chapter is dedicated to applications of PV generators in the range of approximately 10 W to 10 kW. This excludes very small appliances where different storage concepts are used.

There are a number of technical solutions to the problem of energy storage. Storing energy in the electric field of a capacitor is a solution for storage times ranging from microseconds up to 10 s. Storing energy in the magnetic field of a coil is a technology that has been under development for many years (supraconducting coils). It has, however, until today, not resulted in a product that has entered the commercial market.

Medium and high-speed flywheels are being operated in small numbers in grid support, uninterruptible power supplies and in underground railways or buses to overtake

energy from regenerative braking and to support acceleration. However, storage times are in the range of seconds. Compressed air storage in the MWh range, which after decades of development has not reached the market, and pumped water storage are the other technologies that store the energy mechanically. Pumped water storage shows a pronounced economy of scale, which means that larger systems have lower specific investment costs and better storage efficiencies. This is the reason pumped storage has its application in small grids that supply power in megawatt hours per day rather than in the domain of energy systems based on photovoltaics, which are and will be designed to deliver some 10 kilowatt hours per day.

The most promising storage technologies today for the application of which we are discussing here, are electrochemical systems [1]. Therefore, this chapter is dedicated to electrochemical storage systems only.

Although a variety of storage technologies are under development, for the systems focused in this chapter the lead acid battery still is, and will be for some years to come, the working horse for autonomous power supply systems. The ageing effects that limit battery lifetimes are treated in detail. Optimised control strategies allow increasing the battery lifetime and a considerable reduction of the overall system costs.

For storing large energy quantities with low power requirements, electrochemical storage systems with separate storage and power conversion units are under development. These are namely hydrogen storage systems with an electrolyser and a fuel cell as converters and redox-battery systems. The latter use charged ions from metal salts dissolved in liquids as the storage medium and a converter unit quite similar to a fuel cell. These systems are getting more and more interesting as seasonal storage systems and for balancing power generation and power demand in grids with a high penetration of renewable power sources (mainly wind and sun).

There are numerous requirements for storage systems in autonomous power supply systems. Their importance in different applications is different; some of them are in contradiction to each other and therefore they cannot be fulfilled at the same time. Table 18.1

Table 18.1 Requirements to electrical storage systems in autonomous power supply systems (the order of appearance does not imply any weighting of their importance)

<ul style="list-style-type: none"> • High energy efficiency • Long lifetime (years) • Long lifetime in terms of capacity throughput • Low costs • Good charge efficiency even at very low currents • Low self-discharge rate • Low maintenance requirements • High availability worldwide • High power availability • Easy estimation of state of charge and state of health 	<ul style="list-style-type: none"> • Low exposure • Easy recycling • Low toxicity of materials • Fail-safe behaviour at overcharging or deep discharge • Easy extendibility in voltage and capacity through series and parallel connection • Low voltage gap between charging and discharging (allows direct connection of loads to the battery) • Fast charging ability • No memory effect • Low explosive potential • High reliability in operation: high MTBF
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Note: MTBF: mean time between failure

gives an overview of the most important requirements of batteries in autonomous power supply systems.

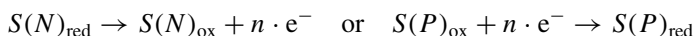
System designs for autonomous power supply systems should track the properties and the requirements of the storage system from the very beginning. Planning of a system and later on just adding the storage will neglect the numerous interactions between the storage, its peripherals and its operation strategy and the overall system design and control. Therefore, only an integrated planning of the system allows to use all synergies and to design systems that can be operated during their lifetime at minimum costs.

18.2 GENERAL CONCEPT OF ELECTROCHEMICAL BATTERIES

18.2.1 Fundamentals of Electrochemical Cells¹

18.2.1.1 *The equilibrium potential*

The basic element of each battery is the electrochemical cell. A positive and a negative electrode are immersed in an electrolyte. The reactive substances (the active materials) are stored in the electrodes.² Chemical and electro chemical reactions, the electrode reactions, occur at both electrodes, which release or absorb electrons according to



N and P indicate negative and positive electrodes, S_{red} and S_{ox} indicate the reduced and oxidised states of the chemical compounds that react and n is the number of electrons involved in the process. The possibility of splitting up the cell reaction into two separate electrode reactions is a decisive prerequisite for the realisation of any electrochemical cell. Only then can the electron exchange connected with the electrode reactions be collected as a current that flows through the consumer (or the charging device), and the energy input or output connected with the chemical reaction be converted into electrical energy. Otherwise, the reaction would occur merely as a chemical reaction. The electrical charge would be exchanged directly between the reacting substances and the released energy would be converted predominantly into heat and to some extent into volume energy.

The electrochemical storage system is based on the conversion of chemical energy into electrical energy and vice versa. The amount of energy that can be stored in a cell is determined by the different energy content of chemical substances that represent the charged and discharged states. Consequently, the characteristic parameters of the system are determined by a number of electrochemical reactions and the energetic changes connected with these reactions. In total, these reactions result in the cell reactions that characterise the battery system.

¹ This section is based on Chapters 2.1, 2.2 and 2.3 from the book of D. Berndt "Maintenance-free batteries" [3] which can be highly recommended for a deeper insight into applied battery technology.

² Please note: the wording used herein is characteristic for classical electrochemical secondary accumulators with solid active masses and a liquid electrolyte. In fact, batteries with solid electrolytes and liquid active masses exist as well. Examples are redox-flow batteries (see Section 18.5.1) or the NaS batteries (liquid Na and S as active masses, solid oxide ceramic as electrolyte).

The laws of thermodynamics generally apply to the equilibrium, which means that all reactions are balanced. In the electrochemical cell, these data can only be measured when no current flows through the cell or the electrodes. On account of this balance, the thermodynamic parameters do not depend on the reaction path; they depend only on the difference between the final and initial components of the electrochemical reaction.

Because of the equilibrium conditions, the laws of thermodynamics describe the possible upper limit of the performance data. As soon as the current flows through the cell, energy losses occur due to kinetic restrictions and ohmic resistance.

The energy exchange, connected with electrochemical reactions, is described by the following thermodynamic parameters. As far as these parameters concern chemical or electrochemical reactions, they actually describe the difference between the parameters before the reaction started and after it was completed. Therefore, they are expressed as the difference between the initial and the final state of the reaction.

- *Enthalpy of the reaction* ΔH , which describes the amount of energy released or absorbed. It is derived from the energy content of the chemical compounds H .
- *Free enthalpy of the reaction* ΔG (also called the Gibbs free energy), which represents the (maximum) amount of chemical energy that can be converted into electrical energy, and vice versa.
- *Entropy* ΔS , which characterises the energy loss or gain connected with the chemical or electrochemical process. The product $T \Delta S$ represents the heat exchange with the surroundings when the process occurs reversibly. This is synonymous with minimal heat loss or gain of the system, which is true only when no current flows through the battery.

T is the absolute temperature. The most important relation among these parameters is given by the following formulae:

$$\Delta G = \Delta H - T \cdot \Delta S$$

As ΔG describes the amount of energy that can be converted into electrical energy, a simple relation between the Gibbs free energy and the equilibrium voltage³ E_0 of the cell can be derived.

$$\Delta G = -n \cdot F \cdot E_0$$

where n is the number of exchanges of electronic charges, F is the Faraday constant (96485 As) and nFE_0 describes the generated electrical energy.

Thermodynamic quantities like ΔH and ΔG depend on the concentration of the reacting components as far as these are dissolved according to the relation

$$\Delta G = \Delta G_S + R \cdot T \cdot \sum_i \ln[(a_i)^{j_i}]$$

³ Occasionally, the equilibrium voltage is called the open-circuit voltage. However, strictly speaking this term only means a voltage without external current flow, and may concern a mixed potential as well. On account of secondary reactions, the rest potential in batteries are usually mixed potentials, but this is not strictly observed in practical languages.

with a_i = activity⁴ of the reacting components i (closely related to the concentration),
 j_i = number of equivalents of this component that take part in the reaction,
 R = molar gas constant for an ideal gas ($R = 8.3413 \text{ J/K/mole}$),
 ΔG_S = standard value when all activities are unity.

From these equations, the Nernst equation describing the concentration dependence of the equilibrium voltage can be derived, where $E_{0,S}$ is the equilibrium potential in standard conditions.

$$E_0 = E_{0,S} + \frac{R \cdot T}{n \cdot F} \cdot \sum \ln[(a_i)^{j_i}]$$

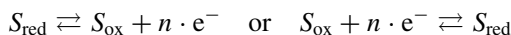
The temperature coefficient of the equilibrium cell potential can be derived from the following thermodynamic relation.

$$\frac{dE_0}{dT} = -\frac{\Delta S}{n \cdot F}$$

Thermodynamic calculations are always based on a complete cell, and the derived voltage refers to the potential difference between two electrodes. The potential difference between the electrode and the electrolyte, the “absolute potential”, cannot be determined. The name electrode potential always refers to a potential difference measured with the aid of a reference electrode. To get a basis for the electrode-potential scale, the zero point was arbitrarily equated with the potential of the standard hydrogen electrode (SHE⁵).

18.2.1.2 Electrode kinetics at current flow

When current flows through a cell, the reaction must take place at a corresponding rate. For each delivered ampere-second, a corresponding number of electron exchanges must have occurred. This means that at the electrodes the elementary processes



must take place $6.42 \cdot 10^{18}/n$ times (reciprocal of one elemental charge). To achieve this current flow, additional forces are required, which intensify the electron and ion flow in the required direction. These additional forces find their expression in deviations from the equilibrium data, which means irreversible energy loss.

⁴ Activity described the “effective concentration”. Thermodynamic rules are derived for dilute solutions. The activity is equivalent to the concentration in very dilute solutions, but the activity can be different at higher concentrations as interactions among the ions in the solution need to be taken into account.

⁵ The standard hydrogen electrode means a hydrogen electrode immersed in acidic solution with H^+ ion activity of 1 mole/dm^3 and H_2 pressure of 1 atm . The specification of the electrolyte concentration is required because the potential of the hydrogen electrode depends on the H^+ ion concentration and is shifted by -0.0592 V when the H^+ concentration is reduced by one decade. The potential of the standard hydrogen electrode at 25°C is synonymous with the zero point of the potential scale. The temperature coefficient of the standard hydrogen electrode is $+0.871 \text{ mV/K}$.

Usually, the reaction path consists of a number of reaction steps that precede or follow the actual charge-transfer step, and the rate of each these reaction steps is determined by its kinetic parameters, such as exchange current density, diffusion coefficient or transport numbers. The slowest partial step of this chain is decisive for the rate of the overall reaction. As a consequence, limitations of the reaction rate are often not caused by the electron-transfer step itself, but by preceding or following steps such as the transport rates of the reacting ions to and from the electrode surface.

Transport processes play an important role, because electrochemical conversion can only take place when reaction partners and electrons are available at the same time. Frequently, the reaction substances must be brought to these places or transported away, for example, when the reactions include substances in the dissolved state.

Electrochemical equilibrium is always composed of two reactions, the actual reaction and its reversal. The resulting current/voltage relation is called the “current/voltage curve” or the “current/potential curve”. It is composed of two curves, one for the forward and the other for the reverse reaction. At equilibrium, both reactions are in balance.

The forward and reverse reactions of an arbitrary electrode are shown in Figure 18.1. The horizontal axis represents the electrode potential related to the equilibrium potential E_0 . The vertical axis represents the current density, which is synonymous with the reaction rate.

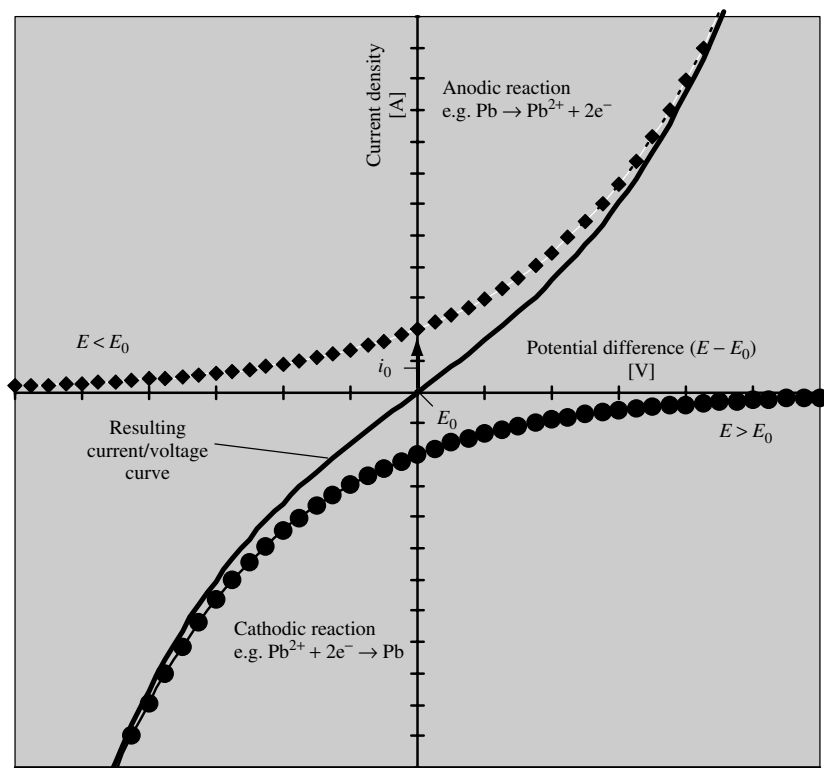


Figure 18.1 Current/voltage curve based on the Butler–Volmer equation (example taken from the lead electrode of a lead-acid battery)

The exponential relation between voltage and current is based on the fact that the charge/discharge reaction, in which the electrons are released or absorbed (the so-called “transfer reaction”) can be approximately described by an exponential law, called the Butler–Volmer equation.

$$i = i_0 \cdot \left\{ \exp \left[\frac{\alpha \cdot F}{R \cdot T} \cdot (E - E_0) \right] - \exp \left[-\frac{(1 - \alpha) \cdot F}{R \cdot T} \cdot (E - E_0) \right] \right\}$$

Therein i is the current density, i_0 the exchange current density, E the actual potential, E_0 the open-circuit electrode potential and α the transfer factor describing the efficiency of the overvoltage on forward and backward reactions. The difference $E - E_0$ is called overvoltage or polarisation. The difference expresses the additional energy voltage required to force the current through the surface. The exponential relation between current and voltage means that the increase in current might be enormous when the overvoltage exceeds certain values.

The equilibrium voltage E_0 is determined by the point at which the forward and reverse reactions are equally fast. In lead acid batteries, this is the point where metal dissolution and deposition balance each other, which means that the current densities of the forward and reverse reaction equal each other. This equilibrium potential represents a dynamic equilibrium: current flow occurs in both directions, but does not appear externally.

The current density for the forward and reverse reactions at the open-circuit potential is called the exchange current density i_0 , which describes the rate at which this equilibrium is adjusted. The exchange current density represents an important kinetic parameter. High exchange current density means that the equilibrium potential is rather stable, while a low exchange current density indicates that the electrode potential will be polarised even when very small current densities flow through the electrode. On the other hand, it is important that unwanted side reactions have rather small exchange current densities. In the lead electrode, the exchange current density for the charge/discharge reaction is of the order of 10^{-5} A/cm² while it is only of the order of 10^{-13} A/cm² for the hydrogen production.⁶ Therefore, the hydrogen evolution at open-circuit voltage is rather small.

In the literature, simplified versions of the Butler–Volmer equation can be found. For high overvoltages caused by the electrochemical charge-transfer (trans) process, the so-called Tafel equation is a proper approximation.

$$(E - E_0)_{\text{trans}} = \frac{R \cdot T}{\alpha \cdot F} \cdot \ln \left(\left| \frac{i}{i_0} \right| \right)$$

Using a semi-logarithmic plot results in straight lines, called the Tafel lines. For mathematical reasons, α is signed positive for positive currents and negative for negative currents.

⁶ It is worth noting that the current density caused by the current flow through the electrode during a charge or discharge of a lead-acid battery (approximately 10 h discharge or charge) is of the order 10^{-5} A/cm² to 10^{-6} A/cm² for the Pb electrode (assumptions: capacity of the lead electrode 3.865 g/Ah, inner surface of Pb active material 0.5 m²/g and discharge current 0.1 A/Ah). This gives a feeling for the very high activity in equilibrium conditions.

For small overvoltage, the first-order approximation of the exponential terms in the Butler–Volmer equation results in the following equation:

$$(E - E_0)_{\text{trans}} = \frac{R \cdot T}{F} \cdot \frac{i}{i_0}$$

Electrochemical reactions, chemical reactions as well as transport processes that precede or follow the charge/discharge step, lead to changes in the concentration of the reacting substances at the electrode surface and thereby may change the current/voltage curves. Each of these steps can cause an overvoltage. If the diffusion of one of the reacting partners to the electrode surface is the slowest partial step, then the concentration of this substance is reduced more and more with increasing overvoltage. A limit is reached when the concentration of the reaction partner is reduced to zero at the electrode surface. From this point, further increase in overvoltage no longer increases the current. In fact, with rising overvoltage typically a side reaction becomes dominant and the current goes into this reaction. This is the case with the hydrogen evolution at the lead electrode. If the electrode is totally charged and the overvoltage is increasing, the current going into the hydrogen-evolution reaction takes over the complete current through the electrodes. This happens even though the current-exchange density for the hydrogen evolution is several decades smaller than that of the lead charging/discharging reaction.

Diffusion processes can be characterised by a limiting current i_{lim} , which describes the maximum flow of charge carriers that can be transferred through diffusion to the reaction site. The overvoltage of this diffusion process (diff) can be described by the following equation.

$$(E - E_0)_{\text{diff}} = \frac{R \cdot T}{n \cdot F} \cdot \ln \left(1 - \frac{i}{i_{\text{lim}}} \right)$$

An effect not often described explicitly is the “production” of the charge carriers from a chemical process. Typically, this is included in the diffusion overvoltage, but for a deeper understanding of the battery processes and the effects of ageing (diffusion itself is not affected directly by ageing) it is worthwhile to separate these effects.

To explain the effect, the lead acid battery is taken as an example. Figure 18.10 in Subsection 18.4.7.1 will describe the process in more detail. From the electrochemical process described by the Butler–Volmer equation or the Tafel equation charged ions are released into the electrolyte during the discharge process. This increases the concentration c of charged ions in the electrolyte above the equilibrium concentration c_0 (defined by the solubility of the ions in the electrolyte) resulting in a concentration (conc) overvoltage. The following equation gives the mathematical formulation of this overvoltage.

$$(E - E_0)_{\text{conc}} = -\frac{R \cdot T}{n \cdot F} \cdot \ln \left(\frac{c}{c_0} \right)$$

As soon as the concentration of any species in a solution deviates from its equilibrium concentration, chemical processes driven by concentration gradients occur. In the case

of the lead electrode, dissolved Pb^{2+} ions form the lead sulphate crystals (PbSO_4) with SO_4^{2-} . The rate of formation of sulphate crystals (and the dissolution of the crystals during charging) determines the concentration of the charged ions in the electrolyte and therefore the concentration overvoltage. The rate of forming and dissolving of sulphate crystals depends strongly on the crystal size, shape and number. These parameters depend on the operating conditions of the battery and on the ageing of the active material. Therefore, battery ageing and active material structure is reflected by the values of the concentration overvoltage and the charge-transfer overvoltage.

The diffusion overvoltage describes the transport of ions that are available in sufficient volume (in the lead acid battery these are the SO_4^{2-} ions), thus a classical transport phenomenon. The concentration overvoltage describes the generation with respect to the absorption of ions from a chemical process.

Chemical processes are always driven by concentration gradients. Electrochemical processes are driven by the external currents. Therefore, the electrochemical process must take place exactly at the rate given by the external current. The rate of the chemical process depends only on ion concentration. With respect to the charge/discharge process in a battery, this means that the electrochemical process follows without delay any changes in the external current flow. Chemical processes have time constants as the rate of the process depends on the concentration in the electrolyte. In steady-state charge and discharge conditions, the rates of the electrochemical process and the chemical process need to be equivalent. This means that the ratio of the ion concentration and the equilibrium concentration in the electrolyte is constant.

All processes strongly depend on the temperature. The temperature dependence of the reaction rate k of a chemical reaction is described by the Arrhenius equation (C is a constant, E_A the activation energy).

$$k = C \cdot \exp\left(-\frac{E_A}{R \cdot T}\right)$$

The activation energy for many processes is of the order of 50 kJ/mole. From this experience, the rule of thumb “*increase of temperature by 10 K increases the reaction rate by a factor of 2*” is derived.

18.2.2 Batteries with Internal and External Storage

Electrochemical accumulators convert electrical energy into chemical energy. The energy is stored in a chemical compound. In secondary electrochemical batteries, this process is reversible. During discharging, the chemical energy is converted back into electrical energy. Thus, the converters determine the charging and the discharging power and the storage determines the energy capacity of the systems. This principle concept is described in Figure 18.2.

In secondary electrochemical batteries with internal storage, the converter and the storage cannot be separated. The interface of the active material to the electrolyte is

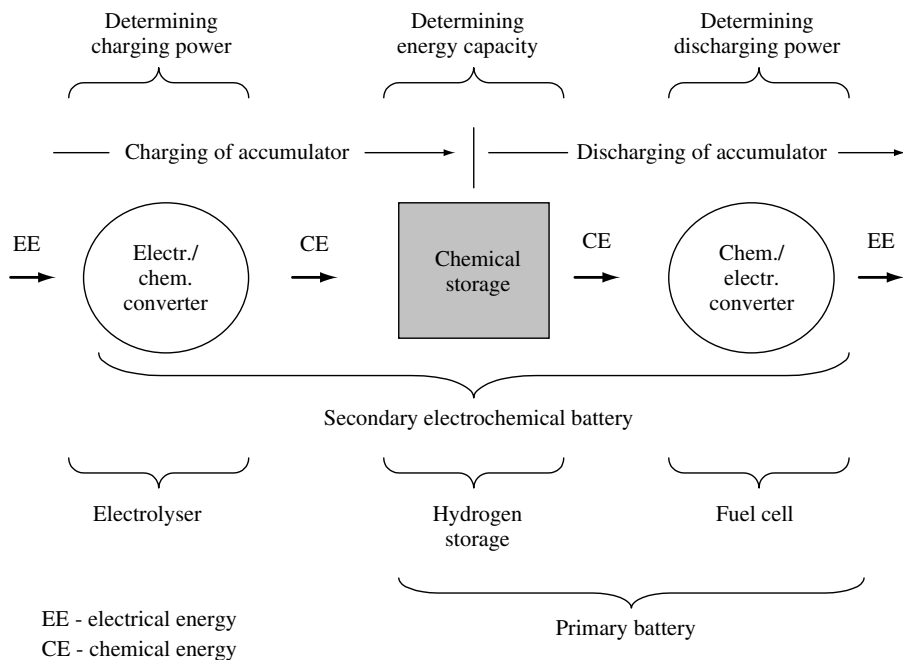


Figure 18.2 Schematics of electrochemical storage systems

equivalent to the converter; the transformed active mass is the storage. In conventional secondary electrochemical batteries, power and capacity depend on each other and cannot be designed independent of each other. In practice, there is a small margin for the design. For high-power and low-capacity requirements, very thin electrodes having a high surface-to-capacity ratio are used. Section 18.4 will go into the details of this type of batteries.

Nevertheless, the margin is limited and this is a drawback for autonomous power supply systems where high energy capacity is required and the power requirement is moderate. Therefore, electrochemical storage systems with separated converters and storage are of interest. The electrolyser/hydrogen storage/fuel cell system is a well-known option for the problem even though it is not yet a common commercially available solution. Details of this system will be discussed in Section 18.5.2.

A second class of storage systems with separated converter and external storage units are electrochemical Redox systems, where the reaction partners like iron and chromium salts or vanadium salts are dissolved in liquids and stored separately in tanks. The converter functions quite similar to a fuel cell. During charging or discharging, the electrolyte is pumped into the converter. These systems are not available in large quantities in the market yet, but there are several R&D activities on these systems. Section 18.5.1 will discuss this technology in more detail.

For a clear understanding of this chapter and to get familiar with the wording used in the “storage community”, the following two sections explain some basics. They are oriented very much on the application of storage systems in autonomous power

supply systems. They are by no means complete but should help to understand this chapter without additional literature. For more information, References [2, 3] are highly recommended.

18.2.3 Commonly Used Technical Terms and Definitions

A battery is made from two or more electrochemical *cells* connected in series. *Primary* and *secondary* electrochemical cells can be distinguished. Secondary batteries – also called accumulators – have reversible reactions and are rechargeable. This chapter is centred around them.

An electrochemical cell consists of two *electrodes*. Commonly, one is called the “positive” electrode and the other, the “negative” electrode. The positive electrode has a more positive potential than the negative electrode with respect to the standard hydrogen electrode.⁷ Each combination of charged and discharged active material has a specific electrochemical potential. The potential difference between the positive and the negative electrode is called the *cell potential* or *cell voltage*. The *equilibrium voltage* of a cell is a function of the electrolyte concentration and the temperature. The *open-circuit voltage* can be measured if no external current flows through the battery. It is identical to the equilibrium voltage if all the internal overvoltages mainly caused by diffusion processes have levelled out. The time until this stadium has been reached depends on the battery technology and the operation condition. It is in the range of some seconds to many hours.

The *capacity* of a cell is measured typically in ampere-hours (Ah). The capacity is determined by a constant current discharge down to a defined *end-of-discharge voltage*. The capacity depends significantly on the discharge current and the temperature. Battery manufacturers can define the discharge current and the end-of-discharge voltage on their own. Therefore, it is very important to check the reference conditions defined by the manufacturer while comparing the capacity of different products.

Typically, nominal cell voltages are in the range between 1.2 and 3.6 V. Therefore, several cells are usually connected in series to build a *string* of higher nominal voltage. The *nominal voltage* of a battery is therefore defined by the number of cells connected in series times the nominal cell voltage of a single cell. Batteries are often sold in so-called blocks or modules. Therein, several cells have been integrated and connected in series with only one set of terminals. A well-known example is the starting, lighting, ignition (SLI) battery for cars where 6 cells are connected in series but are sold as one 12 V block. To increase the capacity of a cell, often several sets of positive and negative electrodes are connected in parallel within a single cell. To increase the capacity even more, two or more strings can be connected in parallel. The *nominal energy* content (Wh or kWh) of a battery is defined by the nominal battery voltage times the nominal battery ampere-hour capacity.

The *state of charge (SOC)* gives the capacity that can be discharged from a battery at a certain moment. Hundred percent state of charge means a fully charged battery, 0% SOC means that the nominal capacity is discharged. State of charge is defined in more

⁷ The standard hydrogen electrode is a platinum electrode rinsed with hydrogen gas in 1 N electrolyte. Its potential is defined as 0 V.

detail in Section 18.2.4. Often, instead of SOC the *depth of discharge (DOD)* is used in the literature or in data sheets. DOD is defined as 0% when the battery is fully charged and as 100% after the nominal capacity is discharged from the battery ($\text{DOD} = 100\% - \text{SOC}$).

When looking up literature related to autonomous power supply systems, typically a *positive battery current* is defined to increase the SOC of the battery while a negative current decreases the SOC. However, please be aware that some authors use the opposite definition.

A *cycle* refers to a discharge followed by a recharge. Cycles used in data sheets always start from a fully charged battery up to a certain DOD. A nominal *full cycle* is a discharge down to 100% DOD. The *cycle lifetime* for a battery is given by the number of cycles as a function of the DOD. Nevertheless, in autonomous power supply systems cycles as defined above do not occur as can be seen from Figure 18.6. Many *partial cycles* within a *macrocycle* (time between two full charging states) occur, where a partial cycle is defined as the charge transfer within the time of the change of the direction of the battery current. Overall, charge transfer of batteries in autonomous power supply systems can be defined by the *capacity throughput*. It is given by the accumulated ampere-hour discharged from the battery divided by the nominal capacity. The resulting number is formally equivalent to the number of 100% DOD cycles delivered during the battery life. This normalised number will be referred herein as the capacity throughput.

The *ampere-hour efficiency* η_{Ah} is defined as the ratio of the ampere-hours discharged from the battery divided by the ampere-hours charged to the battery within a certain period (typically one month or one year or within a period between two full charging processes). Often the *charge factor* is used instead of the ampere-hour efficiency. It is defined as $1/\eta_{\text{Ah}}$. For a sustainable battery operation, charge factors greater than one are necessary.

The *energy efficiency* η_{Wh} is the ratio of the energy discharged from the battery divided by the energy charged to the battery within a certain period (defined as above).

The size of a battery is given by its nominal energy content in the fully charged condition. To express the relative size of a battery concerning the load in autonomous power supply systems, often the term *days of autonomy* is used. The “days of autonomy” is defined by the ratio of the nominal energy content of the battery (kWh) (sometimes the practical capacity according to Figure 18.3 instead of the nominal capacity is also used) to the average energy consumption per day (kWh/day). Therefore, the unit is “days” and expresses how long a system can be supplied only from the fully charged battery.

Battery currents are usually given relative to the battery size. The reason is that the strains and the current-dependent electrical properties are related to the specific current loads to the electrodes with respect to the active materials. For larger capacities just formed from parallel-connected electrodes or cells or from larger electrodes, the normalisation of the current to the capacity is an appropriate measure. Therefore, battery currents are expressed as multiples of the ampere-hour capacity or as multiples of the capacity-defining discharge current. For a battery with a capacity of $C = 100 \text{ Ah}$, a current of 10 A is defined as $0.1 \times C$. In the example, 100 A is called the *C-rate*. I_{10} is the current that discharges a fully charged battery within 10 h down to the defined end-of-discharge voltage. The typical nomenclature for the capacity is C_x where x is the time in which the battery is

discharged. For example: $C_{10} = 10 \text{ h} \times I_{10}$, or $C_{10} = 100 \text{ Ah}$, $I_{10} = 10 \text{ A} = 0.1 \times C_{10}$. Note that $1 \times I_{10}$ is not equivalent to $10 \times I_{100}$ as the C_{100} capacity is typically larger than the C_{10} capacity. For a more detailed example, see Section 18.4.7.3.

The *end-of-charge voltage* defines an upper voltage limit. Charging of the battery usually is not stopped on reaching the end-of-charge voltage (other than the end-of-discharge voltage), but the charge current is reduced accordingly to maintain the end-of-charge voltage over time.

The *lifetime* of a battery depends very much on the operating conditions and the control strategy. Manufacturers usually define two types of lifetime: the *float lifetime* (calendar lifetime) gives the lifetime under constant charging conditions without cycling (typical applications are uninterruptible power supplies), and for continuous cycling (*cycle lifetime*, typical applications are fork-lift trucks). Sometimes, the *shelf lifetime* is given. It defines the time for which a battery can be stored before usage.

Self-discharge describes the (reversible) loss of capacity on open-circuit conditions. It depends very much on the temperature.

The *state of health* is defined as the ratio of the actual measured capacity and the rated or nominal capacity. The state of health indicates to which extent the battery is still able to fulfil the requirements. According to the norms, lead acid batteries are at the end of their lifetime if the state of health is under 80%. However batteries can be operated significantly longer, but the days of autonomy are reduced accordingly and a system might not fulfill the energy requirements any more in a proper way. Batteries operating at a state of health of 50% are found frequently especially in hybrid systems. As a consequence, the share of the motor generator is increasing.

18.2.4 Definitions of Capacity and State of Charge

For operation and energy management in autonomous power supply systems, the battery capacity and the actual state of charge of the battery are the most important parameters. State-of-charge determination is difficult in autonomous energy supply systems with renewable energies because full charging of the battery as it is done frequently with conventional battery chargers is very unusual.

If state of charge is displayed, the question that arises is, what is the meaning of the specific values. Figure 18.3 shows different definitions of the battery capacity and the corresponding definitions of state of charge. The measured capacity of a battery might be smaller or even higher than the rated capacity given by the manufacturer. During the lifetime, the measured capacity decreases more and more due to ageing effects. The practical capacity is less than the measured capacity. Owing to the special conditions of renewable energy sources, batteries are almost never completely recharged (number of charging hours is limited) [4]. The maximum state of charge that is reached during normal system operation is called a “solar-full state of charge”. Further on, the system defines an end-of-discharge criterion to avoid deep discharging of the battery and therefore accelerated ageing, which usually differs from the end-of-discharge criteria used for capacity tests. Therefore, the practical battery capacity is lower than the measured capacity. In the literature and other publications, no common definition of the state of charge is used. Therefore, any data and results must be handled with care.

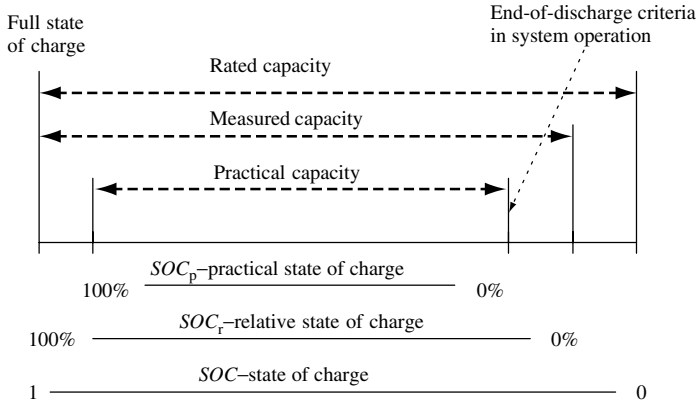


Figure 18.3 A Comparison of the different definitions of battery capacity and the corresponding definitions of state of charge

Within this chapter the following definitions according to Figure 18.3 and [5] will be used.

The rated or nominal capacity is defined as the 10-h discharge capacity C_{10} . This is the basis for the SOC determination. The rated or nominal capacity does not change during the life of a battery whereas the measured capacity changes with time. The state of charge with respect to the measured capacity is called relative state of charge (SOC_r). The practical capacity C_p is always lesser than the measured capacity. The state of charge definition related to the practical capacity is the practical state of charge (SOC_p). SOC_p is 100% if a solar-full state of charge is obtained.

In [5], a complete review of the different definitions for the capacity, state of charge and full state of charge is given. Further on, definitions of open-circuit voltage and state of health are included, because some state-of-charge meters and algorithms use these definitions as well.

18.3 TYPICAL OPERATION CONDITIONS OF BATTERIES IN PV APPLICATIONS

To understand the requirements of storage systems for autonomous power supply systems, an analysis of the typical operating conditions is necessary. The operating conditions vary very much according to the location and application of the system, the load patterns, the installed power generators and the operation strategy.

The most important parameters for the classification of the operating conditions are the charge and discharge currents, the state-of-charge profile and the temperature.

18.3.1 An Example of an Energy Flow Analysis

Photovoltaic stand-alone systems may be roughly separated into two groups. There are systems consisting of the PV modules that charge the batteries. A charge controller prevents

overcharging or deep discharging. The appliances are supplied from the battery either directly or via a DC/AC converter. The typical representative of this first system group is the Solar Home System (SHS), which is operating in hundreds of thousands of rural households. It will supply lights and TV sets and delivers, in a standard version, approximately 0.25 kWh of electricity per day. Larger systems may deliver up to 5 kWh per day.

The second group of systems combine a photovoltaic generator with a diesel gen-set and possibly with additional wind turbines or hydroelectric generators. Including a diesel gen-set as a controllable generator gives an additional degree of freedom to the system sizing.⁸ It allows reducing the battery capacity, especially if the solar radiation undergoes strong seasonal variations. These systems are called hybrid systems. They are designed to deliver from 1 kWh per day to typically between 10 and 100 kWh per day. They may be used to supply power to telecommunication equipment, mountain lodges, hospitals or hotels in non-electrified rural areas and small villages.

A typical hybrid system with a 4.5-kW_p PV generator, a diesel generator and 32 kWh of lead acid battery storage is in operation since 1992 in the Black Forest in Germany. It has to deliver 10 kWh per day to the hikers inn “Unterkrummenhof”. An analysis done in model calculations based on measured data shows the flow of energy in the system and the effect of internal losses (Figure 18.4). Two-thirds of the power delivered (E_{consumer}) is drawn from the battery storage. The numbers given in the diagram are normalised to the nominal energy production of the PV generator under the radiation conditions at the site. A detailed discussion of the energy-flow diagram is given in [6].

Figure 18.4 underlines the key role that battery storage has to fulfil in hybrid systems. More than 80% of the energy used goes via the battery storage. This is a typical value for all hybrid systems and is even higher in many pure PV battery systems.

18.3.2 Classification of Battery-operating Conditions in PV Systems

An intensive study of the operational data of close to 30 batteries in stand-alone PV systems with and without a diesel generator was made. All systems were operated under European radiation conditions [7]. The study resulted in a classification of the battery-operating conditions into four classes. Figures 18.5 and 18.6 show measured data on the annual operating conditions of four systems selected to represent the four different classes. Figure 18.5 shows scatter graphs of the battery current versus battery voltage and Figure 18.6 shows the time series of the state of charge within a complete year.

The hybrid system “Unterkrummenhof”, characterised in Figure 18.4 is a system from Class 2. Class 3 and Class 4 represent systems with an increasing role of the diesel gen-set and relatively smaller PV generators and batteries. The “Class 1” system is a system without a back-up generator, designed to operate with high reliability in Europe.

Solar home systems (SHSs), which were not included in the survey, operating under the favourable conditions of low latitudes would typically be equipped with a three- to five- “day” battery and would not show the pronounced long-lasting period of

⁸ Diesel gen-sets are currently the most common solution for an additional controllable generator. Other solutions like thermoelectric, thermophotovoltaic or fuel cell generators have been developed in many places and might be alternatives in the near future.

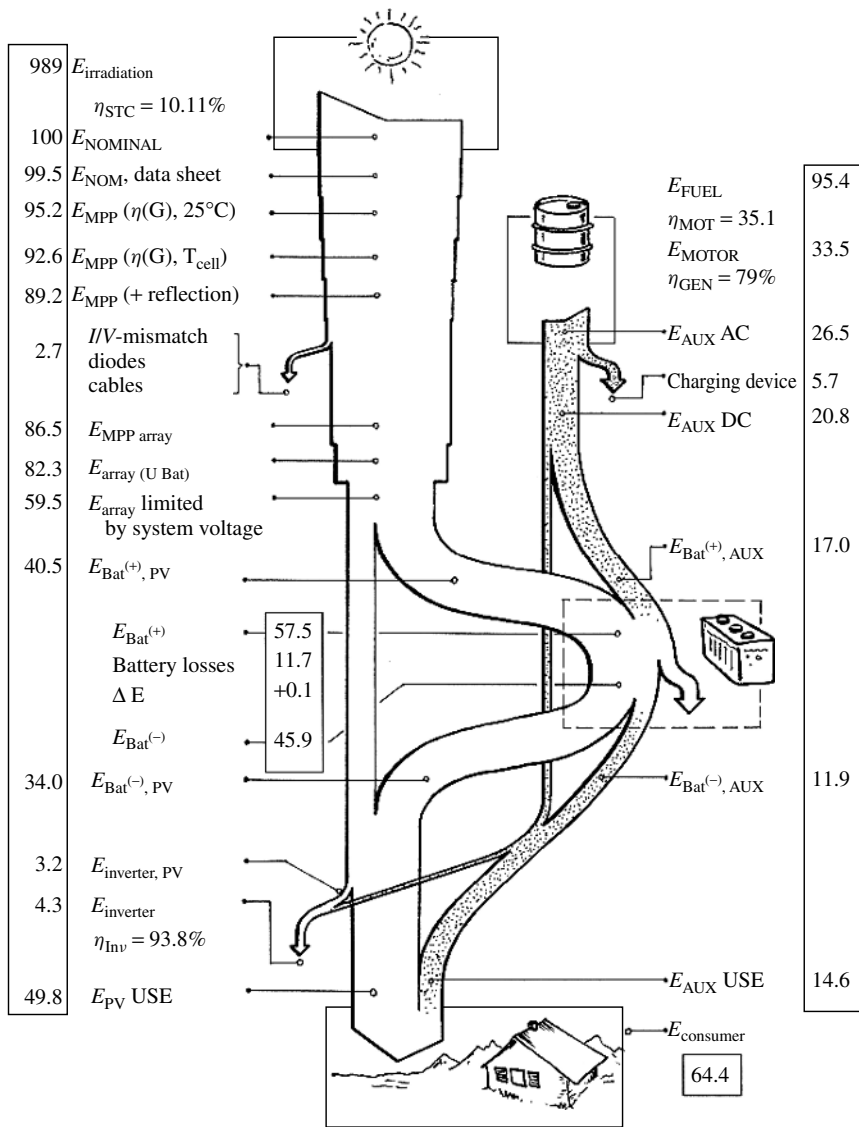


Figure 18.4 Energy-flow diagram on a one-year basis of the autonomous power supply system Unterkrummenhof (PV diesel battery) near Freiburg/Germany [6]

deep discharge during the winter months. Classical SHSs are very much like Class 2 or Class 3 systems and village power supply systems like Class 4.

An extension of the classification including the Southern Europe climatic conditions is necessary but is not available yet.

The time series of a battery's state of charge (Figure 18.6) and the current/voltage representation (Figure 18.5) demonstrate that batteries in stand-alone systems have to operate under very specific conditions such as the following:

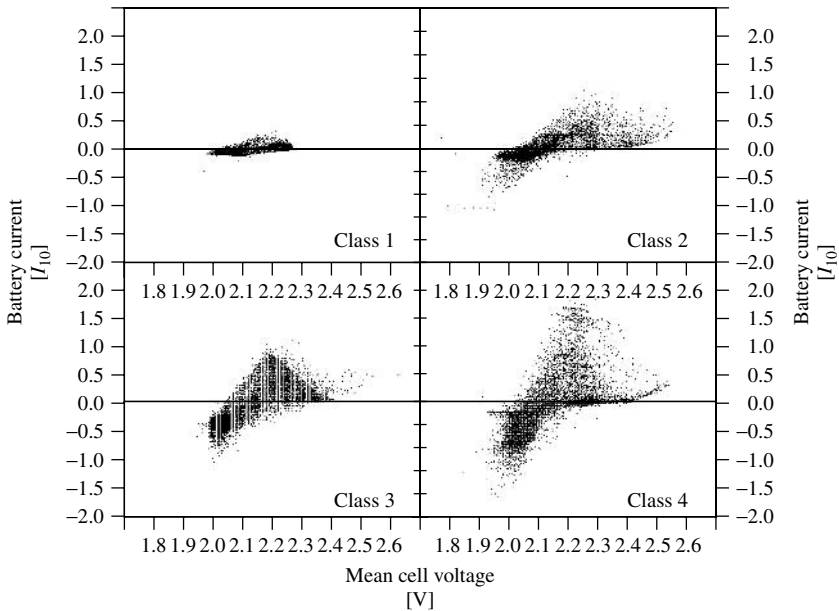


Figure 18.5 Battery current in units of I_{10} versus cell voltage for all data points. For each class, data of a complete year were taken from a representative system

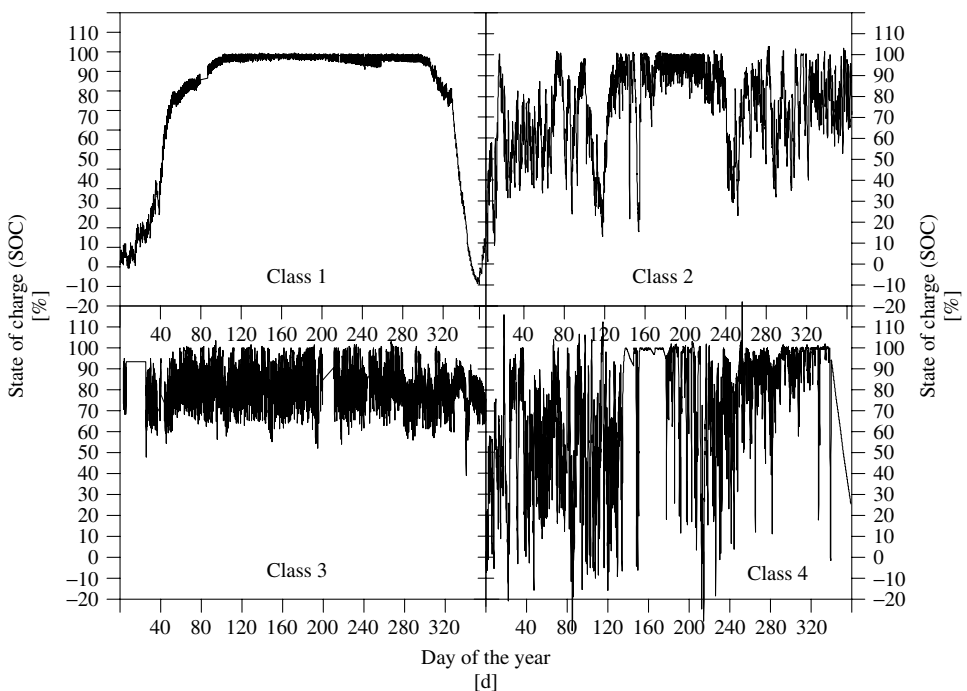


Figure 18.6 Time series of state of charge calculated from current, voltage and temperature using an ampere-hour balance with a voltage and temperature-dependent loss current [5, 8]

- The charging and discharging currents are small compared to the standard 10-h discharging current I_{10} (at least for system Classes 1 and 2).
- For long periods, sometimes weeks or even months, the batteries do not reach a fully charged state (SOC = 100%).

These features are distinct from other battery applications in, for example, uninterruptible power supplies, where the batteries are kept at a full state of charge for the longest time of the year or in vehicle traction applications, for example, fork-lift trucks, where the batteries are fully recharged regularly with high charging current. Figure 18.6 also demonstrates that in systems of Classes 1 and 2 – the same is true for the solar home system application – the daily discharged capacity is between 5% and 30% of the nominal battery capacity. This is equivalent to the annual full cycles between 20 and 100.

Table 18.2 gives a comprehensive view of the requirements of the battery in the different system classes. In Table 18.3, suggestions for the selection of adequate lead acid battery types out of the variety of products available in the market on the basis of this classification are made.

On the basis of this classification, an evaluation of the properties of a battery according to the requirements of the systems is possible. Solar fraction and storage size in days of autonomy are the output of all commercial system design and simulation-software packages. Therefore, the classification allows the system designer to ask the battery manufacturers for an appropriate battery type by showing him the typical operating conditions.

Table 18.2 Identification of classes by typical system indicators (solar fraction, storage size) for the different classes of operating conditions and importance of battery features for the different classes. The storage size is given in units of battery capacity divided by the mean daily load (days of autonomy). The solar fraction is the amount of energy produced by the PV generator divided by the energy produced by all the energy sources within the system (including the diesel generator in hybrid systems) [9]

System indicators	Class 1	Class 2	Class 3	Class 4
Solar fraction	100%	70–90%	About 50%	<50%
Storage size/days of autonomy	3–>10 days	3–5 days	1–3 days	About 1 day
Capacity throughput ⁹	10–25	30–80	100–150	150–200
Necessary battery features				
Number of lifetime cycles ⁹	Low (<300)	→		High (>1200)
Capability to withstand long periods in deep discharged states	Important	←		Less important
Low self-discharge rate	Important	→		Less important
	(<1% per month)			(5% per month)
Measures against acid stratification	Important	Very important		Important
Resistance against corrosion	Important	←		Less important

⁹ The capacity throughput is defined as the number of ampere-hours discharged from the battery divided by the nominal capacity of the battery. The given numbers are typical of the applications in the defined classes of operating conditions. A full cycle with regard to lifetime cycles is defined by a one capacity throughput. This is equivalent to a complete discharge (100% DOD) of a fully charged battery. In data sheets, often the cycle number is given for cycles with a depth of cycle other than 100% (e.g. 80%). This has to be taken into account while comparing the design capacity throughput of different products (see also Figure 18.24).

Table 18.3 Continuation of Table 18.2. Different product groups of lead acid batteries are classified with respect to the different classes as defined in Section 18.3.2 (● optimum, ○ acceptable) table from Reference [9]

Type of battery	Class 1	Class 2	Class 3	Class 4
SLI	—	—	—	—
Stationary	●	●	○	—
Traction	—	○	●	●
Electric vehicle	—	○	●	●
“Solar battery” (from SLI)	●	○	—	—
VRLA	●	●	●	○
Flooded	●	●	●	●

The differences in the operating conditions and the requirements listed in Table 18.2 show clearly that one “solar battery” cannot exist. The range of operating conditions in autonomous power supply systems is very large and requires appropriate individual solutions.

An additional parameter for differentiating the operating conditions of batteries is the amount of capacity throughput caused by an AC ripple. Loads and generators are connected to the battery at the same time. This results, in many cases, in so-called micro-cycles in which the battery current changes from charging to discharging and vice versa with a frequency between 1 and 300 Hz. Measurements and calculation have shown that this can cause an additional capacity throughput of up to 30%. This in fact shortens the lifetime of the batteries. Taking into account the optimum operating strategies, battery ageing is related strongly to the capacity throughput. The amount of this additional capacity throughput depends very much on the system’s sizing and the electrical properties of the loads, the inverters, the converters and the generators [10].

18.4 SECONDARY ELECTROCHEMICAL ACCUMULATORS WITH INTERNAL STORAGE

18.4.1 Overview

There are several secondary electrochemical accumulators available on the market. They differ in parameters concerning the materials of the electrodes and the electrolyte. This results in different electrical properties like energy and power density, efficiency, lifetime, cycle life, operation temperature, inner resistance and self-discharge and last but not the least economic properties like battery costs and maintenance requirements.

Products like lead acid batteries, ZnBr_2 , NiCd , NiFe , NiZn , nickel-metal hydride (NiMH), Zn -air, Li-ion , Li-polymer , Li-metal and rechargeable alkali mangan (RAM) are available. They operate at room temperature, but also high-temperature batteries like NaS and NaNiCl_2 (“ZEBRA”) operating at 300 to 350°C are possible. In addition, there are capacitors storing the energy in an electrostatic field instead of chemical bonds out of which the double-layer capacitors are the most interesting for autonomous power supply systems.

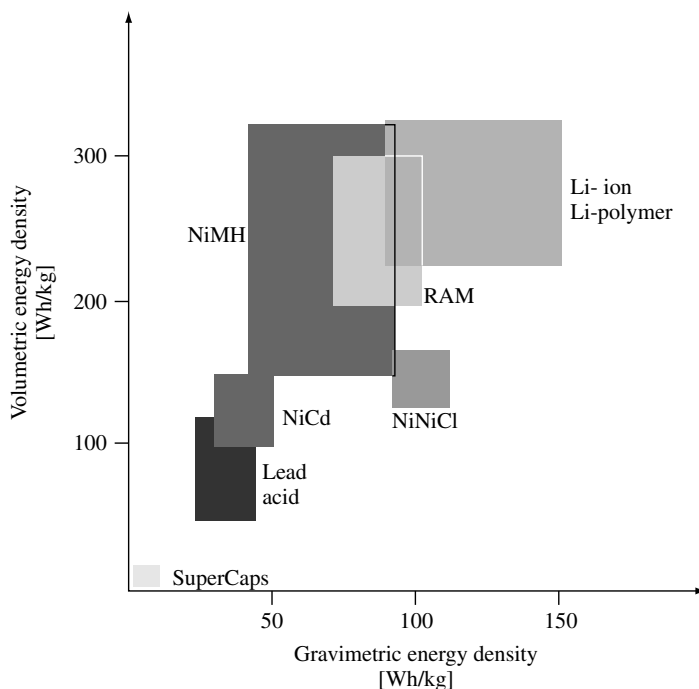


Figure 18.7 Practical specific volumetric energy density (Wh/l) versus specific gravimetric energy density (Wh/kg) for various secondary battery technologies (data from Table 18.4)

The specific energy densities of batteries are an important parameter to characterise the different battery types. For logistic reasons on supplying the batteries to the systems, gravimetric and volumetric energy densities are a relevant cost factor also for autonomous power supply systems. Figure 18.7 shows an overview of the energy densities of different secondary battery technologies based on an analysis of commercially available products. The figure does not show the theoretical limits of the different technologies.

Table 18.4 gives an overview of the most important properties of several secondary electrochemical accumulators. A more detailed description is given on the NiCd (Section 18.4.2), the nickel-metal hydride (NiMH) (Section 18.4.3), the RAM (Section 18.4.4) and the Lithium batteries (Section 18.4.5) as well as on the double-layer capacitors (Section 18.4.6). Lead acid batteries are treated in greater detail in Section 18.4.7. All other battery types have no relevance in the field of autonomous power supply systems. Details on all primary and secondary batteries can be found in [2].

18.4.2 NiCd Batteries

NiCd batteries have been available as a commercial product for many decades and are well-proven products. They have very good properties concerning lifetime and lifetime cycles. They are widely used in heavy-duty applications and in very cold climates. Standard NiCd-battery designs can be operated easily at temperatures of -20°C and specially designed cells can be operated even up to -50°C . Nevertheless, NiCd batteries

Table 18.4 Overview of the technical data of different secondary batteries based on actual available products. All numbers are typical data based on the data sheets of existing products. The data are not the theoretical limits for the different technologies. Products for special applications may have technical parameters outside the ranges displayed in the table

Battery technology	Electrolyte	Energy density [Wh/kg]	Energy density [Wh/l]	Efficiency η_{wh} [%]	Life-time [a]	Typ. cycle-lifetime [cycles]	Temperature for operation		Typical applications (examples)
							Standard charging [°C]	Discharging [°C]	
Lead acid	H ₂ SO ₄	20–40	50–120	80–90	3–20	250–500	–10 to +40	–15 to +50	Stationary application (UPS, autonomous power supplies), traction, SLI
NiCd	KOH	30–50	100–150	60–70	3–25	300–700	–20 to +50	–45 to +50	Power tools, hobby toys, consumer products, traction, applications as for lead acid batteries with higher power requirements or lower ambient temperature, electrical cars
NiMH	KOH	40–90	150–320	80–90	2–5	300–600	0 to +45	–20 to +60	Laptop, mobile phones, camcorder, electric vehicles, hybrid cars, hobby toys
Li-ion, Li-polymer	Organic, polymers	90–150	230–330	90–95	–	500–1000	0 to +40	–20 to +60	Laptop, mobile phones, Camcorder, smart cards
RAM		70–100	200–300	75–90	–	20–50	–10 to +60	–20 to +50	Consumer products, hobby toys
SuperCaps		1–10	2–15	90–95	~10	500 000	–25 to +75	–25 to +75	For applications with typical cycle periods of less than 10 s at very high power requirements
NaNiCl	β -AlO ₂	~100	~150	80–90	–	~1000	+270 to +300	+270 to +300	Hybrid vehicles, electric vehicles (prototypes available)

have a bad image due to the cadmium content, which is, known to be environmentally incompatible.

Several different types of NiCd batteries are in the market with differences in the plate technologies and the handling of evolved gases.

The basic reaction is the same for all construction types of NiCd batteries.



During discharge, trivalent NiOOH is reduced under consumption of water to divalent Ni(OH)₂. Metallic cadmium is oxidised to Cd(OH)₂. The reversible backward reactions proceed during charging.

The potassium hydroxide electrolyte (KOH) does not undergo a significant change in its concentration or density during charging or discharging. Only water, which is present in high concentrations, participates in the reaction. The electrolyte density is about 1.2 g/cm³.

NiCd batteries are available with liquid electrolyte and as sealed, maintenance-free types [3].

The rated voltage of NiCd cells is 1.2 V. Although the discharge rate and the temperature significantly affect the discharging behaviour of all electrochemical cells, the effect is noticeably less pronounced in NiCd batteries than in lead acid batteries. As a result, NiCd batteries can be discharged at higher rates, without the accessible capacity falling much below the rated capacity. Even for discharge rates of $5 \times C_5$ a high-performance NiCd battery can supply 60 to 80% of the rated capacity. Also, the influence of the temperature on the capacity is comparatively small which is due to the fact that diffusion processes have less impact on the reaction kinetics compared with lead acid batteries.

High temperatures in the range of 40°C and more should be avoided as the charging efficiency is getting very low and the self-discharge rate is increasing significantly. Self-discharge rates at 20°C are in the range of 20%/month. The energy efficiency is in the range of 60 to 70%, which is significantly less compared to lead acid batteries.

A NiCd battery can withstand occasional deep discharge, inverse charging and also freezing of the cells without direct damage.

NiCd cells have a low internal resistance. Typical values for the DC resistance are between 0.4 and 2 mΩ for a fully charged 100 Ah cell. The internal resistance is largely inversely proportional to the cell size for all cell types. Falling temperatures and a decrease in the SOC increase the internal resistance, but the internal resistance remains essentially constant up to a DOD of 60 to 80%, and only increases significantly at higher DODs. Thus, the internal resistance is not a suitable indicator to determine the state of charge.

Under normal operating conditions, a NiCd battery can reach up to 2000 100% DOD cycles even under severe operating conditions. Depending on the application and the operating conditions, the lifetime can be between 8 and 25 years. Starter batteries for diesel generators reach lifetimes of about 15 years, batteries for train lighting achieve 10 to 15 years and stationary batteries have lifetimes of 15 to 25 years. Good charging

(charge factors of approximately 1.2), frequent overcharging and frequent full discharges are necessary to achieve long lifetimes.

A number of factors are responsible for the high reliability and the very long lifetime of NiCd batteries: the design is mechanically very robust, the cells are not easily damaged by incorrect technical handling, such as inverse charging, overcharging and long idling periods at medium or low states of charge and the reactants involved are not very corrosive with regard to the electrodes and other components in the cell.

One drawback is the so-called memory effect, which occurs under some operating conditions. This term is used to describe the tendency of the battery to adapt its electrical properties to the cycling conditions in which it has been operated over a long period of time. This means that a battery that is cycled over prolonged periods up to a certain DOD, tends to limit discharging to this DOD even if a higher discharge at high discharge current is planned. This effect can be resolved by discharging the battery several times with a low current. In modern NiCd batteries, this effect is not very pronounced any more.

Despite the good electrical properties, the market share of NiCd batteries in autonomous power supply systems is not very high due to the high costs. Investment costs for NiCd batteries are round about a factor of 3 higher than lead acid batteries.

18.4.3 Nickel-metal Hydride (NiMH) Batteries

The active material of the positive electrodes of a nickel-metal hydride (NiMeH or NiMH) battery in its charged state is NiOOH, the same material as in a NiCd battery. The negative active material in the charged state is hydrogen, a component of a metal hydride. The metal alloy is subjected to a reversible absorption/desorption process during charge and discharge of the cell. The reaction for the reversible charge/discharge process is indicated below [11].



An aqueous solution of potassium hydroxide is the main component of the electrolyte. Only a small amount of electrolyte is used in sealed nickel-metal hydride cells, most of which is absorbed in the separator and the electrodes. In the cell, oxygen can be transported from the positive to the negative electrode and can recombine there with hydrogen to form water. Thus, the cells can be used like dry cells and can also be installed in any desired position.

The discharge characteristics of sealed nickel-metal hydride cells are very similar to those of sealed NiCd cells. The open-circuit voltage is between 1.25 and 1.35 V/cell, and the nominal voltage is also 1.2 V.

The electrical characteristics are quite similar to NiCd batteries even though their energy efficiency is about 80 to 90% and the maximum power available is less than that in NiCd batteries. The latter is of little relevance in autonomous power supply systems. Memory effects are less pronounced than in NiCd batteries. Self-discharge at 25°C is also in the range of 20%/month, but at 45°C it is as high as 60%/month.

Nickel-metal hydride batteries are not as robust against polarity reversal as NiCd batteries. If the positive electrode gains a negative potential, hydrogen is generated at

the positive electrode. Some of the gas can be absorbed by the metal of the negative electrode, but the rest remains as gas in the cell. If the discharge is continued, oxygen is formed at the negative electrode, which further increases the gas pressure and leads to oxidation of the metal electrode. When the overpressure is large enough, the safety vent opens and the gas pressure falls again. To avoid this, appropriate measures must be taken especially if long series-connected strings are used. References [12, 13], and Chapter 19 of this book discuss a number of possible solutions for this problem.

Nickel-metal hydride batteries have replaced NiCd batteries in the market for portable appliances (e.g. mobile phones, camcorders and power tools) to a large extent due to their better environmental compatibility and their higher gravimetric energy density (Figure 18.7). However, NiMeH batteries are not commercially available in larger capacities as necessary for autonomous power supply systems. The reasons for this are mainly the costs that are actually approximately five times higher than the lead-acid batteries. Currently, there is no evidence that NiMeH batteries will play a major role in storage for autonomous power supply systems except for small technical appliances with some 10 Wh. It is more likely that Lithium batteries may enter this market, but NiMeH batteries are seen as an interim technology between NiCd and Lithium batteries.

18.4.4 Rechargeable Alkali Mangan (RAM) Batteries

Alkali-mangan cells are well known as primary batteries for several decades. Over the past few years this technology has entered the market as a secondary battery. In the beginning, the primary batteries were used and recharged. Meanwhile, rechargeable alkali-manganese (RAM) cells are in the market specially designed as a secondary battery. RAM batteries are gas tight. The nominal voltage is 1.5 V/cell and is therefore 25% higher than that of NiCd or NiMeH batteries. Currently, only small batteries with capacities of up to 5 Ah are in the market. They are significantly less expensive than the NiCd batteries. RAM cells have higher inner resistance than all other batteries discussed here. RAM cells are much more environmentally compatible than NiCd batteries as they contain no heavy metals.

The major drawback is the low deep-cycling lifetime of the RAM cells. Up to now only approximately 20 to 50 full cycles (100% DOD) are available. However, if only very shallow cycles are required (1–5% DOD), several thousands of cycles can be achieved. Even though RAM cells are currently not suited to larger autonomous power supply systems, they are interesting storage systems for small appliances with limited lifetime or usually very shallow cycling like, for example, some kinds of toys. Emergency lighting systems may be another field of application where normally only the surveillance electronics need any power (recharged by a small PV generator) and only in case of an emergency the full capacity is needed.

18.4.5 Lithium-ion and Lithium-polymer Batteries

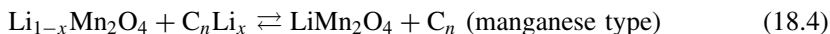
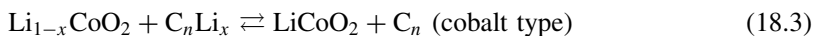
Lithium batteries have been the most emerging battery technology over the last few years. Primary lithium batteries were already well known due to their very high energy density and shelf lifetimes of up to 10 years without any major self-discharge. Nowadays, lithium-ion and lithium-polymer batteries have captured the market for portable applications like

camcorders, mobile and cordless phones and organisers. Even though they are not used in larger autonomous power supply systems today, it is worth having a closer look at this technology. Their electrical properties concerning efficiency and charge/discharge characteristics are very well suited to these applications. At the moment, lithium batteries are by far too expensive for applications where the high gravimetric energy density is of little benefit. However, as this is an emerging technology and cost reductions in the manufacturing process are expected, they might play a role in some autonomous power supply applications in the next few years.

The lithium-ion rechargeable battery's operation is based simply on lithium ions migration between the cathode and anode. Lithium-ion rechargeable batteries are therefore fundamentally different from non-rechargeable lithium and, for example, secondary lead acid or NiCd batteries in that the basic form of the cathode and anode materials does not change.

When the battery is charged, the lithium ions in the cathode material (lithium compound) migrate via a separator into the layer structure of the carbon material that forms the anode, and a charging current flows. During discharging, the lithium ions in the carbon material migrate backwards to the cathode material. This is known as the "rocking-chair" principle. Even though a large number of different material combinations are known under the name of lithium ion batteries, the most important materials for the commercial products are of the LiCo and the LiMn type.

The reactions for the reversible charge/discharge process are indicated below.



Li-ion batteries of the modern types as marketed today have a nominal voltage of 3.6 V. As this is far above the water-electrolysis voltage of 1.23 V, no aqueous electrolytes can be used anymore. The electrolyte here is an organic solvent with dissolved lithium salts. The cathode material is lithium cobaltite (LiCoO_2) or lithium manganese oxide spinel (LiMn_2O_4). The anode material is graphite of coke (graphitised carbon).

Lithium-ion rechargeable batteries have a three-layer structure consisting of a porous separator sandwiched between sheet-like cathode and anode materials, which, in the case of a prismatic cell, are wrapped around in an elliptical form. These materials are impregnated in an electrolyte and sealed in a metal case. This metal case includes a safety vent to protect the battery by releasing gas externally if the pressure inside the cell builds up to extreme levels.

Lithium batteries are potentially risky due to their very high energy density and the reactivity of metallic lithium. Incorrect handling of a lithium rechargeable battery may cause heat, explosion or fire. Therefore, it is even more important with this battery type to assure overcharge protection, over-discharge protection, over-current protection, short-circuit protection and operation at too high temperatures. Today, lithium batteries are only supplied with an integrated control electronic as a protection device. It works independent of all external chargers or monitoring devices and is therefore fully controlled by the battery manufacturer.

The main differences between the lithium-ion and the lithium-polymer batteries can be described as follows. Lithium ion batteries have a fluid organic electrolyte while the negative electrode is made from a lithium/carbon intercalation electrode. The electrolyte has a high conductivity. The non-metal electrode increases the safety in comparison with a Li-metal electrode. What is sold today as lithium-polymer batteries is in fact a combination of a polymer electrolyte and a lithium/carbon intercalation electrode. The use of the polymer simplifies the manufacturing. Strictly speaking the so-called lithium-polymer batteries are polymer lithium-ion batteries.

The lithium-polymer cell is just entering the market. In the long run, it is expected that lithium-polymer batteries can be manufactured at lower costs than lithium-ion batteries. Further, they allow very flexible battery designs. This makes lithium-polymer batteries an interesting solution for chip integration or smart cards, but also larger capacities for power applications are available for field demonstrations now.

Compared to NiCd or nickel-metal hydride batteries, a disadvantage of lithium batteries is that they are less tolerant to operations with high currents, which makes discharge at high currents noticeably more difficult. Also, they currently do not achieve the same cycle life as NiCd or nickel-metal hydride batteries. However, both points are subject to R&D and especially concerning the power rating, significant steps forward have been achieved.

Lithium batteries require constant current/constant voltage charging (Figure 18.23a). The recharge behaviour is very good. Full charging of the battery is not as important as with lead acid batteries to achieve adequate lifetimes. However, the voltage limit must be observed very accurately. The end-of-charge voltage is limited to 4.1 V and must not be extrapolated by more than 50 mV. High voltage causes the formation of metallic lithium. In series-connected cells, it must be assured that the voltage limits are kept within the acceptable limits for each individual cell.

The discharge of lithium batteries must be restricted to the material-specific end-of-discharge voltage. Again, over-discharge leads to the formation of metallic lithium. For the cobalt type, the end-of-discharge voltage is 2.3 V/cell and for the manganese type 2.7 V/cell. Figure 18.8 shows the discharge curves of a lithium-ion battery at different discharge currents. The battery capacity only slightly depends on the discharge current. In addition, Figure 18.9 shows the temperature dependence of the discharge curves. As the ion migration depends strongly on the temperature, the low-temperature performance is not too good.

18.4.6 Double-layer Capacitors

Conventional capacitors have a dielectric between the electrodes. Their capacity is determined by the dielectric number and the area of the electrodes. The so-called double-layer capacitors have an ion-conducting electrolyte between the electrodes. Therefore, an agglomeration of charge carriers at the interface between the electron-conducting and the ion-conducting interface is possible. The interface is called the electrochemical double layer. In contrast to secondary batteries, no chemical reaction and no charge transfer from the electrode to the electrolyte happened. Therefore, no changes in the material structure occur resulting in cycle lifetimes of several hundred thousands. The storing of energy

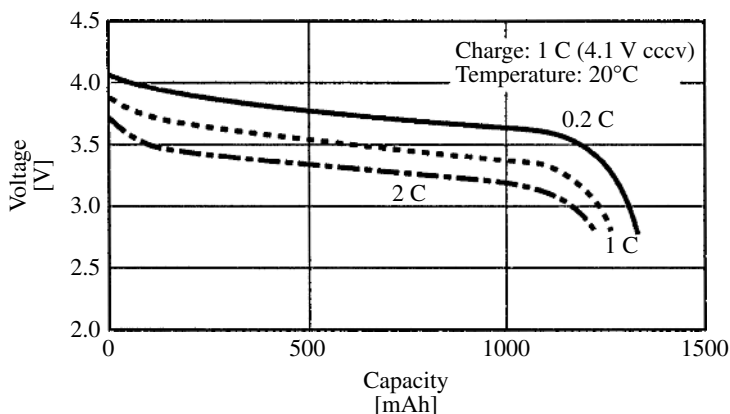


Figure 18.8 Voltage during discharge of a Li-ion battery with $C_5 = 1350$ mAh capacity as a function of the discharged capacity at different discharge currents and a temperature of 20°C. The charging is done with the constant current–constant voltage (cccv or IU , see Sub-section 18.4.7.6.1) regime with a charge current of 1 C and an end-of-charge voltage of 4.1 V [14]

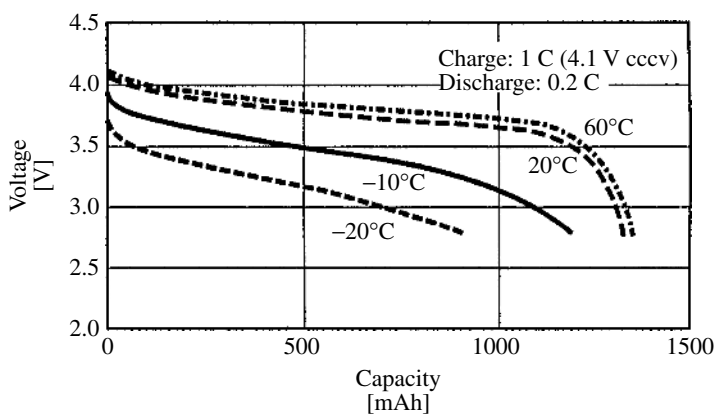


Figure 18.9 Voltage during discharge of a Li-ion battery with $C_5 = 1350$ mAh capacity as a function of the discharged capacity at different battery temperatures at a discharge current of 0.2 C. The charging is done as in Figure 18.8 [14]

only depends on the electrostatic effect. However, in contrast to classical capacitors in which in the dielectric only electrons are moved, in double-layer capacitors a movement of ions and therefore a significant mass movement occurs. This results in diffusion-time constants during charging and discharging in the double-layer capacitor.

Depending on the electrode material, the capacity is approximately 20 to 40 $\mu\text{F}/\text{cm}^2$. The electrode materials are typically made of carbon with very high surface areas of approximately 2000 m^2/g . The number of charge carriers in the double layer is limited because with increasing charge-carrier density the potential increases. If the potential is too high, the charge carriers are forced to penetrate the electrode/electrolyte interface resulting in electrochemical reactions like in secondary batteries. However, in this case

this is an irreversible effect and destroys the double capacitor. An additional problem is that in many double-layer capacitors aqueous electrolytes are used and the gassing must be avoided as well (start of water electrolysis at 1.23 V). Therefore, the maximum voltage needs to be limited to approximately 1.5 to 2.0 V. To avoid the electrolysis problem, organic electrolytes are used which allow maximum voltages of 3 to 4 V, but they have significantly lower conductivity than aqueous electrolytes. Therefore, for applications with very high power requirements capacitors with aqueous electrolytes are used; if higher energy density and lower power is required organic electrolytes can be used. Because overcharging of the double-layer capacitors will destroy them, a careful single-cell control is necessary when they are operated in long strings of series-connected cells.

Double-layer capacitors are often known by their brand names like SuperCaps or GoldCaps. They all are based on the above-described technology.

The self-discharge of double-layer capacitors is in the range of 5%/day at 20°C. Especially at higher temperatures, the self-discharge rate (approximately doubling of the self-discharge rate with a 10-K temperature increase as in all electrochemical systems) is hardly acceptable for autonomous power supply systems.

The electrical characteristics are dominated on one hand by the low inner resistance (resulting in high power) and on the other hand by the linear decrease in voltage with the state of charge. On one hand, this allows easy estimation of the state of charge, but on the other hand the voltage drop is very high and increases the requirements of the electronics or limits the usable energy from the double-layer capacitor (e.g. operation only between 1.7 and 2 volts).

Today, double-layer capacitors are available in units of up to some thousand farads. Their gravimetric and volumetric energy density is very low (Figure 18.7), but they may have power densities up to 5000 W/kg. Therefore, double-layer capacitors are most suited to applications with very high power requirements and low energy demand. As double-layer capacitors are a new and emerging technology, it is difficult to give definite cost figures. For orientation purposes, a cost of approximately 50 000 euro/kWh can be estimated today. However, to supply a current of 200 A at 2 V for 2 seconds the cost is approximately 10 euro for the storage.

For autonomous power supply systems, double capacitors are an interesting technology in applications with peak power demand or for smoothing of power flow. These are, for example, pumping systems where pumps have a very high power demand to overcome the initial inertia. Another application might be grid-connected PV inverters with power quality control functionality. They are more efficient with a milli second storage system. As a rule of thumb, it can be assumed that double-layer capacitors can find their place in applications with discharge times of less than 10 s per cycle (for “power storage”) or in combinations with conventional batteries. The big advantage of the capacitors is their almost unlimited number of cycles until the end of their lifetime (several hundred thousands).

18.4.7 The Lead Acid Battery

Lead acid batteries have been commercially used for more than 100 years for storing electrical energy. It has been the most widely used storage system for electrical energy

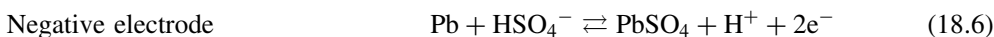
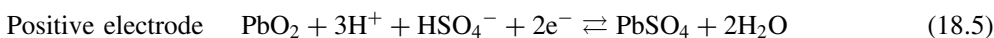
for decades and still remains so. Lead acid batteries cover a wide range of applications from SLI batteries in cars and trucks to uninterruptible power supplies, from load-levelling batteries for grid stabilisation to traction batteries (fork-lift trucks and others) and last but not the least autonomous power supply systems. Different battery designs have been developed for different applications to cover the various requirements.

Lead acid is by far the cheapest battery type in comparison to all other readily available storage systems with appropriate characteristics according to the list given in Table 18.1. A major drawback of the lead acid battery is the low specific gravimetric energy content due to the high molecular weight of lead. However, this is not a parameter of major importance in autonomous power supply systems as the battery is stationary.

It is expected that the lead acid battery will remain as the working horse for autonomous power supply systems for many more years, probably decades. Therefore, this chapter gives a deeper insight into the lead acid battery. The lead acid–battery chemistry, a detailed description of the battery design, ageing effects and recommendations for the operating strategy are the main topic of the following sections.

18.4.7.1 Lead acid–battery chemistry

Lead acid batteries in the charged state consist of a positive electrode with lead dioxide (PbO_2) and a negative electrode with lead (Pb) as the active materials. Both electrodes contain a support grid, which is made from hard lead alloys. Sulphuric acid (H_2SO_4) diluted to 4M or 5M is used as the electrolyte. The following reaction equations describe the main reaction:



PbO_2 and Pb are both converted to lead sulphate PbSO_4 during discharging (double sulphate theory). Sulphuric acid as the electrolyte is used up during the discharging of the battery. Therefore, the concentration of the sulphuric acid decreases linearly with the state of charge. This is an important difference with respect to almost all other battery types, where the electrolyte has only the function of an ion conductor. In lead acid batteries, it is in addition the source for the ions to counterbalance the charge dissolved in the electrolyte from the electrochemical process. Therefore, the electrolyte is subject to “structural” changes like the electrode materials themselves. This is an important reason for several battery characteristics and ageing effects as will be discussed later.

In Section 18.2.1.2, it was described that during charging and discharging not only the electrochemical process described by the Butler–Volmer equation occurs but a chemical process takes place as well. Figure 18.10 shows a schematic of this overall process for the lead electrode which is described by equation (18.6).

The charged electrode consists of lead (Pb) in the solid state. When a discharge current occurs, two electrons are withdrawn from the metallic lead and dissolution of Pb^{2+} ions into the electrolyte occurs. Through diffusion, the charged ions are transported

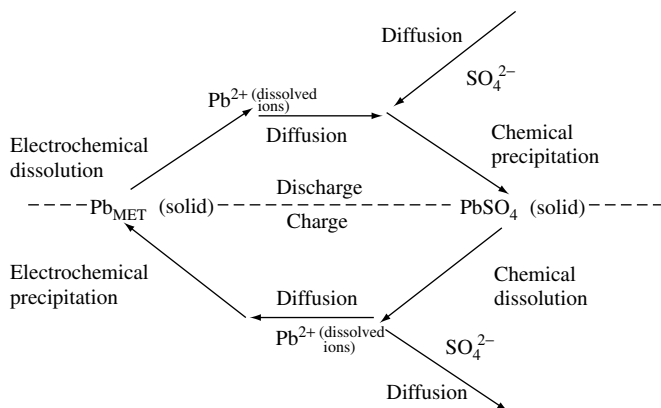


Figure 18.10 Schematic of the charge/discharge process in the lead electrode of a lead acid battery

away from the reaction surface. As the charged ions unbalance the number of positive and negative ions in the electrolyte, negatively charged ions are necessary to counterbalance the positive surplus. They are provided as SO_4^{2-} ions from the sulphuric acid electrolyte. The SO_4^{2-} ions are transported by diffusion from the free electrolyte volume to the reaction site of the electrochemical reaction. There, the Pb^{2+} and the SO_4^{2-} ions meet and form PbSO_4 by a chemical precipitation process. This finally results in the formation of PbSO_4 crystals.

During charging, the reverse process takes place. Pb^{2+} ions are taken from the electrolyte to form solid Pb during the electrochemical precipitation process. These ions are transported by diffusion processes to the reaction site. To stabilise the Pb^{2+} ion concentration in the electrolyte, a chemical dissolution process of the PbSO_4 crystals takes place. Because the positive ions are removed from the electrolyte through the electrochemical precipitation process, the SO_4^{2-} ions need to be transported away from the reaction site to assure electrical neutrality.

All these processes cause overvoltages.

1. Electrochemical dissolution with respect to precipitation described by the Butler–Volmer equation.
2. Transport of Pb^{2+} ions described by the diffusion law resulting in diffusion overvoltages.
3. Transport of SO_4^{2-} ions described by the diffusion law, law of migration of charged ions in an electrical field and fluid dynamics caused by the change in the pore volume during charging and discharging resulting in diffusion overvoltages.
4. Chemical precipitation or dissolution of the PbSO_4 crystals forced by deviations of the ion concentration in the electrolyte from the equilibrium concentration resulting in concentration overvoltages.

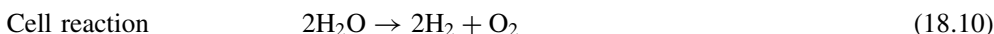
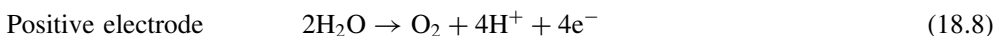
All processes depend on the temperature. Further, the processes depend on the electrolyte concentration. The concentration influences the equilibrium current density of the Process 1, the diffusion rate of ions in Processes 2 and 3 and it has a strong impact on the

equilibrium concentration of the Pb^{2+} ions and hence on the Process 4. Ageing of the battery and the operating conditions (high currents, small currents and pulse currents) have a significant impact on the overvoltages caused by Processes 1 and 4. This is mainly caused by changes in the inner active surface on the charged active material side (Pb) as well as on the PbSO_4 side.

The nominal voltage of a lead acid battery is 2.0 V; the open-circuit voltage of a charged battery is about 2.1 V, depending on the concentration of the electrolyte.

The open-circuit potential of the positive electrode in a fully charged battery is approximately +1.75 V against the standard hydrogen electrode. The negative electrode potential is approximately -0.35 V against the standard hydrogen electrode. The relationship between the electrolyte concentration and the electrode potential with respect to the cell potential can be seen from Figure 18.14. The dependence of the open-circuit potential on the temperature is as small as 0.2 mV/K. Therefore, it can be neglected for practical reasons.

In addition, there is the main side reaction – the water electrolysis. As the electrolyte is aqueous and the cell voltage is approximately 2 V and can be as high as 2.5 V, water electrolysis takes place continuously. Hydrogen and oxygen are produced at the negative and the positive electrodes, respectively. Hydrogen production starts at electrode potentials more negative than 0 V against the standard hydrogen electrode. Oxygen evolution starts at electrode potentials more positive than 1.23 V. Fortunately, the so-called overvoltages at lead electrodes for the gas production are very high and therefore the gas production is inhibited to a high extent. This allows the lead acid battery to be stable even at the high cell potential of 2 V. The self-discharge rate caused by the gassing is approximately 2 to 5% per month.



Very comprehensive handbooks on lead acid batteries have been written by Bode [15] on the fundamentals and by Berndt [3] on valve-regulated batteries.

18.4.7.2 Lead acid batteries – technology, fundamentals, concepts and applications

All the different types of lead acid batteries discussed in the following text are based on the reaction equation presented above. Whereas Figure 18.11 shows a complete battery system in an autonomous power supply system, Figure 18.12 shows the schematic construction of the electrochemical $\text{Pb}/\text{H}_2\text{SO}_4/\text{PbO}_2$ cell.

Solid lead grids, rods or plates serve to conduct the current (grid) and to mechanically stabilise the porous active mass in both electrodes. Depending on the battery type, different lead alloys for the grid are used to increase the stability, improve the tooling properties and to reduce corrosion. The porous active material is attached to the grid



Figure 18.11 A battery in a photovoltaic system with a rated capacity of $C_{10} = 37.5$ Ah and a rated voltage of 168 V (flat-plate technology, 28 blocks of 6 V connected in series, Picture courtesy Fraunhofer ISE)

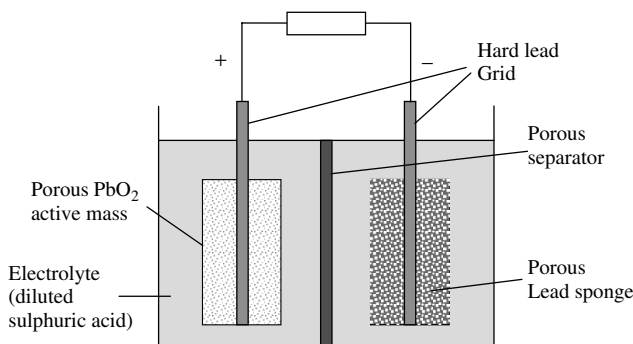


Figure 18.12 Schematic construction of a $\text{Pb}/\text{H}_2\text{SO}_4/\text{PbO}_2$ cell

PbO_2 (lead dioxide) for the positive electrode and to the Pb sponge for the negative electrode. Figure 18.13 shows a more detailed view of the structure of the active material. The active material has an internal surface area of approximately 0.5 to $5 \text{ m}^2/\text{g}$ for the negative and the positive electrode in the fully charged state. The reaction speed and thus the charging and discharging properties are determined by the internal surface. Both electrodes are completely immersed in diluted sulphuric acid (H_2SO_4). As described earlier, the sulphuric acid plays a double role as the ion conductor between the electrodes and a reagent in the charge and discharge reactions. While the battery discharges, the PbO_2 and Pb are converted to PbSO_4 (lead sulphate). The sulphate ions (SO_4^{2-}) are drawn from the electrolyte, causing the electrolyte concentration to fall.

It is worth mentioning that the ratio of the specific volumes of PbSO_4 and Pb is 2.4 and the ratio between PbSO_4 and PbO_2 is 1.96. This means that the solid-phase volume of the active materials increases during discharge. This reduces the free electrolyte volume in the pores and causes mechanical stress on the active material.

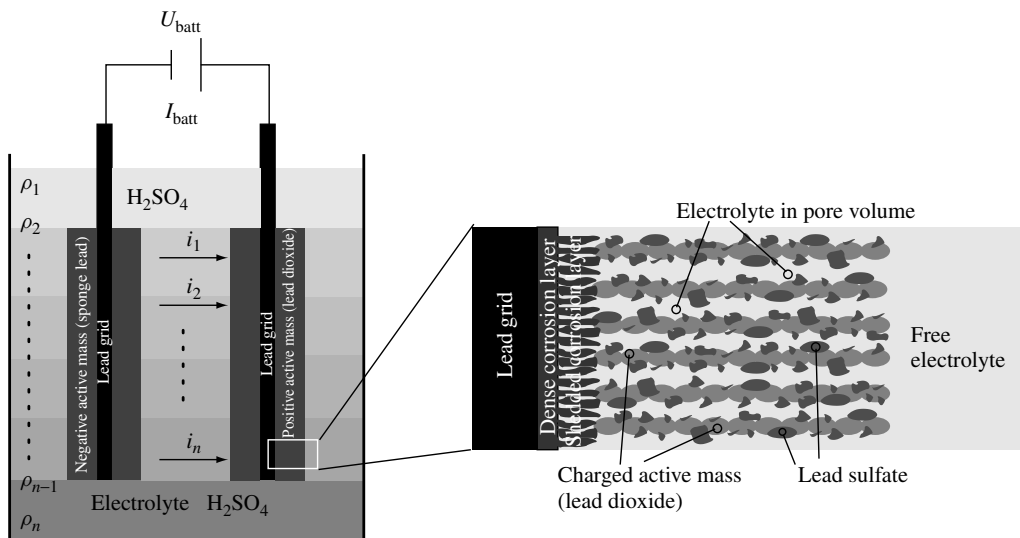


Figure 18.13 A more detailed schematic drawing of the lead acid battery. The left-hand side shows a macroscopic view of the cell including effects like acid stratification represented by the different electrolyte densities in different horizontal heights of the battery followed by inhomogeneous vertical-current distribution within the electrodes. The right-hand side shows a “microscopic” view of the active material in a partial state of charge

A separator is located between the electrodes, intended to prevent short circuits between the electrodes.

The above-described water electrolysis increases significantly as a function of voltage and temperature. As a rule of thumb, an increase in the so-called gassing rate by a factor of two is caused by an increase of 10 K in the temperature and by a factor of 3 by an increase in the cell voltage by 100 mV.

Regarding the hydrogen and the oxygen created as a result of the electrolysis reaction, two different technologies can be distinguished. In so-called flooded batteries, the electrolyte is in the liquid phase. To allow the gases to emerge from the battery, batteries with liquid electrolyte are not sealed gas tight. However, this results in a decrease in the water content of the battery and therefore the electrolyte level decreases and the concentration of the sulphuric acid increases. The water loss needs to be compensated during the maintenance that should take place once or twice a year. Deionised water must be used for refilling and not sulphuric acid or tap water.

The so-called valve-regulated lead acid (VRLA) batteries are sealed gas tight with a valve. The valve allows the release of gas only in the case of overpressure in the battery. In normal operation, the gas is recombined to water within the battery. This effect is achieved by an immobilisation of the electrolyte. Two different techniques are state of the art: the electrolyte is transferred into a viscous gel by adding SiO_2 to the electrolyte or the electrolyte is absorbed within a highly porous glass matt (absorbed glass matt type – AGM). In both cases, the oxygen can pass through the electrolyte to the negative electrode. The recombination of oxygen and hydrogen occurs

at the negative electrode. In VRLA batteries, the electrolyte is not in the liquid phase and therefore no spillage of electrolyte occurs in case of any break of the case or other accidents.

However, if the battery is incorrectly overcharged, more gas is generated than can recombine, so the gas must be able to leave the cell through the valve if an overpressure builds up. At the same time, the valve must prevent ambient air from entering the battery. As these batteries cannot be refilled with water, blowing off the gas from the cell must be reduced to a minimum to prevent the cell from drying out. As a rule of thumb, after more than 10% water loss the battery is at the end of its lifetime. The water loss can be estimated by the weighting of the battery.

To achieve low gassing rates in VRLA batteries, normally lead–calcium alloys are used for the grids. Flooded batteries use mainly lead–antimony alloys with less than 2.5% antimony (Sb). This is a good compromise among the beneficial effects of antimony grids (good grid conditions for casting and good contact of the active material to the grid result in low contact resistance) and the harmful effect of the reduction of the hydrogen overvoltage caused by the antimony. However, as gassing needs to be minimised in VRLA batteries, antimony grids are not an appropriate choice. Especially, in the early days of the VRLA batteries, the antimony-free grids caused a significant reduction in battery lifetime through the so-called antimony-free effect. This effect is described in the literature as premature capacity loss (PCL) [16].

While the rated capacity of a cell depends on the geometry and the number of parallel-connected electrodes, the rated voltage of a cell is 2.0 V. The open-circuit voltage U_0 of the cell depends on the electrolyte concentration as shown in Figure 18.14, but for practical purposes the open-circuit voltage can be determined by the following rule of thumb:

$$\frac{U_0}{V} = \frac{\rho}{\text{g/cm}^3} + 0.84 \dots 0.86 \quad (18.11)$$

where ρ is the density of the electrolyte. Electrolyte concentration and electrolyte density have an almost linear relation. As the electrolyte density can be easily measured, the electrolyte density is often used to express the electrolyte concentration. At 25°C, 30% H_2SO_4 in H_2O has a density of about 1.22 g/cm^3 and 40% H_2SO_4 in H_2O has a density of 1.30 g/cm^3 . Typical electrolyte densities in fully charged batteries are between 1.22 and 1.32 g/cm^3 , depending on the application, the technological type and the climatic conditions. The acid density in the discharged state is between 1.18 and 1.05 g/cm^3 . According to equation 18.11, the open-circuit voltage also varies with the density. It is not a constant by any means.

Figure 18.14 shows the correlation between the electrode and cell potentials and the acid concentration. The acid concentration can be measured by means of the concentration in mol/l, the density in g/cm^3 and the percentage of acid in the solution %_{weight}. This allows the translation of all values to one another.

According to equation (18.7), the electrolyte concentration decreases during discharge. According to equation (18.11) the open-circuit voltage decreases in a manner directly proportional to the acid concentration. VRLA (sealed) batteries have less electrolyte per ampere-hour capacity than flooded batteries. Therefore, the open-circuit voltage

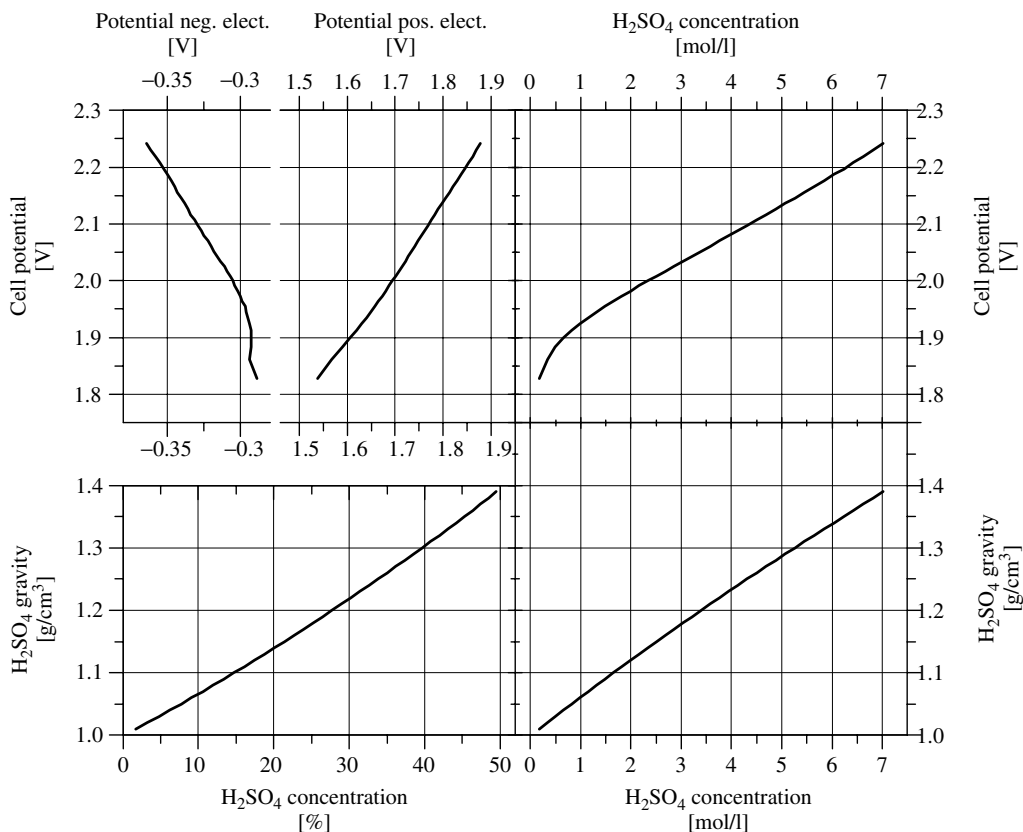


Figure 18.14 Correlation between the acid concentration in percent, mol/l or density and the equilibrium potential of the negative and positive electrodes and the cell potential. The graphs allow converting each value to the other

decreases more rapidly in sealed batteries during discharge than in flooded batteries. This must be taken into account, if the voltage is used as an SOC indicator.

Today, two different plate technologies are commonly used. The most common type of plate is the flat plate (Fauré type). The porous active mass is applied to the hard lead grid as a paste. The flat plate is simple and cheap to produce. The so-called tubular plates¹⁰ are also widespread. A central lead rod, surrounded by active material, is inserted into a protective tube that is permeable to the electrolyte. A plate then consists of a row of adjacent tubes. While flat-plate electrodes have lower internal resistance and therefore higher specific power than tubular plates, the latter show more cycles in their lifetime. Manufacturing of tubular plates is more expensive than the manufacturing of flat plates. Figure 18.15 shows schematics of a flat-plate and a tubular-plate electrode. Currently, wounded lead cells come into the market consisting of a thin lead foil pasted with active material and with a very thin glass-mat separator between the electrodes. These batteries

¹⁰ Tubular-plate electrodes are not very common in North America. Traditionally, tubular-plate batteries are more popular in Europe for cycling applications like, for example, fork-lift trucks.

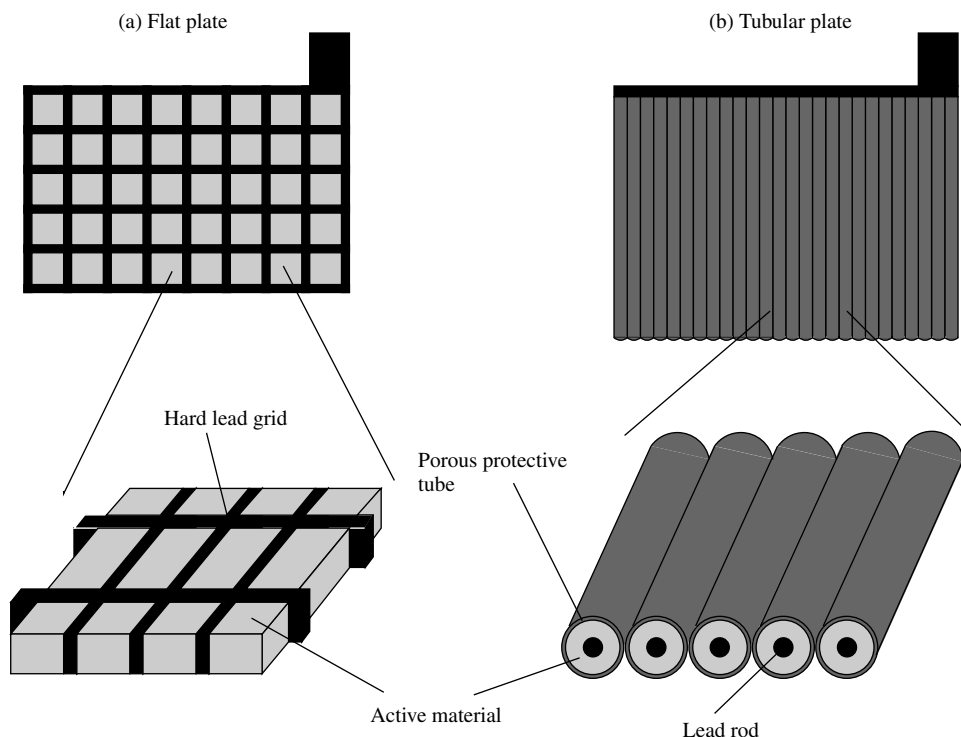


Figure 18.15 Schematic diagram of (a) a flat-plate electrode and; (b) a tubular-plate electrode

are primarily used in high-power applications like the ignition of motors. The first results show good cycle-life behaviour.

Lead acid batteries are used today in many different applications, therefore a large variety of application-specific batteries are in the market. They can be distinguished by their specific power, their cycle life and their float lifetime. Float lifetime is the relevant parameter for batteries in uninterruptible power supplies where the batteries are subjected to only very few cycles in case of failure of the mains, but they should have long operating lifetimes while always being 100% charged. The main battery types for different applications and their typical operating conditions are as follows:

SLI (starting, lighting, ignition) batteries: Used for starting of engines; very high power capabilities even at low temperatures; traditionally only very low capacity throughput; subject to high temperature fluctuations; the largest global market for lead acid batteries with respect to the capacity; production companies in almost all countries throughout the world; the operation profile is changing in modern cars as cars have a very high power demand beside starting owing to numerous electric applications in cars like seat heating, electric window lift or HiFi systems. The batteries are made from very thin flat-plate electrodes to achieve high power. SLI batteries are a mass product, highly automated and are therefore very cheap.

UPS (uninterruptible power supply)/stationary batteries: Long idle periods at full SOC; rapid discharge when required (discharge time in the range of 10 min to 1 h, in some applications even longer); designs for lifetimes of up to 20 years available and market grows strongly in connection with the expansion of telecommunications and computer systems. The electrodes are thicker than for SLI applications to withstand corrosion for long periods.

Traction batteries: Application in fork-lift trucks, traction engines, underground mining vehicles and so on; designed for daily complete cycling with moderate currents and regular and controlled complete charging and cycle lifetimes of 1000 to 2000 cycles with 80% DOD can be achieved. The most common electrode technology in these applications is tubular-plate. Flooded batteries show longer lifetimes than VRLA and are widely used.

Electric-vehicle batteries: Widely fluctuating current profile; partial recharging phases (regenerative braking); inadequate lifetimes to date; expanding market and strong competition from other types of battery technology (see Table 18.3). Low gravimetric energy density is a major drawback in this application. Lead acid batteries based on thin pasted lead foils and wounded design are currently under development and are already available in the market from some manufacturers to serve hybrid vehicles¹¹ that are seen at the moment as a more realistic option than purely battery-powered electric vehicles. Wounded cells have very high power capability and therefore can serve electric motors for accelerating and regenerative braking.

Batteries for photovoltaic systems: Operating conditions corresponding to the load profiles illustrated in Section 18.3; complete charging very seldom and many partial cycles. Two classes of so-called “solar batteries” are in the market. One class is the modified SLI battery with typically thicker grids than those used in SLI batteries, quite cheap (often from local production in developing countries [17]) but with limited lifetime. The other class of “solar batteries” are modifications from high-quality batteries originally used for cycling or standby applications. In general, flooded batteries show better lifetimes in autonomous power supply systems than VRLA batteries. On the other hand, VRLA batteries have significant advantages concerning electrolyte spillage, maintenance and transport and very little release of corrosive and explosive gases. This reduces the requirements on the battery housing significantly. Therefore, a final choice must be made according to the specific application and the boundary conditions.

Operational experience, however, reveals that the lifetime of batteries in stand-alone applications based on solar energy is in general unsatisfactory compared to battery lifetimes in traditional applications. Batteries in solar home systems normally have to be exchanged after 2 to 3 years and batteries in hybrid systems after 3 to 8 years. Lifetime extensions to 5 years in solar home systems and 10 years in hybrid systems are achievable with advanced batteries designed for the purposes of autonomous power supply systems and appropriate system designs and operation strategies.

¹¹ Hybrid vehicles have a conventional motor but with less power than in traditional cars. Acceleration is supported by electric motors powered by the batteries. The batteries are charged during regenerative braking and from the main motor. This concept allows the conventional motor to run with small variations in power and therefore at higher efficiencies. Fuel consumption was reduced with this concept in prototypes down to 2 l/100 km.

18.4.7.3 Discharge capacity

The capacity that can be withdrawn from lead acid batteries depends strongly on the discharge conditions.

For stationary batteries usually the C_{10} or C_8 capacity, for starter batteries usually the C_{20} capacity and for traction batteries usually the C_5 capacity is specified. Solar batteries often are rated as C_{100} and C_{120} at 100 or 120-h discharge current, respectively. Typical end-of-discharge voltage is 1.8 V/cell or 1.85 V/cell for C_{10} , C_{20} and C_{100} . For C_5 , 1.7 V/cell is commonly used. All other ratings and voltage limits can be found as well.

The measured and the practical capacity increase when the discharge current decreases. If a battery is discharged with a lower current than the rated current, a higher capacity than the rated capacity can be withdrawn. If the state of charge is specified with respect to the rated capacity (a reasonable convention), negative values for the state of charge can arise. This is the reason Figure 18.6 displays negative states of charge.

Figure 18.16 shows the voltage during discharge as a function of the discharged capacity at different discharge currents. The lead acid batteries' capacity depends very much on the discharge current.

As a rule of thumb, it can be assumed that a battery with a nominal capacity of 100 Ah at C_{10} has approximately 50 Ah at C_1 and approximately 130 Ah at C_{100} . Please note the fact that the corresponding currents I_1 and I_{100} are not equivalent to $10 \times I_{10}$ res. $0.1 \times I_{10}$. In this example, I_1 is 50 A and I_{100} is 1.3 A.

With respect to the electrical properties, the temperature influences the inner resistance (increasing conductivity of the electrolyte with increasing temperature), the diffusion

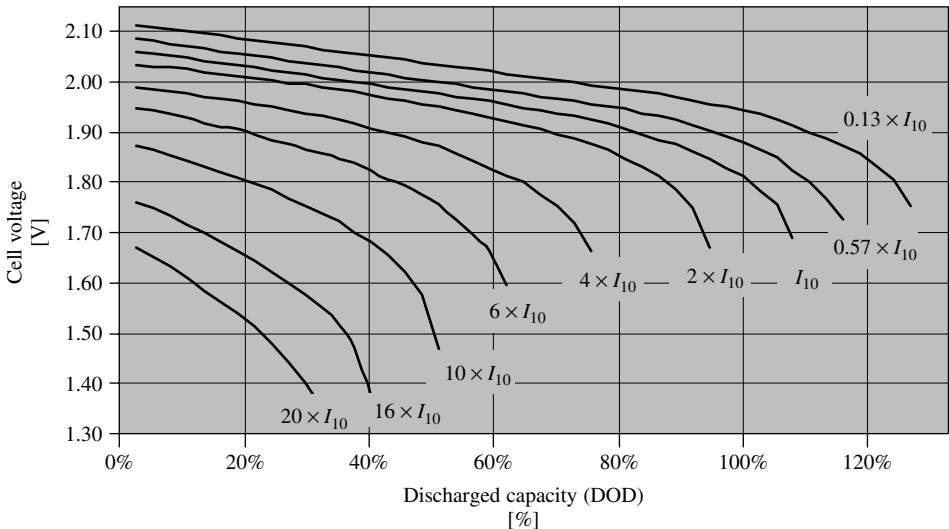


Figure 18.16 Voltage during constant discharge as a function of the discharged capacity at different discharge currents (tubular-plate lead acid battery, C_{10} capacity defined at I_{10} and 1.8 V), data from Berndt D, *Blei-Akkumulatoren* (Varta), VDI-Verlag, 11. Auflage, Düsseldorf (1986) [18]

processes and the reaction at the electrochemical double layer. Therefore, the capacity of lead acid batteries depends strongly on the temperature. The capacity increases almost linearly by approximately 0.6%/K with an increase in temperature. The capacity decreases in the same way with decreasing temperatures. Depending on the battery technology, the temperature coefficient can be as high as 1.0%/K.

18.4.7.4 Ageing processes and their influence on the battery properties

A comparison with other battery systems, for example, NiCd batteries, reveals that the relatively short lifetime of lead acid batteries is a significant disadvantage. However, the operating behaviour of the batteries is already affected during the lifetime by the processes responsible for ageing. Thus, it is helpful to be aware of the most important ageing processes and to avoid the conditions that accelerate them.

18.4.7.4.1 Acid stratification

Acid stratification is not an ageing process but affects the operating behaviour of the battery. On one hand it reduces the available capacity and changes the current/voltage characteristics. On the other hand it leads to inhomogeneous current distribution at the electrodes. The latter effect accelerates sulphation (Section 18.4.7.4.2), which is a major ageing effect. Therefore, acid stratification is a reason for ageing and not an ageing effect by itself. Acid stratification in flooded batteries can be removed immediately by stirring the electrolyte.

Because the electrolyte functions as an active component of the electrode reaction, local variations in the density can arise, with the result that the acid density decreases in the upper part of the cell and increases in the lower part. The potential difference associated with the concentration difference leads to discharging of the lower section of the electrodes, which can result in irreversible ageing effects (e.g. sulphation).

In batteries with liquid electrolytes, the acid stratification can be eliminated by deliberate overcharging, associated with gas production. The same mixing effect can be achieved by active circulation of the electrolyte. Such electrolyte stirring systems are made from an air bubbling system (Figure 18.22).

Electrolyte stratification can also occur in batteries with immobilised electrolytes. In a gel battery, the effect is very small and therefore is of little relevance. In AGM batteries, the strength of acid stratification depends very much on the quality of the glass mat. Large battery cells from AGM technology are mounted vertically to avoid any acid stratification. While purchasing the batteries, it is important to check the manufacturer's specifications regarding vertical installation of the battery. The problem with VRLA batteries is that an existing acid stratification cannot be removed.

From theoretical consideration [19, 20], it is obvious that small currents in conjunction with acid stratification lead to a significant undercharging of the lower part of the electrodes. This effect is getting more and more pronounced with smaller battery currents. When an acid stratification occurs, the upper part of the electrodes is charge preferential and the lower part is discharge preferential. This results in differences in the local state of charge between the upper and the lower part of up to 30%. During the limited charging

times, the upper part can reach a very high state of charge while the lower part is by far not completely charged. This means, that the lower part of the electrode is cycled in lower states of charge than from the average state of charge of the electrode. Further, the lower part is cycled without a full charge for extended periods.

These findings are confirmed twofold by experimental results. On one hand, it was possible to show experimentally the effect of inhomogeneous current distribution and the state of charge within the electrode as a function of the charge/discharge currents [20]. On the other hand, almost all physicochemical analysis of lead acid batteries from PV systems at the end of their lifetime shows a high degree of sulphation in the lower part of the electrodes [21, 22].

Another problem related to acid stratification in batteries with liquid electrolytes is that a measurement of the acid density, made at the only accessible position above the electrodes, does not give any direct information on the battery's state of charge.

As an example, Figure 18.17 shows the correlation between the acid density above the electrodes in a flooded battery and the battery's state of charge for a battery from a PV system, with a large number of partial cycles.¹² Without acid stratification, a measured acid density of, for example, 1.18 g/cm³ corresponds to a real state of charge of approximately

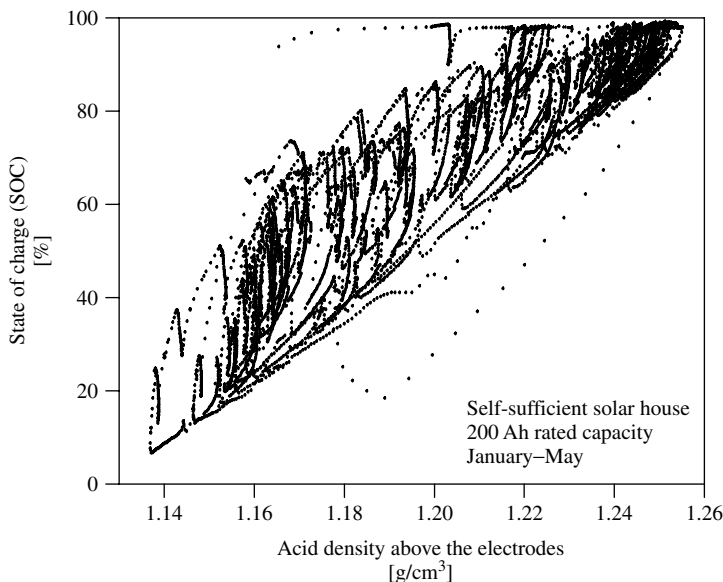


Figure 18.17 Acid density above the electrodes versus the actual state of charge, measured over five months for a battery from a photovoltaic system (200 Ah cells, simulated acid densities based on measured initial data 10-minute average values)

¹² Figure 18.17 is based on a detailed battery model including modelling of the vertical acid-density distribution. The model was verified by measurements in a battery. The model and verification are described in [19]. Therefore, the state of charge and the acid density above the electrode displayed in Figure 18.18 are calculated by the model. The calculations are based on detailed measurements of the battery current, voltage and temperature in the system.

30%, whereas it can range between approximately 30% and 75% if the acid is stratified. This measurement only allows a lower limit to be estimated. A measurement of the acid density above the electrodes can lead to appreciable errors in determining the state of charge and thus in associated operation-management measures.

18.4.7.4.2 Sulphation

When the electrodes are discharged, the active masses, PbO_2 and Pb , are transformed into PbSO_4 . The size of the sulphate formed depends on the strength of the discharge current – high discharge currents result in small sulphate crystals. If a battery is not recharged soon after its discharge, the sulphate crystals grow as a result of recrystallisation processes. The rate of recrystallisation is linearly correlated with the solubility of sulphate ions. Unfortunately, the solubility of sulphate ions increases with decreasing acid concentration [15]. Therefore, periods of low states of charge (and hence low acid concentrations and high sulphate solubility) harm the battery by accelerating the growth of large sulphate crystals. During subsequent charging, large sulphate crystals with their relatively smaller active surface are re-dissolved more slowly than smaller ones, so that sulphate crystals are still present when charging is nearly finished. Figure 18.18 illustrates that for the same volume, small crystals have a larger surface area than large ones (two-dimensional representation of the three-dimensional effect).

During the course of the operation, these remaining sulphate crystals can accumulate, reducing the active mass and thus the accessible capacity [23]. Sulphation can be reduced to a minimum if each discharging process is rapidly followed by sufficiently complete charging. The effect of acid stratification is that complete charging is seldom achieved for the lower part of the electrode, so that strong sulphation occurs there. This sulphation effect can be clearly seen in the cross-sections of Figure 18.19.

As a result of sulphation, the amount of active material available for normal charging and discharging operations decreases. This reduces the capacity, and the voltage during discharge is also shifted to lower values. If sulphation is too pronounced (as in the lower section shown in Figure 18.19), larger areas of the electrodes can become completely inactive.

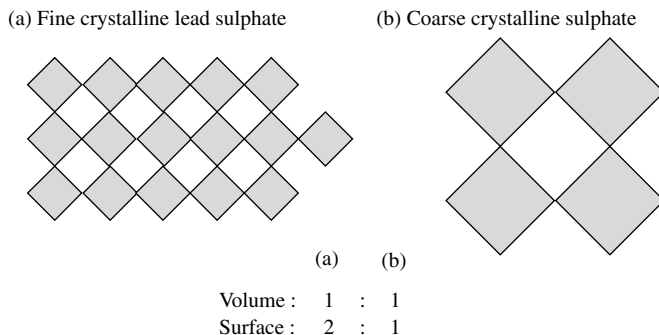


Figure 18.18 An example illustrating the effect of the crystal size on the active surface area of the electrodes. Mass ratio a:b = 1:1, surface area ratio a:b = 2:1

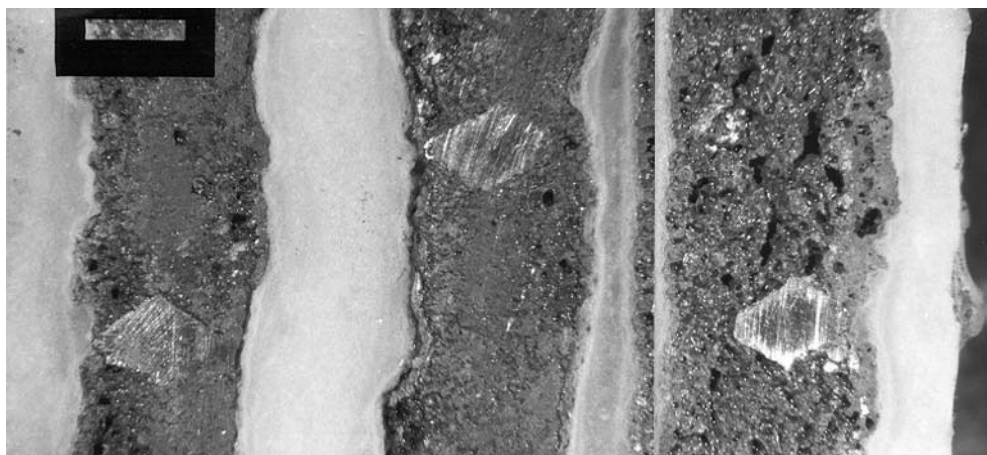


Figure 18.19 Cross-section of a negative flat-plate electrode after 3.5 years of operation in a photovoltaic system. The sections were taken from the upper, central and lower parts of the electrode (from left to right, respectively). Sulphation is clearly indicated in the lower section by the very coarse pores between large crystals, and by the noticeable broadening of the electrode, due to the difference in the specific volumes of Pb and PbSO_4 (Photo source: ZSW)

18.4.7.4.3 Corrosion

The high positive potential at the positive electrode results in the corrosion of the lead grid [24]. On one hand, this causes the cross-section of the grid to decrease, so that the grid resistance increases. On the other hand, a layer consisting of lead dioxide, lead oxide and lead sulphate forms between the grid and the active material, which also raises the contact resistance. This becomes evident during charging and discharging as an increased ohmic voltage drop. Figure 18.20 shows the cross-section of a tubular electrode from a battery after 3.5 years of operation. The lead core (grid rod in the centre of the tube) has almost completely disappeared due to corrosion.

The corrosion rate depends on the acid density, the electrode potential, the temperature, the grid alloy, the active material coverage [25] and a most important factor, the manufacturing quality of the grid. Corrosion is particularly pronounced for cell voltages below 2.0 V and above 2.4 V [24]. Corrosion is minimal for cell voltages around 2.23 V. Corrosion is an irreversible ageing effect and increases the internal resistance of the battery. An indirect consequence is that the current distribution becomes more inhomogeneous in the vertical direction, so that sulphation is accelerated in the lower parts of the electrodes. In batteries for PV systems, thicker grids are used to reduce the effect of corrosion and thus extend the lifetime.

18.4.7.4.4 Erosion

Both electrodes are subjected to strong mechanical loads during cycle operation. The reason is that up to 50% of the active material is converted to lead sulphate during discharge. Lead sulphate has a volume per mole, which is 1.94 times larger than lead dioxide and 2.4 times larger than lead.

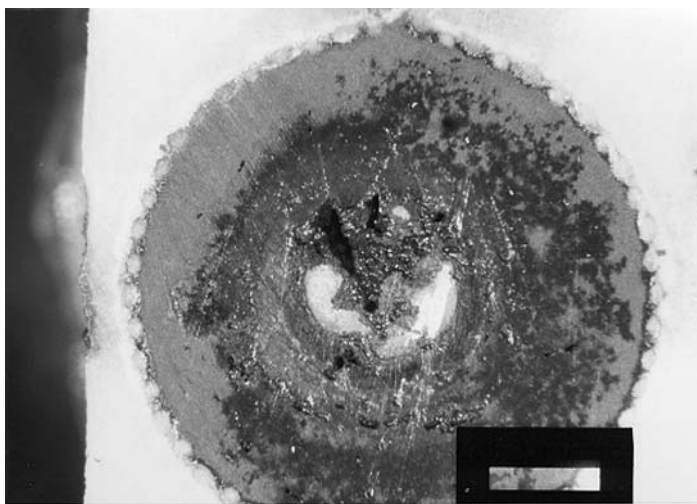


Figure 18.20 Cross-section through a tubular electrode of a battery after 3.5 years of operation. The lead rod (light-coloured area in the centre) has almost completely disintegrated as a result of corrosion. The diameter of the electrode is 8 mm. (Photo source: ZSW)

These large changes in volume act to loosen the active material. This effect increases with increasing depth of discharge. Thus, deep discharge with low currents has an additional negative effect on sulphation. Once the active material has become loose, it can be separated from the electrode, for example, by gas movement, and gathers as sludge at the base of the battery. If the volume below the electrodes that contains the sludge is not large enough, there is a danger of short circuits between the electrodes.

The erosion effect is much less pronounced in sealed batteries, as the electrodes there can be mounted under pressure. The pressure compensates the forces arising from the volume change and increases the stability of the active masses.

The available active mass at the electrodes is reduced by the loss due to erosion. This corresponds directly to a reduction in the accessible capacity. Accordingly, the battery will be discharged earlier.

18.4.7.4.5 Short circuits

In addition to the danger of short circuits in the sludge volume of batteries with liquid electrolytes, there are two further risks for short circuits.

The plate connectors from the positive electrode above the active material are also subject to corrosion. This results in detachment of large corrosion flakes, which can fall onto the electrodes and cause short circuits. This risk can be eliminated by including separators that extend upward well over the electrodes.

Further, there is a risk for all battery types that dendrites (microscopic short circuits) may grow from the positive to the negative electrode through the separators. These dendrites are so fine that they are usually not visible even when the battery is investigated

in the laboratory. Their growth is accelerated by long periods at a low state of charge and thus low acid concentrations. As described in Section 18.4.7.4.2, the solubility of PbSO_4 increases at low acid concentrations. For example, the solubility of PbSO_4 is 2 mg/l at a sulphuric acid density of 1.28 g/cm³, and is already 35 mg/l at a density of 1.02 g/cm³. The higher the solubility the higher is the rate of recrystallisation and hence the rate of formation of large sulphate crystals and dendrites. The danger of dendrite growth can be counteracted by thicker separators and by operating the battery at high states of charge.

In general, a short circuit is a defect that causes a sudden and complete breakdown in the battery. Short circuits can occur from dendrites between the electrodes and the sludge in flooded batteries from active material accumulated as a result of active-material shedding under the electrodes. If the amount of material exceeds the free-electrolyte height under the electrodes, short circuits occur through the “mud”. Microscopic short circuits through the separator affect particularly the self-discharging properties of a battery.

18.4.7.4.6 Reverse charging

If a battery is subjected to a discharging current even after the battery has been fully discharged, the potential changes its sign.

Reverse charging of an individual cell can occur in strings of series-connected cells. The battery voltage and therefore the depth of discharge protection are controlled on the basis of overall string voltage. A single cell within the string may have lower capacity due to manufacturing deviations or due to accelerated ageing. In consequence, the low-capacity cell can be over-discharged resulting in reverse charging.

In case of reverse charging, PbO_2 is formed at the original Pb electrode and vice versa. Although this type of reverse charging can sometimes increase the capacity for a short time, it is certainly detrimental to the cell lifetime in the long term. The main cause of damage is the oxidation of additives in the lead sponge of the negative electrode, which are included to maintain the high porosity of the electrode. If these additives are destroyed, large lead crystals form in the negative electrode resulting in a loss of internal surface area and therefore in an irreversible loss of capacity.

The danger of reverse charging can be reduced if the voltage of the individual cells is monitored and used as the criterion to end discharging (rather than the total voltage of the battery). Alternatively, it can be prevented by allowing charge equalisation between the cells of a series connection [12].

18.4.7.4.7 Ice formation

Figure 18.21 shows the dependence of the freezing point of diluted sulphuric acid on the electrolyte concentration. Ice must be prevented from forming in a battery under all circumstances, as it is then practically impossible to operate the battery (in particular, a frozen battery can hardly be charged) and it is possible that the cell housing may burst (battery breakdown and contamination of the surroundings with sulphuric acid).

For operating modes with very low discharge currents, or if the deep-discharge protection is inactive or non-existent, it is possible to reach extremely deep discharge,

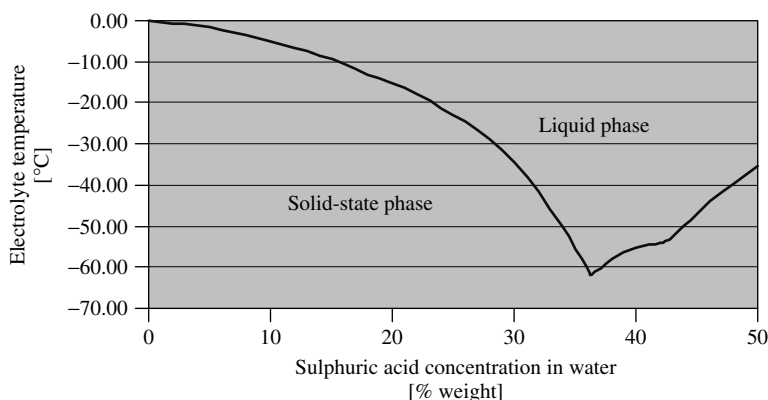


Figure 18.21 Freezing point of diluted sulphuric acid as a function of the acid concentration

as the voltage does not break down until very late in the process. Batteries that are subjected to temperatures below the freezing point should be dimensioned such that after withdrawing $1.3 \times C_{100}$ or $1.7 \times C_{10}$, the acid density is still so high that freezing is not expected, according to Figure 18.21.

18.4.7.5 Battery peripherals

For proper battery operation, several battery peripherals must be used. The following gives a brief description of the most important devices.

Charge controller: Charge controllers are responsible for the charging strategies and the deep-discharge protection. They limit the power from the PV generator if necessary. More details on the operation strategies are given in Section 18.4.7.6 and on the hardware in Chapter 19.

Chargers: Chargers are AC/DC converters that use the power from motor generators to recharge the battery. They need a charge control as well to avoid overcharging of the battery. The charging regime should be the same as for charge controllers.

Charge equaliser: In long strings of series-connected cells, problems with individual cells like overcharging and reverse charging can occur owing to differences in the ageing processes or tolerances in the production. Charge equalisers avoid the detrimental effects by individual treatment of the cells. More details are given in [13] and in Chapter 19.

Monitoring: To get actual information of the state of the battery, monitoring systems can be used. A wide range of commercial products is available. They range from simple voltage monitoring of the complete battery to complete monitoring of temperature, current and voltage of individual blocks and cells as well as impedance of the battery.

State-of-charge meters: For proper battery operation (Section 18.4.7.6) and for the orientation of the user, it is helpful to have proper information on the actual state of charge of the battery. Several devices and algorithms are available, but only very few are really suited to autonomous power supply systems [26].

Electrolyte-agitation systems: To avoid the detrimental effects of acid stratification in flooded batteries, electrolyte-agitation systems are an effective solution. Figure 18.22 shows a battery with an agitation system. Most systems are based on compressed air that is pumped to the bottom of the cells. The ascending air bubbles cause an electrolyte circulation and mixing.

Recombinators: To reduce the loss of water from flooded batteries, recombinators are used. They consist of a catalyser that recombines the hydrogen and oxygen gas evolving from flooded batteries. Figure 18.22 shows a battery with recombinators.

18.4.7.6 Operation strategies

The operation strategy and the charging strategy have an important impact on the battery lifetime. Therefore, in the following paragraphs some ideas on appropriate strategies are discussed.

In most PV systems, the system and the battery control are realised through the charge controllers; in some cases energy management systems take over this job. The battery requires proper handling of frequent full charges, gassing for electrolyte-stirring in flooded batteries, control of end-of-charge voltage and deep-discharge protection.



Figure 18.22 Flooded, tubular-plate battery (2×240 Ah in parallel connection, 12 V) with gas recombinators for reduction of water loss through gassing and an electrolyte-stirring system to avoid acid stratification (only connected to the right hand unit), the membrane air pump is mounted on the wall, operation of the pump: twice a day for 15 min, (Picture courtesy Fraunhofer ISE)

18.4.7.6.1 Charging

As a result of the specific operating conditions, full charging occurs very rarely. Charge and discharge cycles follow each other very frequently. Long charging times at constant power supply as available in grid-connected systems do not occur. Nevertheless, field experience showed that full charging is necessary to achieve long battery lifetimes.

The most common charging strategy is the constant current/constant voltage mode (IU or cccv, Figure 18.23(a)). In autonomous power supply systems, this means that the battery is charged with the fully available power until the battery voltage reaches the defined end-of-charge voltage. From this moment, the charging power to the battery is limited in a way that this voltage limit is not exceeded (constant voltage mode). The voltage drops at the moment when the battery charging is not high enough (due to decreasing power generation or increasing load) to maintain the battery voltage at the given limit. Most charge regulators and battery chargers use this charging procedure.

A more advanced charging method is shown in Figure 18.23(b). The charging starts with a constant current/constant voltage charging, but the maximum voltage is reduced after a certain time to a lower limit (IU_0U). This allows higher voltages during the first constant-voltage phase, but avoids negative effects like gassing and corrosion due to long durations of the high voltage. Therefore, this charging method allows overall faster charging but avoids hazardous conditions in the battery. More and more sophisticated charge controllers in the market use this charging procedure.

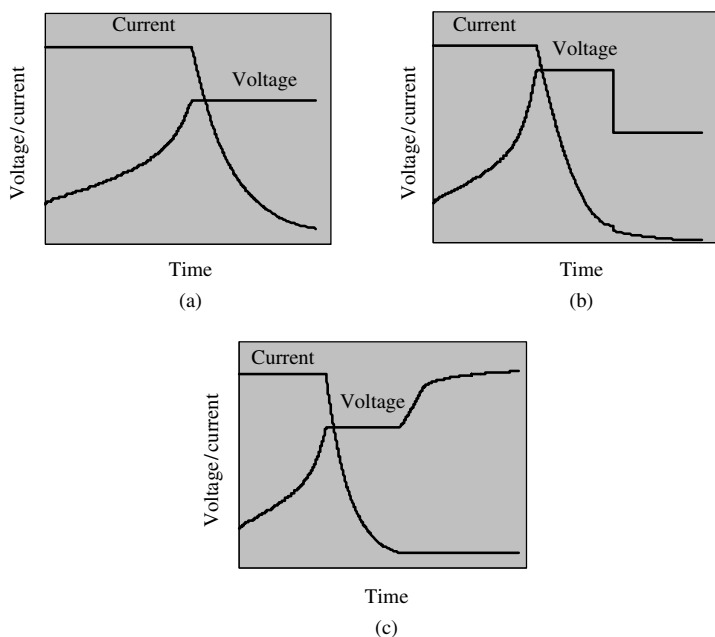


Figure 18.23 Schematics of different charge regimes. (a) Current and voltage during a constant current/constant voltage charge IU or cccv; (b) a constant current/constant voltage charge with two end-of-charge voltage limits IU_0U ; and (c) a constant current/constant voltage charge followed by a limited constant current phase $IU I_a$ are shown

Especially for VRLA batteries, it turned out that longer lifetimes can be achieved with the constant current/constant voltage/constant current (IUI_a) charging as shown in Figure 18.23(c) ([4]). After the current drops during the constant-voltage phase below the limit for I_a charging, the charging is continued for a limited time or amount of charge with a constant current. The voltage is not limited during this phase, but the I_a current must be limited in the range of I_{50} to I_{100} . No commercial device in PV applications uses such a scheme these days.

It is necessary to take into account that the batteries in PV systems hardly ever get fully charged due to the limited charging time per day [4]. Therefore, the term full charge has to be distinguished in a real full charge, defined by the point at which the complete active material is converted into charged material, and a practical or solar full state of charge (Figure 18.3). The latter is defined by the maximum state of material conversion that can be achieved during a sunny summer day or the maximum operation time of the back-up generator that is accepted by the system operator. A “solar full charge” requires at least 5 h at a battery voltage of 2.4/cell.

In hybrid systems, a solar full charging can be achieved by operation of the back-up generator or from the PV generator. Full charging every four weeks is recommended. A detailed analysis of the operational data from systems showed that this has little impact on the overall energy balance, but is obviously enhancing the battery lifetime.

For batteries in systems of Class 1, according to Figure 18.6 an end-of-charge voltage of 2.4 V/cell is appropriate. However, the duration per day at this voltage should be limited to two hours. During the rest of the day (if the charging power is available), the battery voltage should be limited to 2.3 V/cell (charging regime as in Figure 18.23(b)).

In systems of Classes 2, 3 and 4, the end-of-charge voltage should be 2.45 V/cell also limited to 2 hours per day. An end-of-charge voltage of 2.35 V/cell for the rest of the day is appropriate (charging regime as in Figure 18.23(b)).

The values are valid for flooded and for VRLA batteries. In addition, for flooded batteries an increase of the end-of-charge voltage up to 2.6 V/cell periodically for a maximum of 5 hours per 14 days is appropriate. This causes gassing and therefore stirring of the electrolyte. Nevertheless, an active electrolyte-stirring system as shown in Figure 18.22 is the best and most efficient solution.

A significant lifetime extension can be achieved if the battery is charged to a really full SOC at least twice a year. This can be achieved by charging the battery normally to a solar-full SOC followed by a complete discharge with approximately I_{10} . The discharge must be followed by a recharge according to the IUI_a charging regime (Figure 18.23c) where the battery gets charged with 110 to 120% of the ampere-hour capacity taken from the battery in the previous discharge or the nominal capacity (whatever value is higher).

The end-of-charge voltage limit depends on the battery-operating condition and on the temperature. All values for the voltage limits given here are for a battery temperature of 25°C. At increasing temperatures, the voltage must be reduced by 4 to 5 mV/(K*cell) but not below 2.25 V/cell. At temperatures below 25°C, the voltage must be increased accordingly but not above 2.6 V/cell. To protect DC loads or electronic devices connected directly to the DC bus bar, it might be necessary to limit the maximum voltage accordingly.

18.4.7.6.2 Deep-discharge protection

Lead acid batteries suffer from deep discharge for several reasons. An increasing depth of discharge results in a decreasing acid concentration and due to the increased sulphate solubility in accelerated sulphation (Section 18.4.7.4.2), corrosion (Section 18.4.7.4.3) and higher sensitivity to freezing (Section 18.4.7.4.7). Further, the mechanical stress is increased because of the changes in the specific volume of the active materials and in long battery strings, the risk of reverse charging of single cells (Section 18.4.7.4.6) increases.

Therefore, the maximum depth of discharge should be limited during normal operation.¹³

While choosing the appropriate DOD for the operation strategy, the data-sheet information given by the manufacturers should be analysed. They often give the number of cycles during the lifetime of a battery as a function of the depth of discharge. However, for the system design the number of cycles is not the most important parameter. The level of capacity throughput that can be realised during the battery lifetime is of more relevance. A cycle with 50% DOD means that only 50% of the capacity is used and therefore the overall capacity throughput for, for example, 200 cycles with 50% DOD is equivalent to 100 cycles with 100% DOD. However, from the point of view of the system design a battery which is limited to 50% DOD during normal operation must have double the size with respect to a battery with 100% DOD during normal operation. This is worthy of mention because batteries are always limited by the capacity throughput on one hand and by operation life on the other hand. Therefore, it makes no sense to operate a battery which is, for example, rated for 10 000 cycles at 20% DOD in autonomous power supply systems even though this might promise the highest capacity throughput. Assuming that on a daily basis 10 000 cycles take place, it would take more than 25 years to achieve this. However, the battery lifetime would not last that long due to other ageing processes.

Figure 18.24 shows for two different batteries the cycle life as a function of the DOD (data taken from data sheets) and the resulting capacity throughput. It is obvious that for the battery Type 2, the capacity throughput is almost independent of the DOD but for battery Type 1 there is a strong dependency leading to higher throughputs at lower DODs.

For practical purposes, the following “rules” can be used, which have proved their suitability in the field. In Classes 1 and 2 (Section 18.3.2), the maximum DOD should be 60 to 70% and in Classes 3 and 4, 80 to 90%. The lower values are for flooded batteries and the higher values are for VRLA batteries. Low-cost “solar batteries” should be operated to a maximum of 50% DOD. It is very important to take into account that the mentioned values for the DOD are given on the basis of the C_{10} capacity. Using, for example, 80% of the C_{100} capacity means using more than 100% of the C_{10} capacity and this is hazardous.

Control of the maximum DOD can be realised either by deep-discharge disconnecting voltage or on the basis of the state of charge. Most commercial charge controllers

¹³ As stated in the subsection on charging, a complete discharge of the battery to 100% DOD twice a year is of benefit to the battery. This is not in contradiction to a limited DOD during normal operation. The defined discharge is done within a short time and is followed directly by complete recharging of the battery. In normal operation, discharge times and duration in deep states of charge can be very long and the next full charging may occur only weeks or month later.

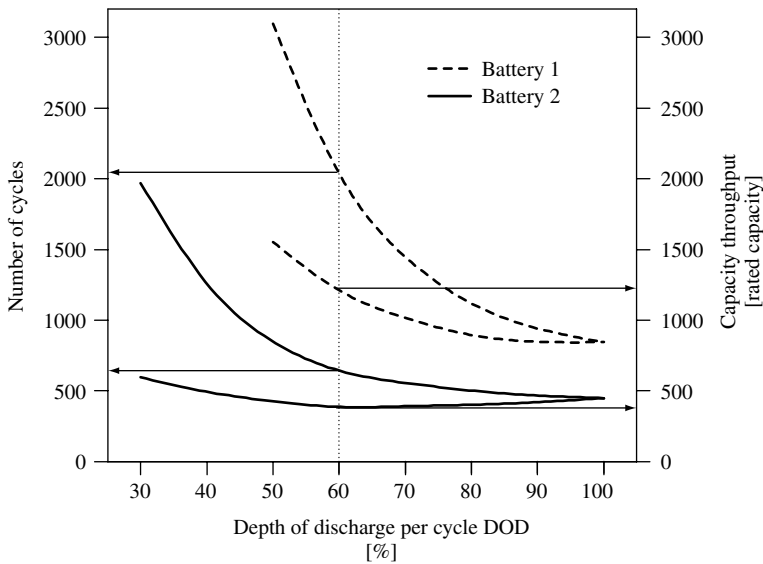


Figure 18.24 Number of cycles and overall charge transfer (capacity throughput) in units of the rated capacity during the battery lifetime as a function of the depth of discharge during cycling. Data from data sheets from battery manufacturers

Table 18.5 Typical end-of-discharge voltages up to which 100% of the C_{10} capacity has been discharged from the battery at different discharge currents at room temperature

$I_{\text{discharge}}$	U [V/cell]
$1.0 \times I_{10}$	1.80–1.85
$0.5 \times I_{10}$	1.85–1.90
$0.2 \times I_{10}$	1.90–1.95
$0.1 \times I_{10}$	1.95–2.00

control the maximum DOD by the voltage. The drawback of this method is that the discharged capacity up to a certain voltage limit depends very much on the discharge current. Table 18.5 shows typical end-of-discharge voltages up to which 100% of the C_{10} capacity has been discharged from the battery. This shows the problem of an efficient DOD control. If the maximum DOD is assured by a high voltage limit even at small currents (e.g. 1.95 V/cell), the available capacity at higher currents is very limited [27]. Figure 18.25 shows a more pronounced version of the problem. A given voltage limit might be appropriate for one battery type, but for another with the same technology (flat plates, lead acid and flooded electrolyte) the discharge curve looks quite different and the same voltage limit results in significant differences in the maximum DOD with respect to the minimum SOC defined to protect the battery as shown in the figure. The difference

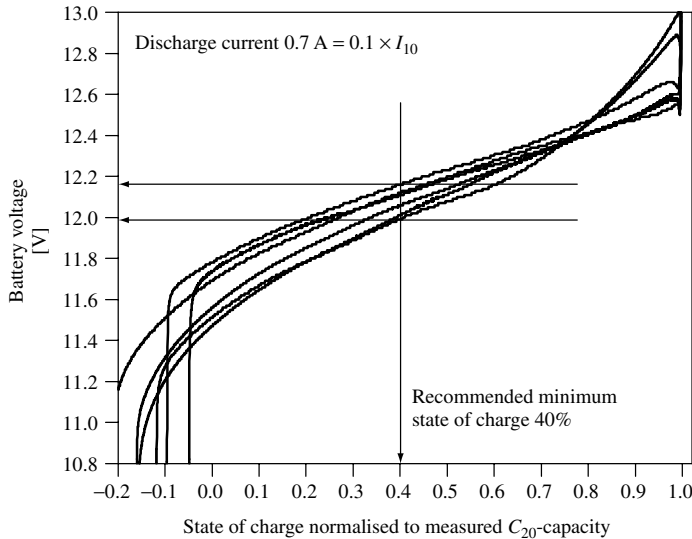


Figure 18.25 Discharge curves of six batteries rated for the same capacity, with the same technology (flat plate, flooded lead acid and all batteries new). The voltage is shown as a function of the state of charge of the batteries. The state of charge is calculated on the basis of the discharge ampere-hour and the nominal (not measured) capacity. Capacity tests were performed with $0.1 \times I_{10}$. The voltage is given for a 12-V block battery made from 6 cells connected in series (a typical design as used for SLI batteries for cars)

in SOC for the same voltage limit could be as high as 25%. Taking into account different battery technologies, the differences in SOC are even higher. In autonomous power supply systems, low and high currents occur (Figure 18.5, [9]).

Two solutions for the problem are available. One is a current-compensated end-of-discharge voltage threshold and the other is the use of state-of-charge determination. The latter solution is the most appropriate for autonomous power supply systems. There are various methods for state-of-charge determination in lead acid batteries, which are appropriate for autonomous power supply systems [26].

18.5 SECONDARY ELECTROCHEMICAL BATTERY SYSTEMS WITH EXTERNAL STORAGE

The secondary batteries described in Section 18.4 use electrodes both as part of the electron-transfer process and to store the energy via electrode solid-state reactions. Consequently, both energy storage capacity and the power rating are intimately related to the electrodes' size and shape.

Electrochemical batteries with external storage overcome this drawback. The reaction occurs within an electrochemical cell and the energy is stored in two tanks separated from the electrochemical cell. The electrochemical cell has two compartments, one for each storage medium, physically separated by an ion-exchange membrane. This allows the designing of the battery power and the energy content separately.

Here, a distinction between the so-called redox-flow batteries in which salts are dissolved in liquid electrolytes and the hydrogen/oxygen storage systems based on the electrolyser and the fuel cell will be made.

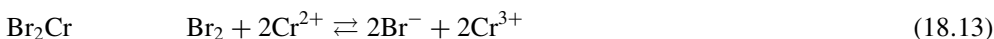
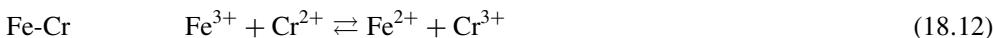
The costs for the converters and therefore the power sizing are independent of the storage size. Therefore, these systems show an economy of scale concerning the energy storage. The larger is the storage, the lower are the specific storage costs. This makes the systems interesting for seasonal storage or other long-term storage applications.

18.5.1 Redox-flow Batteries

In redox-flow batteries, the active material is made from salts dissolved in a liquid electrolyte. The electrolyte is stored in tanks. As the solubility of the salts is typically not very high, the energy density is in the range of lead acid batteries. The electrochemical charge/discharge reactions take place in the converter, which determines the power of the system. Therefore, redox-flow batteries belong to the group of batteries with external storage. Redox-flow batteries were already under investigation for stationary applications in the 1970s and 1980s. An overview of these activities can be found in [28]. Owing to problems with the materials, the investigations were almost stopped but were again started in the last year.

Redox-flow batteries work with electrolytes in two circulations. Each circulation contains a redox system whose valence is changed during charging and discharging. The change in the valence of the two redox systems should take place at preferably high potential difference as this forms the equilibrium voltage of the battery. Figure 18.26 shows the principle of the redox-flow battery with the vanadium battery (equation (18.14)) as an example. The valence of all ions during each step can be seen in the figure.

Several different combinations of salts were and still are under investigation.



Several problems with redox-flow batteries have occurred and are still unsolved. The stability of the separator and the mixing of the electrolytes through the separators are severe problems. Therefore, the vanadium system became the centre of interest in the last few years as the materials and electrolytes are similar for the positive and the negative electrodes. Therefore, a crossing of ions through the separator just causes coulomb losses, but causes no deterioration of the electrolytes.

Defining the specific energy densities is difficult because of the independent sizing of the converter and the storage. Typical values for 20 kW/20 kWh vanadium redox-flow batteries are about 20 Wh/kg and 50 W/kg. For mobile applications in electrical cars, this is not enough, but for stationary, especially in load levelling, applications it is an interesting option. Figure 18.27 shows a prototype of a redox battery at laboratory scale

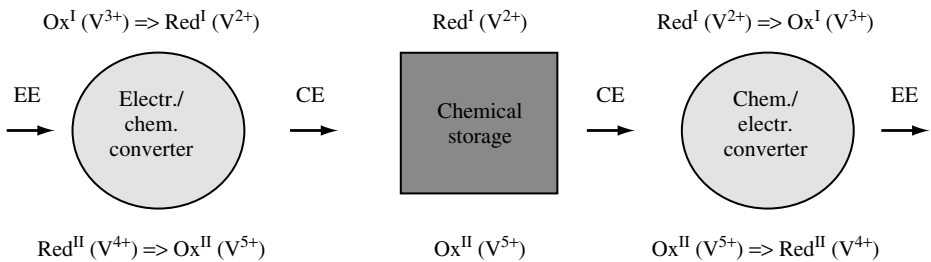


Figure 18.26 General concept of a redox-flow battery with two electrolyte/active mass circulations. The circulation in the upper row is equivalent to the negative electrode, the lower row denotes the positive electrode. In brackets, the vanadium battery is given as an example. The figure is based on an idea from [29] (EE: electrical energy, CE: chemical energy)



Figure 18.27 Prototype of a vanadium redox-flow battery with 32 cells and 14 Ah (Picture Courtesy by ZSW [29])

and Figure 18.28 shows a schematic of a redox-flow battery in the megawatt hour. As there have been no commercial products in operation for a long time, data on lifetimes are hardly available. Theoretically, long lifetimes can be expected as no part of the system undergoes structural changes as they occur in most other battery technologies. In literature, data for a vanadium battery with more than 13 000 cycles have been reported [30]. In any case, a regeneration of the electrolyte/active mass is possible. The influence of vanadium batteries on the environment is described in [31]. No material loss or “down cycling” of the electrolyte including the vanadium occurs.

What is true for the lifetime is also true for the costs. Rough estimations show, for the vanadium battery, costs of approximately 200 €/kWh for batteries with more than

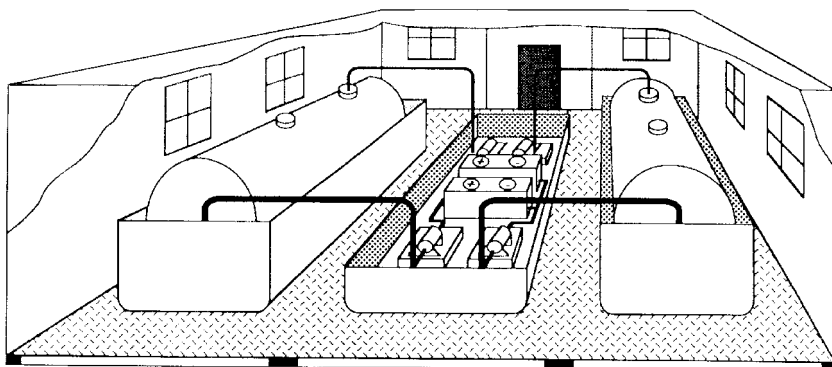


Figure 18.28 Schematic of a redox-flow battery in the megawatt hour range [29]

20 h of discharge time at full power [29]. As no mass production is established, these data are subject to speculations on the mid-term achievable cost figures.

The energy efficiency for the vanadium battery has been demonstrated to be 80 to 85% for the cell itself. As the system requires peripherals (mainly pumps for the electrolytes), the system efficiency can be in the range of 75%, which is considerably better in comparison with the hydrogen system described in Section 18.5.2. No self-discharge of the electrolytes in the tanks occurs. An optimum operation temperature for redox-flow batteries is defined by an optimum of the solubility of all the salts in the electrolyte while avoiding any recrystallisation of a salt.

18.5.2 Hydrogen/Oxygen Storage Systems

The other major technology with external storage is the use of liquid water (discharged state) and its gaseous components hydrogen and oxygen (charged state) [32].

Water can be split into hydrogen and oxygen gas by the fundamental reaction (18.16).



Electrolysis of water starts at 1.23 V/cell. A hydrogen storage system consists of three major components that are listed below:

1. An electrolyser for the production of the gases from electric power,
2. Gas storage for the hydrogen and, depending on the system's design, for the oxygen. Hydrogen is commonly stored either in pressure tanks or metal-hydride tanks.
3. A fuel cell to reconvert the gases into water and electric power. Hydrogen is taken from the storage and oxygen either from gas storage or from air.

Electrolyser/fuel cell systems have been demonstrated; the technology, however, still has to go through a long process of maturation until it reaches the market at acceptable costs and with high reliability.

18.5.2.1 Electrolyser

Electrolysers are needed to produce hydrogen and oxygen gas from water by using electric power. Electrolysis is used in many industrial processes apart from hydrogen production. Two technologies for low-temperature water electrolysis are available today:

- Alkaline electrolyzers
- Polymer electrolyte membrane (PEM) electrolyzers.

In addition, high-temperature steam electrolyzers are under investigation, which are in general good for higher efficiencies (see [33]).

Special electrolyzers can release the gases already under pressure without using an additional compressor. PEM electrolyzers can have efficiencies of 80 to 85%. They are commercially available, but are very expensive because only a few units are sold and expensive materials (membrane, catalysts) are needed. Presently, there is no important market for PEM electrolyzers in the kW range. However, larger alkaline electrolyzers for use with wind or water power plants are commercial and in operation. Reference [34] gives an overview on a research project on electrolyzers operated by wind turbines.

18.5.2.2 Gas storage

Three major technologies for hydrogen gas storage are available today:

1. Pressure tanks (low pressure up to 30 bar, medium pressure up to 200 bar and high pressure up to 700 bar).
2. Metal hydrides with adsorption of hydrogen.
3. Liquid hydrogen storage (only for large scale applications).

Low-pressure tanks can be used in conjunction with pressure electrolyzers. Specially designed electrolyzers [35] produce hydrogen and oxygen at 30 bar without any compressor and therefore a minimum of energy loss due to compression. Medium-pressure tanks or bottles can be fitted to compressors. Today, hydrogen mechanical compressors with a high efficiency for small gas volumes are hardly available. Presently, no compressors for hydrogen with flow rates below approximately 10 Nm³/h are available.¹⁴ Another technology for gas compression is thermal compression with metal hydrides. The pressure in a metal-hydride storage unit increases significantly with an increase in temperature. As different metal alloys have different pressure/temperature curves, gas compression in a multi-stage process is possible. High-pressure gas bottles from composite materials are under development and in operation in R&D and demonstration projects.

Metal hydride is an interesting material for hydrogen storage. The hydrogen is adsorbed within the highly porous metal hydride. In fully loaded metal-hydride tanks, 1 to 2% of the overall weight is hydrogen. The volumetric energy density of metal hydrides is comparable with a 200 bar pressure bottle. The pressure in a metal-hydride tank depends

¹⁴ Nm³ is the typical dimension for a gas amount. It is a gas in a volume of 1 m³ at a pressure of 1 bar and a temperature of 0°C.

on the temperature, the alloy and the state of charge. For outdoor applications, it is important to be aware that the pressure in the metal-hydride tank at constant hydrogen load approximately doubles with an increase of 20 K in temperature.

The energy content of 1 Nm³ of hydrogen gas is approximately 3.5 kWh. Depending on the fuel cell system and power-converter efficiency, between 1 and 1.8 kWh of net energy can be drawn from 1 Nm³ of hydrogen gas.

A standard 200 bar pressure bottle contains 8.8 Nm³ of hydrogen gas. The cost for metal-hydride storage systems is currently in the range of 500 to 1500 € per Nm³.

For oxygen storage, currently only pressure tanks are commercially available. Materials with adsorption properties for oxygen are under investigation. A reduction in volume by a factor of 3 has been achieved.

Nanotubes for hydrogen storage are under investigation. After a very optimistic period some years ago, the optimism has been reduced, but meanwhile there are several activities to investigate this technology which promises very low costs.

18.5.2.3 Fuel cell

As fuel cells can only replace batteries in conjunction with the hydrogen gas generation, only the polymer electrolyte or proton exchange membrane fuel cell (PEMFC) is considered here. A very comprehensive overview of all the fuel cell technologies is given in [36].

The basic reactions are given in equations (18.17) and (18.18).

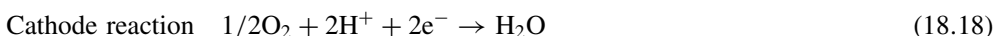
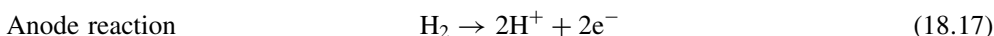


Figure 18.29 shows a schematic of a PEM fuel cell. If hydrogen and oxygen are stored, a closed-loop operation with water and gases can be realised. Then, the water demand for refilling is limited. If air is used instead of pure oxygen, the water produced in the fuel cell process gets lost with the air throughput. The water household of the membrane is one of the most challenging problems in fuel cell operation and control.

PEMFCs operate best at temperatures between 60 and 90°C. The fuel cell stack itself can operate at an efficiency of 50 to 60%. The overall fuel system has additional components beside the stack like air compressors, electronics, valves and security devices. They cause a self-consumption of the fuel cell system and therefore reduce the overall efficiency to 35 to 50%. The efficiency is higher if pure oxygen is used instead of air, but this requires an additional oxygen tank. The stack efficiency is calculated from the ratio of the fuel cell voltage during power generation and the electrochemical potential of the reactants, which is 1.23 V. The coulomb efficiency is considered as 100% even though some gas losses synonymous with coulomb losses due to the penetration of gas through the membrane occur as well.

A big advantage of fuel cells in comparison with motor generators are the high efficiency even at partial loads. Usually the stack efficiency increases with decreasing power output.

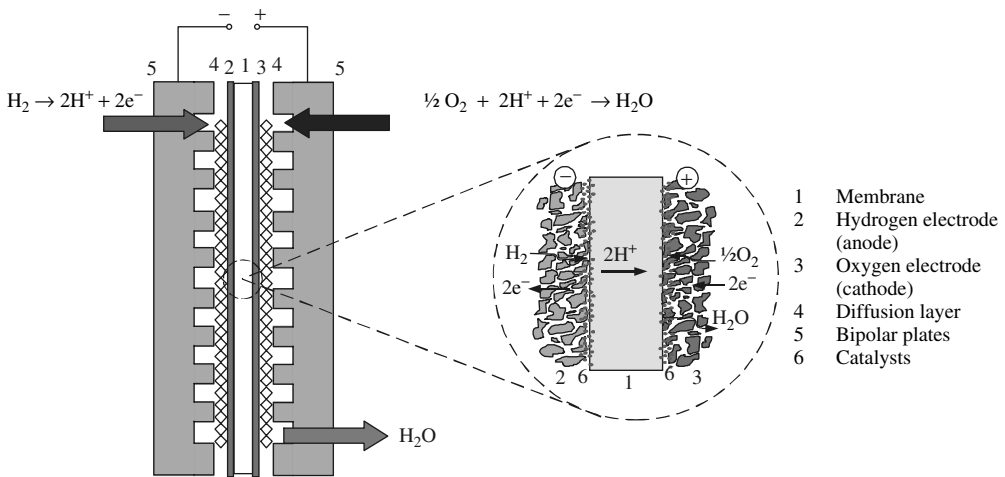


Figure 18.29 Schematic of a polymer electrolyte membrane fuel cell (PEMFC)

The current/voltage characteristic of a fuel cell is quite similar to the characteristic of a PV cell. Unlike secondary electrochemical batteries, the voltage depends very much on the current. To supply a load with a constant voltage, power electronics are necessary. The power electronics are also needed to adjust the point on the I/V curve corresponding to the actual power demand. Therefore, the operation of a fuel cell in applications with varying load demands without power electronics is impossible. Charging of a battery with a fuel cell is in principle possible. However, the fuel cell must not exceed certain current limits for a safe operation. Power electronics that limit current and voltage according to the requirements are highly recommended. Power electronics are necessary in any case if a controlled charge of a battery according to one of the charging regimes given in Figure 18.23 is necessary.

Presently, no cost figures for marketable fuel cells can be given as all available PEM fuel cells are prototypes for R&D and demonstration. However, there is a huge bunch of activities in fuel cell research. They are mainly driven by the automobile industry and by the combined heat and power generation CHP space-heating applications. The target figures for fuel cell systems in these applications are approximately 100 euro/kW for automobiles and 1000 euro/kW for CHP space-heating systems.

18.5.2.4 Applications

Hydrogen storage systems have a low overall efficiency. Even under the assumption of a fuel cell system efficiency of 50%, an electrolyser system efficiency of 85%, no energy losses for the hydrogen storage and efficiencies of 97% each for the two power-converting steps, an overall storage system efficiency of 40% maximum is achievable. Compared with approximately 90% efficiency in lead acid or lithium batteries, this is rather small and rules out the hydrogen system as the principle and only energy storage unit in autonomous power supply systems. This will be the fact as long as the power production is as expensive as it is now. Secondly, the specific storage costs per kilowatt

hour with the hydrogen system must come down to the values of today's lead acid batteries and thirdly, the technical reliability of the complex hydrogen system must be as high as with conventional batteries. The hydrogen storage system is far away from all these goals and these goals will be hardly achieved within the next decade.

One interesting line of development is the reversible fuel cell RFC. RFCs fulfil the functionality of the electrolyser and the fuel cell at the same time. As the process is completely reversible, this is an obvious solution. Technical problems concerning the catalysts and the gas and water management within the cell have to be solved [37]. No commercial products for field applications are available in this technology today.

Applications in autonomous power supply systems will have a combined storage system made from a conventional battery and the hydrogen system. Figure 18.30 shows a principle system design as it is currently under development within an R&D project [38]. The hydrogen system here substitutes the conventional motor generator, which is used today in hybrid systems to bridge the energy gap between summer and winter. A conventional lead acid battery (five days of autonomy) is assisted by the hydrogen storage systems. During summer, the energy excess from the PV generator is used to produce hydrogen in the electrolyser (oxygen is released to the atmosphere). The hydrogen is stored in a metal-hydride tank. During winter, in long periods with low energy supply

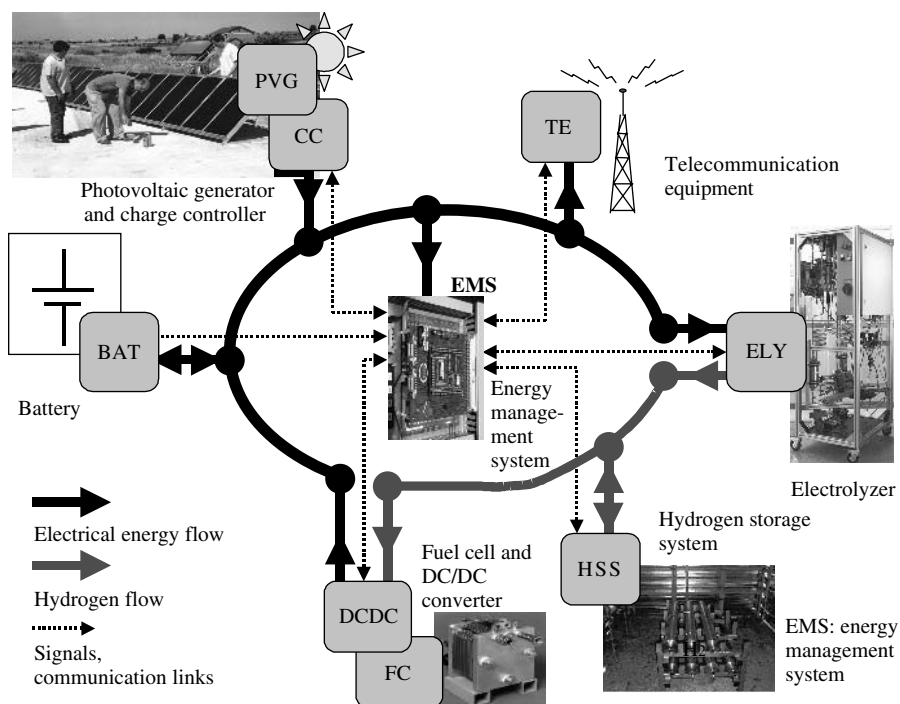


Figure 18.30 Example of an autonomous power supply system for telecommunication with a PV generator, a lead acid battery for short-term storage (five days of autonomy) and a hydrogen storage system for seasonal energy storage. The system and components have been developed by partners in the EC co-financed project FIRST [38]

from the PV generator the fuel cell takes the oxygen from the air and the hydrogen from the tank to produce electrical power.

This concept allows operating the system with very high reliability with respect to the power supply throughout the year without any conventional fuel. The shift of energy from the summer to the winter is beneficial, as, otherwise, in Central Europe a larger PV generator or motor generator would be required to fulfil the energy requirements during winter. Numerous other systems of this type for different applications have been developed and installed by R&D projects within the last decade (e.g. [39–41]).

18.6 INVESTMENT AND LIFETIME COST CONSIDERATIONS

While designing an autonomous power supply system, it is essential to face the lifetime costs rather than looking only into the initial investment costs. The battery has major impacts on the system design, system operation and overall costs.

- The battery causes a considerable part of the initial investment costs.
- The size of the battery influences significantly the solar fraction of the power supply system.
- Typically, more than two-thirds of the energy flow in an autonomous power supply system goes across the storage system. Therefore, the battery acts as an important consumer of electrical energy due to its efficiency of less than 100%.
- The battery voltage influences the selection of the electronic components or vice versa.
- The battery is subject to ageing. Ageing depends very much on the operating conditions of the battery. Operating conditions depend on system sizing and control strategy.
- The lifetime of the battery determines the running costs through the replacement investment.
- The battery needs regular maintenance.
- Depending on the type of the battery, the different requirements of the battery room have to be considered. The requirements are defined in the standards.

These facts are valid for all battery technologies. For the system design, the characteristics of the chosen battery technology must be taken into account. For the following considerations, only lead acid batteries are taken into account.

Investment costs for lead acid batteries depend very much on the technology and the quality of the battery. Typical costs for end users are in the range of 75 to 250 €/kWh. Lifetimes are – depending on the operation conditions – 3 to 8 years. Depending on the sizing of the system (days of autonomy) and the lifetime, the battery will be subjected to 100 to 1000 capacity throughputs. This results in electricity costs of 0.20 to 0.75 €/kWh dedicated to the storage unit. Additional costs occur for the peripherals, the charge controllers res. chargers and maintenance.

Lead acid batteries need maintenance once or twice a year to check the cell connectors, to measure all cell or block voltages to identify weak cells, to clean the tops of the batteries to avoid creeping currents between the poles, to refill water for flooded batteries

and to check the general state of the battery. The set points of the charge controllers or the battery management should be checked. For a 48 V battery system with single cells, 30 to 60 min for the maintenance are necessary.

Figure 18.31 gives an example of the cost share of the battery in a PV battery system. The system is designed to supply power with 100% reliability at a location in Mexico. The left-side graphs show a system that was designed to minimise the initial investment costs under the given boundary conditions. The right-side graphs show the results of a minimisation of the lifetime costs. The calculation includes the initial investment costs, maintenance, repair and replacement of the components, capital costs and other operating costs. It can be seen from the graphs that the lifetime costs are 288% or 248% of the costs for the initial investment. Sizing of the system with respect to lifetime costs resulted, in this example, in an overall cost reduction of 14%. It is interesting to see that this was achieved by approximately 20% higher investments in the PV generator. This allows on one hand a reduction of battery size by approximately 25% and on the other hand the larger PV generator allows a more frequent complete charging of the battery and therefore a lifetime extension. This altogether resulted in a cost reduction for the battery of more than 40% and – as mentioned above – for the overall system of 14%.

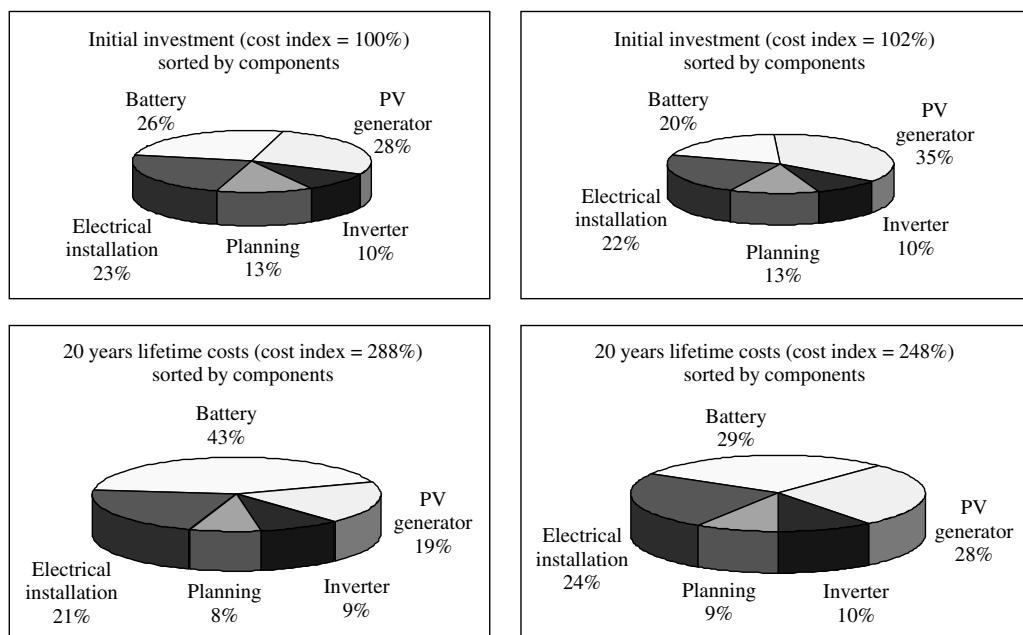


Figure 18.31 Comparison of costs for a PV battery system derived under different assumptions. Left-side graphs show the costs for the system optimised by initial investment costs, right-side graphs show the costs for a system optimised by lifetime costs. The overall costs for the initial investments (upper graphs) and the overall lifetime costs (lower graphs) calculated according to the annuity method are normalised to the initial investment costs for the system optimised by initial investment (cost index = 100%). Location, Mexico; annual power consumption, 1500 kWh; effective interest rate, 6%; lifetime of components: PV generator 20 years, electronic components 15 years, battery according to sizing and operating conditions, calculations and optimisation done with the simulation tool TALCO[42]

This example is just to illustrate the importance of an integrated system planning and design. Powerful tools are necessary and available [42]. The battery is the component with the highest cost share in autonomous power supply systems. Other than in photovoltaics, cost reductions on battery investment costs will be small within the next few years as lead acid batteries are already a commercial product today with a market of more than 10 billion euro per year in the different applications. Cost reductions can occur from improved lifetimes and optimised operation strategies. These figures also show that little tolerance for higher battery costs is given. This is important for the estimation of the market entry of other or new storage technologies. Higher specific costs per kilowatt hour of energy supply and significantly lower efficiency than that achieved today with lead acid batteries will hardly be accepted by a commercial market.

18.7 CONCLUSION

Even though there is a wide range of possible solutions for storage in autonomous power supply systems, the economic boundary conditions focus all solutions on lead acid batteries. This will not change significantly for some years. Their electrical properties are very good. Nevertheless, they have a bad reputation among system designers and operators, which is mainly due to the fact that batteries have a limited lifetime. Owing to their electrochemical nature, they have very complex operation and ageing patterns. Technically speaking, batteries have several time constants. Rapid levelling out of microcycles occurs in the millisecond range, diffusion processes in the seconds and minutes range, state of charge in the hour and day range and ageing effects in the day, month and year range. Batteries have a memory with regard to operation conditions. Faults in the operation can often hardly be repaired, but might show their negative impact much later. Further, currently no method exists that allows a determination of the state of health of the battery within minutes. Nevertheless, it is most likely that lead acid batteries will be the leading storage technologies in autonomous power supply systems for many years to come. This will be especially true if the still available improvements in the lead acid technology concerning lifetime in autonomous power supply systems can be realised.

Mainly lithium batteries have enormous growth rates in the portable market segment. Today, it is difficult to forecast the costs for larger units in terms of capacity for lithium batteries – actual forecasts expect costs in the range of 150 €/kWh and from the technical parameters the lithium batteries are most suited to autonomous power supply systems.

Double-layer capacitors will have their market in applications with very high power demands in the range of a few seconds or less and most probably in combination with an electrochemical battery.

In general, a battery is considered to be “used up” when it has less than 80% of the rated capacity guaranteed by the manufacturer. Nevertheless, this usually does not mean that the battery is completely non-functional. From field experience, it is well known that batteries can be used easily down to 50% of the rated capacity. However, the users must be aware that the days of autonomy are reduced according to the capacity loss and the power available from the battery is reduced due to ageing.

In hybrid systems, the solar fraction reduces with decreasing battery capacity. However, as ageing proceeds, the danger of the so-called “fatal defect” increases. This results in a more or less sudden breakdown of the battery, and can create considerable problems for the user. They are usually due to short circuits, caused by erosion sludge, corrosion flakes from the poles or dendrite growth between the electrodes. This risk should be considered when the decision is made about replacing a battery with clearly reduced capacity.

The operation strategy has a significant effect on the battery lifetime. It is necessary to take this into consideration when planning and designing an autonomous power supply system. Some additional investments in the battery peripherals will result in significant savings within the system lifetime. Frequent additional full charging and deep-discharge protection on the basis of a state-of-charge determination are highly recommended.

Hydrogen storage systems and redox batteries are options for the future, but the hydrogen storage systems have a fundamental drawback concerning the efficiency and the complexity of the system. Nevertheless, important impulses for their development will come from load-levelling applications in grids with a high penetration of renewable energy sources.

Further development on the conventional battery systems is necessary and will happen within the coming years. After almost one century (1880–1980) with no sustainable market entry of different fundamental battery technologies, we have seen within the last decade great achievements with nickel-metal hydride and lithium batteries, which were not expected. Further, improved battery technologies and a more integral system design and operation resulting in longer lifetimes will allow a decrease in the specific costs for electrical energy storage within the next decade by approximately a factor of two. Further cost reduction can hardly be seen from today's point of view.

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