Chapter 8
Battery Storage for Off-Grid Systems

8.1 Introduction

Energy storage devices are incorporated into off-grid systems to provide flexibility between when energy is produced and when it is consumed. The operation of a solar-powered mini-grid with a lead–acid battery illustrates this point. The battery is charged during the day when there is an abundance of input power and is discharged in the evening when the input power is lower than the output power required by the load (including losses). The battery can be thought of as “inhaling” during the day and “exhaling” in the evening, as shown in Fig. 8.1.

There are several energy storage technologies compatible with electrical systems. The most common type used in off-grid systems is the chemical battery, hereafter referred to simply as a battery. The basic concept of a battery is straightforward. A battery is a device that converts chemical energy into electrical energy. Batteries in which the conversion is reversible are referred to as “rechargeable” or “secondary batteries.” Within this category, there are several chemistries as shown in Fig. 8.2. There are two general battery chemistries used in off-grid systems: lead–acid and lithium–ion (LI), which we discuss in this chapter.

Batteries are sometimes modeled as ideal voltage sources. While this might be reasonable under short-term low-loading conditions, in actuality, batteries exhibit nonlinear behavior. The characteristics are dependent primarily on the battery’s temperature and chemical state. The chemicals in a battery are continuously reacting, and so their properties are always changing at some level. Although conceptually simple, the ideal voltage source model is inadequate.

Due to their complex internal behavior, batteries are often treated as black boxes, without regard to the mechanisms that give rise to their nonlinear characteristics. For most applications, the black-box treatment can be justified if the characteristics of interest—typically the voltage and energy availability—are documented in the

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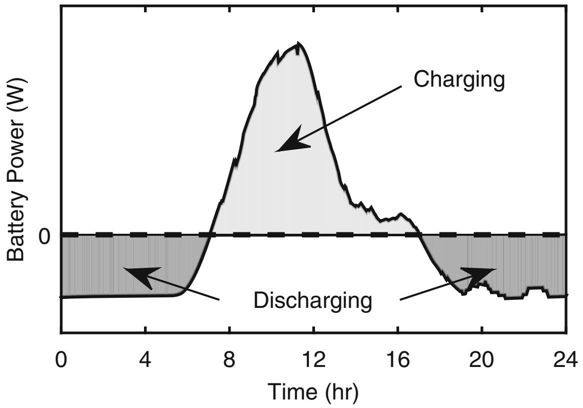

Fig. 8.1 The battery bank in a solar-powered mini-grid discharges during the evening and recharges during the day

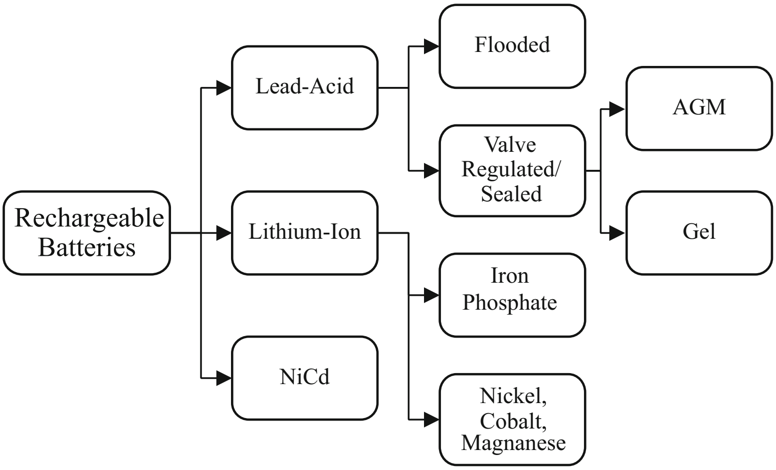

Fig. 8.2 Types of rechargeable batteries

battery's specification sheet. In this chapter we discuss the external characteristics of batteries using a black-box approach. Coverage of the underlying electrochemical mechanisms is limited. However, understanding these mechanisms at least on a basic level is beneficial in de-mystifying the complex and nonlinear behavior exhibited by batteries. It is also important in the context of off-grid systems where the conditions encountered might vary considerably from the "typical" conditions found in specification sheets. A deeper treatment of the underlying electrochemistry in general or specifically for lead–acid and lithium–ion batteries is found in other textbooks [1, 2, 7, 9].

8.2 Basic Description

The first battery was developed by Alessandro Volta in 1799. A battery is comprised of one or more electrochemical cells. Each cell consists of two electrodes, which are usually strips or plates of different metals. One electrode is designated the positive electrode and the other the negative. By convention, the positive electrode is also referred to as the cathode and the negative electrode the anode.[1] A diagram of two cells connected in series is shown in Fig. 8.3. Actual batteries also include insulating separator is used to prevent the electrodes from touching.

Each electrode is partially submerged in a solution known as the "electrolyte." In some batteries, the electrolyte is a liquid; in others it resembles a paste (as used in so-called "dry cell" batteries) or gel. Traditional automotive batteries use liquid electrolytes. Batteries used to power consumer devices are often of the dry cell type. The primary purpose of the electrolyte is to allow ions to flow between the electrodes when the battery is charging or discharging. In a lead–acid battery, the electrolyte is comprised of sulfuric acid dissolved in pure water; in lithium–ion batteries, it is a lithium salt in an organic solvent.

The electrodes of several cells are often connected in series and encased into a single unit to form a battery. For example, an automotive battery consists of

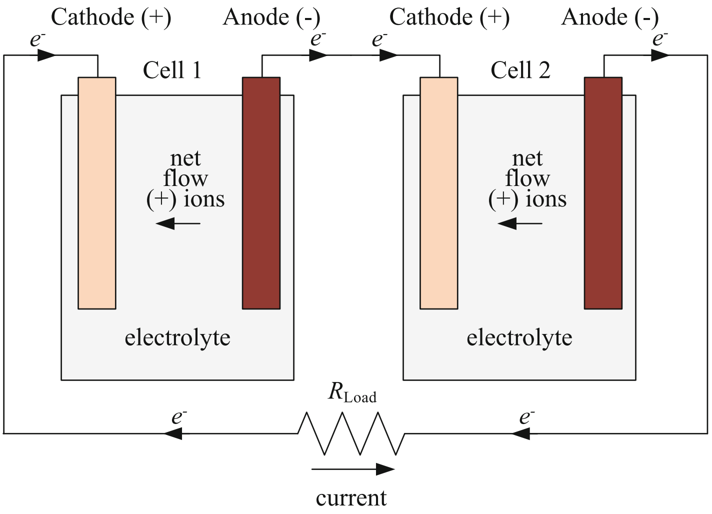

Fig. 8.3 Diagram of anodes, cathodes, and electrolytes of two cells in series and the flow of electrons and ions during discharge. Note that by convention, the direction of current is opposite to the flow of electrons

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[1] Technically, the designation of anode and cathode depends on whether or not the cell is being charged or discharged, but this tends to add confusion, and so we will always refer to the positive electrode as the cathode and negative as the anode.

Fig. 8.4 A 48 V battery bank for a mini-grid in Kenya consisting of a string of eight, six-volt batteries arranged in series (courtesy of author)

six series-connected lead–acid cells. Only two electrodes are accessible. They are known as the “terminals” of a battery. One is positive and the other negative, just like an individual cell. The load or charging circuit is connected to the terminals. Several batteries can be connected together to form a battery bank as in Fig. 8.4. Series connections increase the overall voltage; parallel connections increase the available current.

A cell relies on electrochemical reactions to establish a charge imbalance between its electrodes. Wherever there is a charge imbalance, for example, between the plates of a charged capacitor, an electrostatic field is present and voltage exists. When an external circuit is connected to the electrodes, the voltage causes electrons to flow from the anode to the cathode, while there is a net flow of negative ions from cathode to anode. This is different from a circuit powered by a generator, in which only electrons flow.

It is the nature of the chemical reactions occurring within a cell, not its physical size, that determines its voltage. In other words, the voltage is an *intrinsic* property. The chemicals involved in the reactions that produce the voltage are known as the “active materials” of a cell. This includes the electrodes and, for some cells, including lead–acid, the electrolyte. The complete depletion of any of the active materials will halt the chemical reaction and the cell’s ability to power an external circuit. Cells also contain non-active material to enhance their performance, for example, by improving the conductivity of the electrodes.

Different cell voltages can be achieved by using different combinations of active materials. A lead–acid cell has a typical open-circuit voltage of 2.10 V, whereas a lithium iron phosphate cell has an open-circuit voltage of approximately 3.2 V. But these voltages vary depending on the conditions. Alkaline batteries, such as those found in R6 (AA) batteries, use zinc and manganese oxide electrodes and have a typical open-circuit voltage of 1.43 V. These voltages are too low for high-power applications, and so several batteries or cells are connected together in series.

8.3 Lead–Acid Batteries

We begin by discussing the particularities of lead–acid batteries. Lead–acid batteries are commonly used in mini-grids due to their low cost, wide availability, and technical maturity. Because they are stationary once installed, their size and heavy weight are less of a consideration.

The lead–acid battery was developed by Gaston Planté in 1859. Lead–acid batteries have been continually refined to improve their efficiency and lifespan ever since. Lead–acid batteries can be designed for specialized uses, for example, in automobiles, forklifts, and backup energy supplies. For most off-grid electrification applications, the battery is designed to supply power over a long period of time and has a long cycle life. A "cycle" refers to a charge/discharge sequence. For most mini-grids a cycle is completed every day. Lead–acid batteries used in mini-grids are known as "deep-cycle" batteries. This is in contrast to automotive batteries—also called starting, lighting, and ignition (SLI) batteries—which are designed to supply a short burst of current to start the vehicle. An SLI battery used in an off-grid application will quickly fail. The internal makeup of a typical lead–acid battery is shown in Fig. 8.5.

8.3.1 Electrolyte

The electrolyte in a lead–acid battery is sulfuric acid (H_2SO_4). The sulfuric acid is mixed with pure water where it is dissociated into SO_4^{-2} ions and two H^+ ions. The concentration of a fully charged lead–acid battery is typically 6 moles per liter. A mole is the measurement of the amount of a substance. The number of particles of a substance in 1 mole is 6.022×10^{23}, Avogadro's constant. The concentration drops to around 1 to 2 moles per liter when completely discharged. As we will discuss later, a "fully discharged" battery still stores some energy; it just cannot be meaningfully used because the battery voltage is too low or its use might permanently damage the battery. The fact that the concentration of sulfuric acid in the electrolyte varies as the battery is discharged is important.

8.3.2 Electrodes

The lead at the anode resembles a sponge. This increases its surface area so that more of it can interact with the electrolyte. The electrodes are usually formed around a metallic grid, which also improves the conduction of the electrons to the cell's terminals. The electrodes are close together. A plastic or other insulating material is used as a spacer to prevent accidental contact (an internal short circuit). When fully charged, the anode of a lead–acid cell is lead (Pb), and the cathode is lead dioxide (PbO_2), as shown in Fig. 8.6.

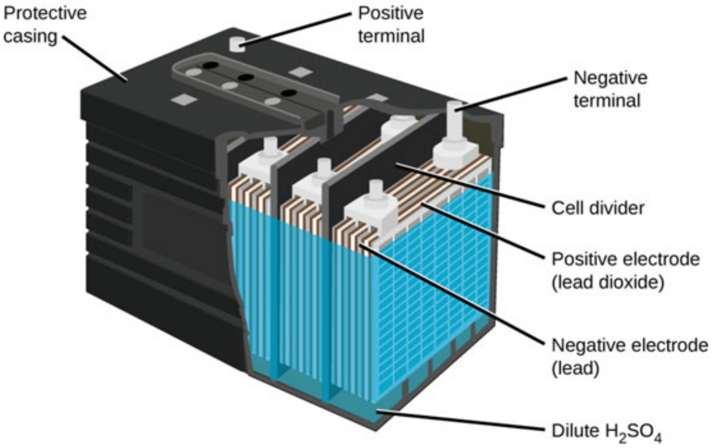

Fig. 8.5 Internal components of a typical multicell lead–acid battery (from https://opentextbc.ca/chemistry/chapter/17-5-batteries-and-fuel-cells/ and is licensed under CC BY 4.0 https://creativecommons.org/licenses/by/4.0/)

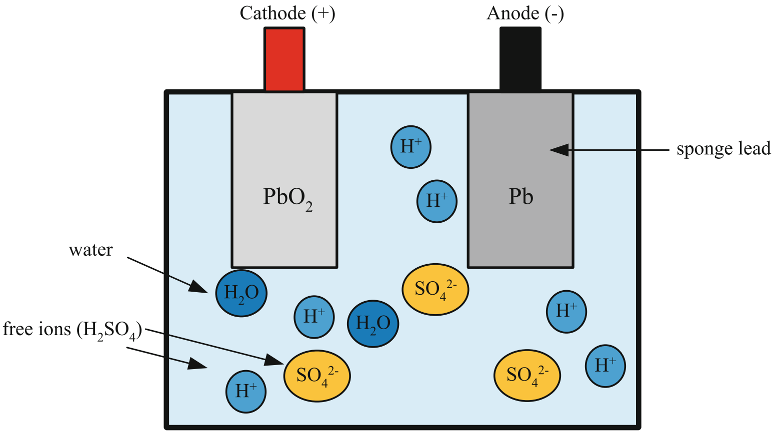

Fig. 8.6 A cell of a fully charged lead–acid battery consists of a lead anode, lead dioxide cathode, and diluted sulfuric acid electrolyte

8.3.3 Discharging Reactions

When connected to an external circuit, as shown in Fig. 8.7, a charged battery begins to discharge, and chemical reactions at both electrodes occur. There are two reactions at the anode. The first is an oxidation reaction of lead which frees two electrons:

$$Pb(s) \rightarrow Pb^{2+}(s) + 2e^{-} \tag{8.1}$$

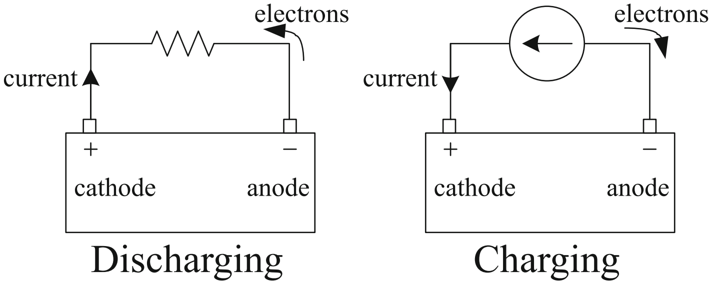

Fig. 8.7 Discharging and charging circuits of a battery

here the (s) indicates the substance is in solid form. The second is

$$Pb^{2+}(s) + SO_4^{-2}(aq) \rightarrow PbSO_4(s). \tag{8.2}$$

Here (aq) indicates that a substance is aqueous. The complete anode reaction is therefore written as

$$Pb(s) + SO_4^{-2}(aq) \rightarrow PbSO_4(s) + 2e^-. \tag{8.3}$$

The reaction converts the solid lead electrode into lead(II) sulfate ($PbSO_4$), which we will refer to as lead sulfate. The reaction consumes some of the SO_4^{-2} ions from the electrolyte. The reaction releases two electrons into the electrode which can flow through an external circuit, supplying power.

The electrons flow to the cathode where the following reduction reactions occur. The lead dioxide and liquid (ℓ) water react at the electrode, resulting in five ions

$$PbO_2(s) + 2H_2O(\ell) \rightarrow Pb^{+4}(s) + 4OH^-(aq). \tag{8.4}$$

The lead ion combines with two electrons from the external circuit (provided by the anode) to form

$$Pb^{+4}(s) + 2e^- \rightarrow Pb^{+2}(s). \tag{8.5}$$

As with the anode, the Pb^{+2} reacts with the SO_4^{-2} ions in the electrolyte to form

$$Pb^{2+}(s) + SO_4^{-2}(aq) \rightarrow PbSO_4(s). \tag{8.6}$$

The OH^- ions from (8.4) react with H^+ ions in the electrolyte to form water

$$4OH^-(aq) + 4H^+(aq) \rightarrow 4H_2O(\ell). \tag{8.7}$$

Written more concisely, the total cathode reaction during discharge is

$$PbO_2(s) + SO_4^{-2}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(\ell). \tag{8.8}$$

The reaction at the cathode transforms the lead dioxide into lead sulfate and produces pure water while consuming the sulfuric acid in the electrolyte.

The total reaction of the battery considering the anode reaction (8.3) and cathode reaction (8.8) during discharge is

$$PbO_2(s) + Pb(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4 + 2H_2O(\ell). \tag{8.9}$$

Discharging a lead–acid battery therefore converts each electrode to the same substance, lead sulfate, while consuming the sulfuric acid but producing water. We now see why the concentration of the sulfuric acid decreases as the battery is discharged.

Example 8.1 The discharge reaction of a lead–acid battery yields 2 moles of electrons for every mole of lead. What is the mass of lead that is needed to provide 1 A of current for a period of 1 h? The molar mass of lead is 207.2 g/mole.

Solution A battery supplying 1 ampere of current for 1 h provides

$$1 \text{ amphour} = \frac{1 \text{ coulomb}}{\text{second}} \times \frac{3600 \text{ second}}{\text{hour}} = 3600 \text{ coulombs}.$$

The number of electrons that must be supplied is

$$\begin{aligned} 1 \text{ amphour} = 3600 \text{ coulombs} \times 6.24 \times 10^{18} \text{ electrons/coulomb} \\ = 2.246 \times 10^{22} \text{ electrons}. \end{aligned}$$

Each mole of lead provides 2 moles of electrons, which, per Avogadro's constant, is equal to

$$\begin{aligned} 2 \text{ moles of electrons/mole of lead} \times 6.03 \times 10^{23} \text{electrons/mole of electrons} \\ = 12.06 \times 10^{23} \text{ electrons/mole of lead}. \end{aligned}$$

Therefore, a total of $\left(2.246 \times 10^{22}\right) / \left(12.06 \times 10^{23}\right) = 0.0186$ moles of lead are needed to supply 1 ampere of current for 1 h. This weighs $0.0186 \times 207.2 = 3.8$ g. We could similarly show that the required lead dioxide and sulfuric acid bring the total mass of the active material required to supply 1 ampere for 1 h to 11.9 g. In practice, only a portion of the active material is accessible, and the added mass of non-active materials that increase the mechanical strength or conductivity of the battery makes the practical value closer to 50 g.

8.3.4 *Charging Reactions*

It is not possible to extract energy from a battery whose electrodes have each transformed into lead sulfate. However, it is possible to recharge the battery by connecting a battery charger, as shown in Fig. 8.7. The battery charger is modeled as an ideal current source. As we add electrons to the anode, the electrode will return to lead, and the SO_4^{-2} ions will return to the electrolyte

$$\mathrm{PbSO_4(s)} + 2e^- \rightarrow \mathrm{Pb(s)} + SO_4^{-2}. \tag{8.10}$$

At the cathode:

$$\mathrm{PbSO_4(s)} + 2\mathrm{H_2O}(\ell) \rightarrow \mathrm{PbO_2(s)} + 4\mathrm{H^+(aq)} + SO_4^{-2}\mathrm{(aq)} + 2e^-. \tag{8.11}$$

We note that a fully charged lead–acid battery has an anode made of lead, and the cathode is lead dioxide. The electrolyte concentration is higher than in the discharged state as water is consumed and sulfuric acid (ions) is produced.

The complete chemical reaction for charging is thus

$$2\mathrm{PbSO_4(s)} + 2\mathrm{H_2O}(\ell) \rightarrow \mathrm{PbO_2(s)} + \mathrm{Pb(s)} + 2\mathrm{H_2SO_4(aq)}. \tag{8.12}$$

This is the same equation as (8.9), but the products and reactants have been reversed.

8.3.5 *Other Reactions*

The charge/discharge reactions enable the battery to store and supply energy. There are other reactions that also occur and affect the performance of the battery. These reactions are unwanted but inevitably occur at least to some degree.

8.3.5.1 Overdischarge

If a lead–acid battery is deeply discharged, then the lead sulfate can evolve into a dense crystalline form. This is known as sulfation. The crystals physically prevent the active material of the electrodes from interacting with the electrolyte. They also act as electrical insulators making electron exchange less likely. Sulfation reduces the energy that can be provided by a battery. The crystals can be difficult to remove. Once sulfation occurs, the battery can be permanently damaged or derated. When a component is “derated,” it means that its effective rating is lower than its initial rating. Sulfation can be minimized by never letting the battery state-of-charge remain low for prolonged periods of time, by avoiding operation at high temperatures, and by preventing any deep discharge of the battery.

8.3.5.2 Self-Discharge

A charged lead–acid battery will discharge even in the absence of an external circuit. The discharge is internal to the battery and is called "self-discharge." Self-discharge occurs because a charged battery, be it fully or only partially charged, is not thermodynamically stable. In other words, there is a natural tendency for the lead and lead dioxide to react with electrolyte. The reaction occurring at the cathode is

$$\mathrm{PbO_2(s) + H_2SO_4(aq) \rightarrow PbSO_4(s) + H_2O(\ell) + 0.5O_2(g)} \tag{8.13}$$

and at the anode:

$$\mathrm{Pb(s) + H_2SO_4(aq) \rightarrow PbSO_4(s) + H_2(g).} \tag{8.14}$$

These reactions are different from the discharge reactions in (8.3)–(8.8). Nonetheless, the stored energy is decreased because the active material on both electrodes is converted to $PbSO_4$, and the electrolyte becomes depleted. We see that self-discharge also produces oxygen and hydrogen gas (g) which may be vented from the battery. This irreversibly reduces the water in the electrolyte. The anode and cathode reactions are independent of each other and occur at different rates, with the anode reaction being more rapid. Lead–acid batteries are designed to limit self-discharge. Most lose about 5% or their capacity each month. This is one reason why an automobile that has not been driven for a long period of time will have trouble starting.

8.3.5.3 Overcharging

When a battery is charged, its terminal voltage increases. As it approaches fully charged, the voltage is such that hydrogen and oxygen gas are rapidly evolved. Two overcharge reactions take place. At the anode, the electrons combine with the hydrogen ions in the electrolyte:

$$\mathrm{2H^+(aq) + 2e^- \rightarrow H_2(g)} \tag{8.15}$$

and in the cathode, the water in the electrolyte electrolyzes, splitting into oxygen and hydrogen:

$$\mathrm{H_2O(\ell) \rightarrow 0.5O_2(g) + 2H^+(aq) + 2e^-.} \tag{8.16}$$

The result is the production of hydrogen and oxygen gas. This is known as "gassing." Some gassing occurs even before the battery is fully charged. Gassing should be avoided for two important reasons. The first is that hydrogen gas is explosive, and therefore it poses a fire risk if allowed to escape the battery and accumulate in a

Fig. 8.8 Flooded lead–acid batteries—from left to right: 6V, 290 Ah; 6V, 525 Ah; 2V, 1400 Ah (courtesy of OutBack Power)

poorly ventilated space. The second is that water is consumed in the process. The lost water must be replaced, which is a maintenance consideration.

8.3.6 Lead–Acid Battery Types

Nowadays there are several types of batteries designed for off-grid systems. They come in different shapes, sizes, nominal voltages, and types. Several are shown in Fig. 8.8. The choice of which to use is not arbitrary as each has different technical performance, cost, safety, and maintenance considerations.

8.3.6.1 Flooded Lead–Acid

Flooded lead–acid batteries are the most common and mature type of lead–acid battery. They are also referred to as “wet” cell batteries. The electrolyte is liquid and the electrolyte and electrodes are at atmospheric pressure. The battery is not permanently sealed—the interior is designed to be accessed. This allows pure (distilled) water to be added to replace water lost to gassing, and the electrolyte sampled to estimate the charge remaining, as discussed later in Sect. 8.5.1. Personnel must be trained to safely maintain the battery. Care must be taken not to over- or under-water the battery and to protect against any accidental spilling or splashing of the electrolyte, which, because it is acidic, is potentially harmful. Flooded lead–acid batteries are the mechanically weakest of the batteries and can leak. Precautions should be made to contain any leak, for example, by installing a short curb around the batteries. The open-circuit voltage for a given state-of-charge tends be somewhat lower than the other types of lead–acid batteries.

8.3.6.2 Sealed Lead–Acid

Sealed lead–acid (SLA) batteries are sealed from the external environment under most operating conditions. Sealed lead–acid batteries as a class are also known as valve-regulated lead–acid (VRLA) batteries. This term stems from the one-way valve that separates the battery interior from the external environment. Only if the pressure inside the battery becomes high enough will the valve operate, emitting whatever gas caused the pressure to build, for example, the hydrogen or oxygen that forms during self-discharge or overcharge. This should not happen during normal operation.

An advantage of the sealed container is that any gases produced might recombine. For example, the hydrogen and oxygen can reform into water. The sealed container also prevents spillage, and so SLA batteries are common in non-stationary applications, for example, in solar home systems. SLA batteries do not require maintenance because any gassed hydrogen and oxygen can recombine to form water, eliminating the need for adding water (regardless, the electrolyte is inaccessible). For this reason, SLA batteries are sometimes marketed as "maintenance-free" batteries. SLA batteries tend to be more expensive than flooded. There are two general sub-types of SLA batteries: gel and absorbed glass mat.

The electrolyte in gel batteries has been thickened, for example, by introducing silica. The electrolyte does not move in bulk, but nonetheless the ions are able to travel within it. Some gel batteries use tubular plate cathodes. These batteries are known as OPzV—from the German phrase Ortsfest PanZerplatte Verschlossen (stationary tubular plate sealed). Tubular plate batteries are more common with European manufacturers. Absorbed glass mat (AGM) batteries use a fiberglass structure to absorb the electrolyte. Gel and AGM batteries offer similar advantages—they are maintenance-free, are leak-proof, and can be operated in any orientation. Presently, AGM seem to be preferred over gel for off-grid applications. However, the relative advantages of each largely depend on the specific model and manufacturer.

8.3.6.3 Comparison

Although there are many differences between flooded and sealed lead–acid batteries, in the context of off-grid systems, the important differences are cost, maintenance, lifespan, and efficiency. Flooded batteries tend to be less expensive—perhaps 50% less. They can have a somewhat longer lifespan, but this depends on the specific application. Sealed batteries are more efficient and are maintenance-free—an important feature if the off-grid system does not employ local staff. Another important distinction between flooded, gel, and AGM batteries is that their charging voltages and times are different. VRLA tend to charge somewhat faster. It is important that the battery charger set-points are matched to the particular battery used.

8.4 Basic Electrochemistry

The chemistry of batteries is not terribly complicated, but it does involve a number of intricacies that are not immediately obvious to the non-expert. These details are described in the following sections. One thing to keep in mind throughout is that the charging and discharging of a battery, although basically reverse actions, are not simply symmetrical opposites to one another.

You might wonder what causes a voltage to appear across the electrodes of a battery. Without going into extreme detail, in this section we describe the basics of the electrochemistry underlying battery operation. A functioning battery requires at least two features: voltage must exist between its terminals, and there must be a mechanism of continuously transporting charge within the battery. Transportation of charge within the battery is accomplished through the flow of charged ions in the electrolyte. A separation of charge can occur when two dissimilar substances with reasonable conductivity come into physical contact. This is true even if the substances, when apart, have no net charge. The voltage between two substances when in contact is known as the *Galvani potential*. The substances can be of any phase, for example, two metals, or in the case of many batteries, a metal and a liquid. In a lead–acid battery, there is voltage between the anode and the electrolyte and another, different, voltage between the cathode and electrolyte. It can be helpful to think of these voltages as being in series, with the voltage appearing across the electrodes the combined effect of the voltages.

When the electrode/electrolyte first comes into contact, some of the electrons from the electrode are accepted by the positive ions in the electrolyte, and some of the negative ions in electrolyte donate electrons to the electrode. Think of this as diffusion occurring. There are two flows of electrons, one to the electrode and one from it. If the two flows do not have the same rate, then the electrode and electrolyte become charged—one positive and one negative with respect to the other. Let us assume the electrode is positive. As the magnitude of the charge difference increases, it becomes harder for the electrons in the electrode to be accepted by the ions in the electrolyte. The reason is that the electrons have to "push" against the electric field caused by the net negative charge of the electrolyte. Therefore, the charge transfer in this direction slows. Eventually a steady-state equilibrium of charge transfer is reached where the diffusion tendency is balanced by the electric field. For lead–acid cells, the voltage corresponding to the equilibrium is approximately 2.04 V when measured across the cell's electrodes. But the exact cell voltage depends on several other factors, as discussed next.

8.4.1 Standard Cell Potential

It is possible to devise batteries using a variety of substances as electrodes and electrolytes. Although a voltage might be developed, it also might not be practical.

Electrochemists have measured and tabulated the equilibrium open-circuit voltages for a wide variety of substances and reactions. The measurements are conducted under *standard conditions*. Standard conditions are defined as reactions occurring at a pressure of 100 kPa and for the effective concentration of solutes to be 1 mole per liter. The temperature is not stipulated, but most tables report the measured voltage, known as the standard cell potential E_{cell}^0, at 25°C.

8.4.2 Nernst Equation

The open-circuit voltage of a lead–acid cell at equilibrium is dependent on the concentration of the electrolyte. Moreover, the concentration of the electrolyte, which is actively involved in the chemical reaction of a lead–acid battery, is almost never at the standard effective concentration of 1 mole per liter (it would be very deeply discharged). Therefore, the standard cell potentials tabulated by electrochemists cannot be directly used.

More generally, and for any cell, the open-circuit equilibrium voltage E_{cell} between its electrodes (terminals) can be adjusted for nonstandard concentrations by the use of the Nernst equation:

$$E_{\text{cell}} = E_{\text{cell}}^0 - (RT/nF)\ln(Q_{\text{r}}) \tag{8.17}$$

where E_{cell} is the cell voltage under equilibrium conditions, R is the universal gas constant (8.314 J/mol/K), T is the temperature in Kelvin, n is the number of moles of electrons transferred in the reaction, F is the Faraday constant (96,485 C/mol), and Q_{r} is the reaction quotient of the reaction. The reaction quotient requires additional explanation. Consider a reaction with reactant chemicals generically named A and B and products C and D written as

$$a\text{A} + b\text{B} \rightarrow c\text{C} + d\text{D}. \tag{8.18}$$

The reaction quotient is

$$Q_{\text{r}} = \frac{\alpha_C^c \alpha_D^d}{\alpha_A^a \alpha_B^b} \tag{8.19}$$

where α_i is the "activity" of chemical i. The activity of a chemical can be thought of as the "effective" concentration.[2] Often, the concentration in moles per liter can be used as an approximation for the effective concentration. The activity of a solid is constant and equal to one, and the activity of pure water is often assumed to be one.

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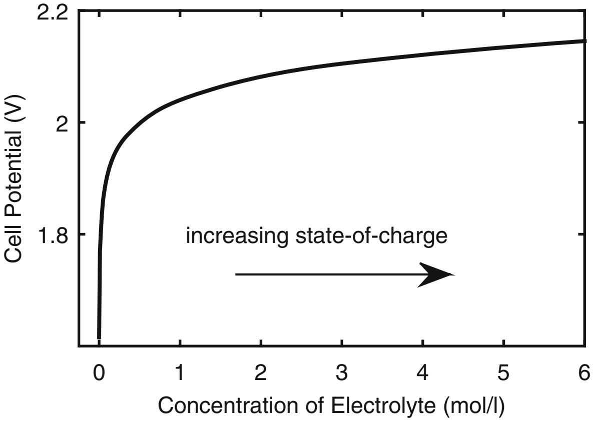
[2] The activity of a chemical is related to the concentration as $\alpha_i = \gamma_i c_i$ where γ_i is the activity coefficient and c_i is the concentration; often an activity coefficient of one is assumed.

Fig. 8.9 As the concentration of the electrolyte decreases during discharge, the open-circuit voltage also decreases according to the Nernst equation



With these assumptions, the open-circuit equilibrium voltage of a lead–acid cell for different concentrations of sulfuric acid in a lead–acid battery is shown in Fig. 8.9. We would expect the actual voltage to be somewhat different due to the simplifying assumptions made [12].

Note that if (8.17) is applied to a reaction that occurs at standard state, then the reaction quotient is one, and $E = E^0_{\text{cell}}$ because $\ln(1) = 0$. The natural logarithm introduces nonlinearity in the relationship between the voltage and the concentration and state-of-charge in lead–acid batteries. The presence of temperature in (8.17) acts to scale the effect of activity-based deviations from the standard state. However, this does not capture the complete effect of temperature on battery voltage. These aspects are discussed further in Sect. 8.5.7.

Example 8.2 Assume that the standard cell voltage for a lead–acid battery is 2.04 V. The battery is fully charged, and so the concentration of the sulfuric acid in the electrolyte is 6 moles per liter. Compute the corresponding cell voltage. Approximate the activity of the sulfuric acid by its concentration. Assume the temperature of the battery is 25°C.

Solution The battery is not under standard conditions due to the increased concentration of the sulfuric acid. We can apply the Nernst equation (8.17) to adjust the open-circuit voltage. This requires the reaction quotient to be computed. For the reaction of a lead–acid battery (8.9), we let activities of the reactants be assigned as A→ PbO_2; B → Pb, and E → H_2SO_4. Note that we accommodated a third reactant, E, just like the first two. The products are assigned as C→ $PbSO_4$ and D→ H_2O so that a reasonable approximation of the reaction coefficient is

(continued)

$$Q_{\mathrm{r}} = \frac{\alpha_C^c \alpha_D^d}{\alpha_A^a \alpha_B^b \alpha_E^e}$$

$$= \frac{1^2 \times 1^2}{1^1 \times 1^1 \times 6^2} = \frac{1}{36}.$$

We also see from (8.9) that the reaction yields 2 moles of electrons, so that $n = 2$. Applying the Nernst equation (8.17):

$$E_{\mathrm{cell}} = E^0_{\mathrm{cell}} - (RT/nF)\ln(Q_{\mathrm{r}})$$

$$= 2.04 - ((8.314 \times 298.15) / (2 \times 96,485)) \ln\left(\frac{1}{36}\right) = 2.086\mathrm{V}.$$

This roughly corresponds to the open-circuit voltage of a fully charged lead–acid cell.

8.5 Basic Characteristics

Now that we have a basic understanding of how a battery functions, we can discuss the characteristics that are especially relevant to off-grid systems. They are:

1. Open-circuit voltage
2. Current–voltage relationship
3. Battery resistance
4. Charge capacity and energy capacity
5. Cycle life
6. Efficiency
7. Self-discharge
8. Effect of temperature

8.5.1 Open-Circuit Voltage

The terminal voltage of a battery V_{B}, measured from the positive terminal to the negative terminal, along with the battery's charge or energy capacity, are the most important characteristics of a battery. The terminal voltage dictates what other components a battery is compatible with—for example, you cannot replace your laptop battery with your automobile's battery and expect it to function, even though your automobile's battery stores a greater quantity of energy. If the battery bank in

Table 8.1 Battery state-of-charge and corresponding open-circuit voltage and specific gravity for lead–acid batteries

Open-circuit cell voltage	Approximate state-of-charge (%)										
	0	10	20	30	40	50	60	70	80	90	100
Flooded (V/cell) (V/cell)	1.90	1.92	1.94	1.96	1.99	2.01	2.03	2.05	2.07	2.09	2.11
AGM (V/cell)	1.94	1.96	1.98	2.00	2.02	2.04	2.06	2.08	2.10	2.12	2.14
Specific gravity (g/ml)	1.048	1.072	1.096	1.119	1.142	1.165	1.187	1.207	1.227	1.246	1.260

an off-grid system is rated at 48 V, then every component connected to it must be compatible with this nominal voltage.

The Nernst equation tells us that the equilibrium open-circuit voltage of a battery depends on the temperature, chemical composition, and state of the battery's active materials. We are most interested in how the open-circuit voltage varies with the state-of-charge of the battery. A formal definition of *state-of-charge* (SoC) is given later, but for now it suffices to think of it as the percentage of the charge remaining in the cell or battery that can be meaningfully used. The open-circuit voltage as it relates to the SoC for flooded and AGM batteries is shown in Table 8.1. These values are approximate and representative—they vary somewhat from manufacturer to manufacturer and from one battery type to the next. For example, the open-circuit voltage of an SLI battery will be different from those shown. If the cells are connected in series, then multiply the values in the table by the number of series-connected cells.

You might have heard of the lead–acid battery in most automobiles as being a "12 V" battery. A 12 V lead–acid battery has six series-connected cells. According to Table 8.1, the fully charged open-circuit voltage for 12 V battery is $6 \times 2.11 = 12.66$ V not 12 V. In fact, if a 12 V battery has an open-circuit voltage of 12.0 V, it has less than 50% of its charge remaining. Despite the added confusion, we often describe batteries by their "nominal[3]" voltage, rather than their actual open-circuit voltage. If we know the nominal voltage of a cell and that of the battery, we easily can compute how many cells are connected in series and then can apply a table such as Table 8.1. For example, certain lithium–ion chemistries have a nominal cell voltage of 3.6 V. Therefore, we refer to a battery with five of these cells connected in series as an "18 V" battery (3.6×5), which are commonly used in cordless power tools. Note that some manufacturers do not adhere to this convention. They inflate their nominal voltages slightly so that their batteries seem superior.

We emphasize that the values in Table 8.1 and those reported by manufacturers are the *open-circuit voltage* as measured at the battery terminals during *equilibrium conditions* and at a certain temperature, usually 25°C. If the battery is being charged and discharged or has recently been charged or discharged, the table should not be

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[3] The nominal voltage itself approximately refers to the average terminal voltage when discharged.

used. The battery must be isolated from other components and allowed sufficient time—usually several hours—to rest before the SoC can be inferred from the battery terminal voltage V_B. It is often impractical to disconnect the battery from the system to measure the open-circuit voltage.

An alternative way of estimating the SoC is by measuring the concentration of the electrolyte. This can only be done in flooded lead–acid batteries because the electrolyte is accessible in these types of lead–acid batteries. The concentration of sulfuric acid in the electrolyte of a fully charged lead–acid battery is usually 6 moles per liter. The specific gravity of pure water is 1.0 g/ml and 1.85 g/ml for sulfuric acid. Since sulfuric acid is denser than water, the specific gravity of the electrolyte will increase from unity as the concentration of sulfuric acid increases. The specific gravity is measured using a hydrometer. The measured value can be compared to a table that relates specific gravity to state-of-charge, as shown in Table 8.1. The reading should be adjusted for the temperature of battery, typically by 0.00075 g/ml for every degree increase above 25°C. Note that stratification of concentration does occur in the electrolyte, and so samples taken at the top of the electrolyte might not accurately measure the average specific gravity.

8.5.2 *I–V Characteristic*

We next consider the electrical characteristics of a battery or cell when connected to an external circuit. The I–V curve of a typical battery when charging and discharging is shown in Fig. 8.10. This curve is also known as a "polarization curve." We see that as the discharge current increases, the terminal voltage decreases. The decrease is not linear—there are steep drops at low current and high current. The current–voltage relationship is influenced by several factors, including the temperature, SoC, and the shape and separation distance of the electrodes. An I–V curve therefore is valid only for a given set of parameters and conditions. In particular, the curve can change dramatically for the same battery as the SoC increases or decreases.

The I–V curve of an idealized battery would be a horizontal line located at the battery's open-circuit voltage, with no variation in terminal voltage as the discharge current increases. That of course would be impossible because it suggests infinite power capability. The downward sloping, nonlinear curve of a practical battery is caused by three types of "polarizations": ohmic, activation, and concentration [2, 7]. Each of these can be thought of as a voltage drop that causes the I–V curve to deviate from the ideal.

Ohmic polarization is the voltage drop caused by the battery current passing through the resistance of the electrodes and the electrolyte (the resistance of the electrolyte can be thought of as how easily the ions can be transported through it). The magnitude of the resistance varies somewhat with the SoC and whether the battery is charging or discharging. Most notably, there tends to be a sharp increase when the battery is discharging and at a low SoC. For example, the resistance of lead sulfate ($0.3 \times 10^{10}\ \Omega$ cm) is several orders of magnitude greater than for lead or lead

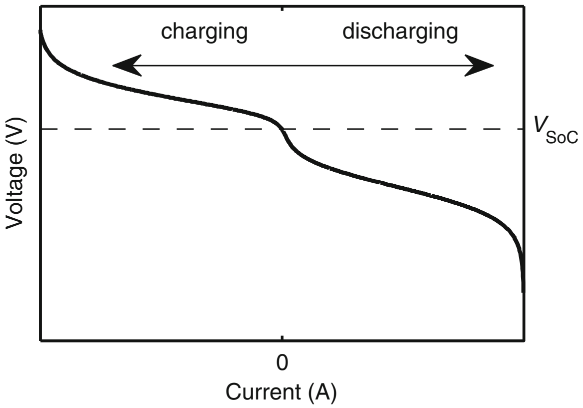

Fig. 8.10 I–V characteristic of a typical battery during charging and discharging

dioxide; and the resistivity of the sulfuric acid electrolyte increases by about 60% from full SoC to empty. Ohmic polarization is largely responsible for the nearly linear middle portions of the curve while charging or discharging in Fig. 8.10.

The activation polarization is related to the kinetics of the chemical reactions. For there to be a net flow of current at the electrode, as is the case whenever the battery is charged or discharged, the equilibrium of the charge exchange described in Sect. 8.4 must be upset. When charging, a voltage higher than the equilibrium is needed. When discharging the voltage is lower. Conceptually, activation polarization can be thought of as a voltage drop (when discharging) or voltage rise (when charging). The voltage drop/rise is generally not the same for the same discharge/charge current. In other words, the polarity of the current matters. The activation polarization increases very rapidly as the battery is charging and approaches a full SoC. Activation polarization is responsible for the steep drop (rise) in voltage in the I–V curve at low discharge (charge) current.

The concentration polarization reflects that at high current, there can be a localized reduction in concentration of the electrolyte—caused by a mismatch in the ion transportation rate in the electrolyte with those being transformed at the electrodes. From the Nernst equation, we expect any change in concentration to affect the developed voltage. The concentration polarization is responsible for the large voltage drop (rise) at high discharge (charge) current. Like the activation polarization, the voltage drop (rise) associated with concentration polarization increases rapidly when charging at a near full SoC.

How might we model the effects of polarization using circuit elements? A simple model of a cell is shown in Fig. 8.11 where we find a voltage source connected in series with two resistances [14]. The voltage source itself is shown to be a function of the cell's SoC and temperature. Under open-circuit conditions:

$$V_{\mathrm{cell}} = V_{\mathrm{SoC,cell}}. \tag{8.20}$$

The resistance $R_{\Omega,\mathrm{cell}}$ represents the ohmic polarization. As discussed, this is dependent on the SoC but also the temperature. The other resistance $R_{\eta,\mathrm{cell}}$ models the concentration and activation polarizations. Its value is a function of SoC,

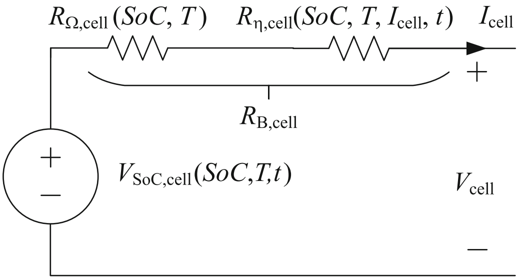

Fig. 8.11 Polarization resistance model of a battery

temperature, current as well as how long the current has been applied and how long since it was applied. These resistances can be combined into a hypothetical battery resistance $R_{\text{B,cell}}$ which depends on the same parameters as $R_{\Omega,\text{cell}}$ and $R_{\eta,\text{cell}}$. Therefore

$$V_{\text{cell}} = V_{\text{SoC,cell}} - I_{\text{cell}} R_{\text{B,cell}}. \tag{8.21}$$

Using this model, the terminal voltage of a battery with N_{cells} in series is

$$R_{\text{B}} = N_{\text{cells}} \times R_{\text{B,cell}} \tag{8.22}$$

$$I_{\text{B}} = I_{\text{cell}} \tag{8.23}$$

$$V_{\text{SoC}} = N_{\text{cells}} \times V_{\text{SoC,cell}} \tag{8.24}$$

$$V_{\text{B}} = V_{\text{SoC}} - I_{\text{B}} R_{\text{B}} \tag{8.25}$$

In interpreting R_{B} we must always remember it is not a resistor, but it is resistance. It is variable with the state and characteristics of the battery and reflects a number of physical phenomena, including the battery's age [5]. Further, R_{B} should not be confused with the "internal" resistance reported by manufacturers. The reported resistance is usually the resistance associated with the ohmic polarization only. Hereafter, whenever the resistance of a battery is discussed, it is in reference to the battery resistance R_{B}, not the "internal" ohmic resistance. The model also does not represent all of the dynamic characteristics of a battery. More sophisticated models[4] include a capacitive element [8]. This models a battery's"inertia"—that a battery's terminal voltage takes some time to return to V_{SoC} after the sudden disconnection of the charging circuit or load.

The value of the battery resistance for a larger flooded lead–acid battery—one that could supply 1 kWh of energy—typically ranges from about 1 mΩ/cell to about 25 mΩ/cell during charging. Smaller capacity batteries tend to have larger battery resistances.

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[4] See, for example, the widely used Randle's model.

Example 8.3 The equilibrium open-circuit cell voltage of a 24 V lead–acid AGM battery is 24.96 V. An external circuit is connected to the battery that draws 21 A. Assume the battery resistance R_B under the these conditions is 0.060 Ω. Compute the terminal voltage. Estimate the SoC using Table 8.1. How does this estimate compare to SoC if the open-circuit voltage is used? Which is more accurate?

Solution The terminal voltage will be less than the equilibrium voltage because the battery is discharging. Applying (8.22)

$$V_B = 24.96 - 21.0 \times 0.060 = 23.70 \text{ V}.$$

Normally, we do not know R_B, but if we do we can compute V_{SoC} and estimate the SoC. The corresponding cell voltage is found by dividing the voltage by the number of cells: 23.70/12 = 1.975 V/cell. If this is wrongly used to estimate the SoC according to Table 8.1, then the estimated SoC would be approximately 17.5%. However, the SoC should be estimated using the equilibrium open-circuit cell voltage of 24.96/12 = 2.08 V/cell, corresponding to an SoC of 70%. This illustrates why the terminal voltage is a poor estimator of SoC unless the battery is open-circuited.

Figure 8.12 is a typical plot of the terminal voltage of a lead–acid battery during a discharge and charge cycle if the magnitude of the current is constant throughout. As the battery is discharged, the voltage drops immediately from the open-circuit value (approximately 2.1 V). This is due to the voltage drop associated with the battery resistance. Over time, the terminal voltage decreases, primarily due to the decrease in V_{SoC} brought about by the dilution of the electrolyte concentration and the increasing value of R_B at low SoC while discharging. When the battery transitions from discharging to charging, the terminal voltage immediately and abruptly increases. This is primarily due to the voltage drop across the battery resistance now having the opposite polarity. As the battery is recharged, its terminal voltage rises nonlinearly due to the increasing V_{SoC}. The sharp rise near the far right of the figure is caused by the rapid increase in R_B—primarily due to increases in the activation and concentration polarization—that occurs when a battery with a full SoC continues to be charged.

8.5.3 Battery Capacity

The capacity of a battery tells us how long it can meaningfully supply a constant current load. Although this is conceptually simple, there is some nuance to its

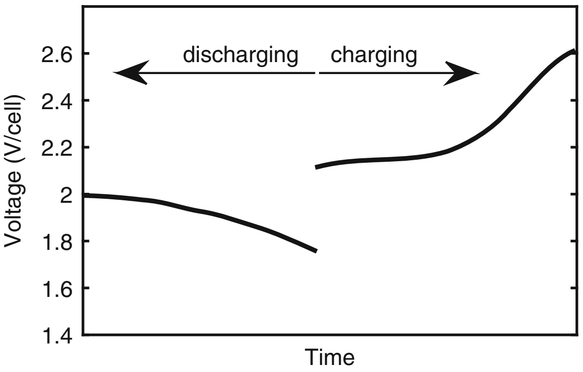

Fig. 8.12 Cell voltage during a discharge/charge cycle with constant battery current magnitude

interpretation, and the reader should pay particular attention to how capacity and the related state-of-charge (SoC) and depth-of-discharge (DoD) are defined. Capacity refers to either the amount of *charge* or the amount of *energy* a battery can provide to an external load.

8.5.3.1 Charge Capacity

The most common method of quantifying the capacity of a battery is the charge capacity. The charge capacity is the amount of electric charge that can be supplied to an external load. Recall that the relationship between current and charge is

$$1 \text{ Ampere} = 1 \text{ coulomb/second.} \tag{8.26}$$

Out of convenience, the charge capacity of a battery is specified in terms of amphour (ampere-hour, Ah), rather than coulombs. One amphour is equivalent to 3600 coulombs. It follows that since it takes the charge of 1.602×10^{19} electrons to equal 1 coulomb, 1 amphour is also equivalent to 2.246×10^{22} electrons. The number of electrons that a battery can supply is directly related to the mass of the active material (see Example 8.1). This explains why higher-capacity batteries are necessarily physically larger than smaller-capacity batteries.

We can devise a simple test to determine the charge capacity of a battery. We do this by discharging a fully charged battery through a variable resistor. The resistance is varied so that the discharge current has constant value of x as R_B and V_{SoC} change. The charge supplied by the battery in amphours during constant current discharge is

$$c_x = xT_{d,x} \tag{8.27}$$

where $T_{d,x}$ is the discharge time.

If we were also measuring the terminal voltage, we would notice that the terminal voltage decreases over time, for example, as shown in Fig. 8.13. As can be expected, the terminal voltage decreases nonlinearly as the discharge progresses, even as the

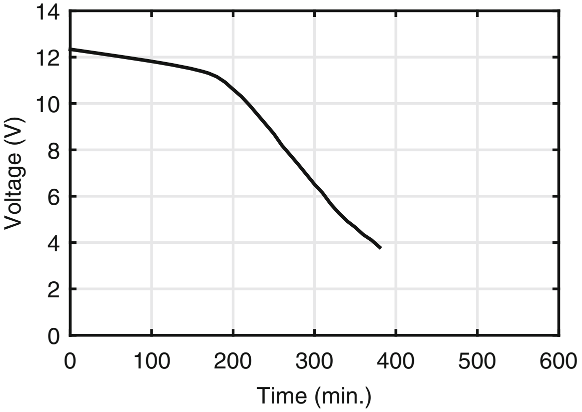

Fig. 8.13 Discharge curve of a 12 V, 40 Ah, gel battery at a rate of $x = 8$ A

current is held constant. Of particular importance is that the decrease is first gradual and then rapid. The battery is unable to supply $x = 8$ A after about 390 min ($T_{\mathrm{d},x} = 6.5$ h). The charge supplied by the battery shown in Fig. 8.13 is therefore approximately $8 \times 6.5 = 52$ Ah. The discharge ceases when the battery is no longer able to supply 8 A. However, we note that at the end of the discharge cycle, the voltage of the battery was far below its nominal value of 12 V. In practice, it is unlikely that the load connected to the battery would properly function across the range of voltages exhibited. Moreover, the battery is almost surely permanently damaged due to overdischarge. In other words, we are not able to meaningfully extract all 52 Ah of charge. But at what point should the test be terminated and the charge capacity calculated?

The standard practice is to consider a battery "fully" discharged when the terminal voltage reaches a predefined *cut-off voltage*. The cut-off voltage is selected so that, when reached, the load will likely still function and the battery will not be seriously damaged. The cut-off voltage typically corresponds to the point at which the battery voltage sharply decreases (slightly above 10 V for the battery in Fig. 8.13). For lead–acid batteries this is usually 1.75 V/cell; for lithium–ion batteries it is typically between 2.0 and 3.0 V/cell.

The presence of the battery resistance makes it so that the amount of charge provided before the cut-off voltage is reached will vary with the magnitude of the discharge current. In other words, a battery discharged at a current of x will provide somewhat less charge before the terminal voltage reaches the cut-off voltage than if it were discharged at $0.5x$. This is because the voltage drop across R_{B} will be approximately twice as large when discharged at x. There might also be an increase in unwanted side reactions. We therefore must associate the charge capacity rating of a battery with the current it was discharged at. Mathematically, the capacity c_{x} at discharge rate of x amperes is

$$c_{\mathrm{x}} = \int_0^{T_{\text{cut-off}}} x \, \mathrm{d}t \tag{8.28}$$

where $T_{\text{cut-off}}$ is the time when the terminal voltage equals the cut-off voltage. Note that it is common for manufacturers to decrease the cut-off voltage when determining the rating of a battery at a high discharge current to account for the increased voltage drop across the battery resistance. Values of 1.67 V/cell or 1.33 V/cell are typical for high discharge current. Note that as soon as the discharge ends, the battery voltage will rebound past the cut-off value. This is partly due to the absence of a voltage drop across the battery resistance when the current is zero. Also, the electrolyte gradually mixes, removing any localized areas of low concentration around the electrodes that might have lowered the voltage. If we wait long enough, we could discharge the battery further before the cut-off voltage is again reached. However, rest periods are not used when determining a battery's capacity.

In the case of the battery in Fig. 8.13, the cut-off voltage specified by the manufacturer is 10.2 V (1.7 V/cell). This occurs after approximately 3.75 h of discharge. The corresponding capacity is 8 A × 3.75 h = 30 Ah. This is considerably less than the charge extracted if the cut-off voltage is ignored.

We emphasize that the capacity rating of a battery depends on its terminal voltage during discharge. The capacity is therefore related to, but not a direct measurement of, the accessible active material that can supply charge. Regardless of the discharge rate, the same mass of active material is used to supply each electron to the external circuit [6]. Thus, the same active material will be consumed if a battery is discharged at 10 A for 1 h or 1 A for 10 h.

8.5.3.2 State-of-Charge

We know that we can extract charge in excess of a battery's capacity rating if we are willing to discharge it past the specified cut-off voltage. However, we do this to the detriment of the battery, and so this additional capacity should be considered "off-limits." We often describe the charge that a battery can meaningfully provide in its present condition as its state-of-charge (SoC). The SoC is always in reference to the capacity rating.

$$SoC = 100 \times \frac{c_x - \int_0^{T_{\text{use}}} i_{\text{B}}(t)\,\text{d}t}{c_x} \tag{8.29}$$

where SoC is the state-of-charge, in percent, $i_{\text{B}}(t)$ is the battery current—which is positive when discharging and negative when charging—and T_{use} is the time the battery has been in use. Despite the mathematical exactness of this definition, there are several practical limitations to its use. First, it requires that the current be measured and integrated throughout the life of the battery. This is known as "coulomb counting." Because integration is involved, any measurement bias in the current sensor will accumulate over time leading to large errors in the SoC. Second, this definition does not account for the effects of self-discharge. The SoC of a fully charged battery that has never supplied current will decrease over time. Third, it is possible in some situations for the SoC to be negative or exceed 100%. A negative

SoC occurs when the battery has been discharged past the cut-off voltage. An SoC in excess of 100% can occur in lithium–ion batteries that are overcharged. Lastly, the selection of the capacity c_x upon which to calculate the SoC is somewhat arbitrary, and the discharge current will likely differ from x. For example, if the SoC calculation is based on a capacity of c_{10} (10 A discharge), but the battery is actually discharged at 30 A, then the cut-off voltage will be reached before the SoC is zero. In practice then, the SoC should not be viewed as a precise indicator of how much charge is remaining in a battery. Rather, it is a general indicator. Despite these drawbacks, the SoC is very useful because several characteristics of the battery can be related to the SoC, as we have seen with the open-circuit voltage.

8.5.3.3 Depth-of-Discharge

The complementary measure to the SoC is the depth-of-discharge (DoD). The DoD is the percent of rated capacity that has been discharged:

$$DoD = 100 \times \frac{\int_0^{T_{\text{use}}} i_{\text{B}}(t)\,\mathrm{d}t}{c_x}. \tag{8.30}$$

The DoD and SoC are related by

$$DOD = 100 - SoC. \tag{8.31}$$

Example 8.4 A nominal 6 V battery is discharged at a constant current of 15 A. After 20 h the terminal voltage reaches the cut-off voltage (5.25 V). The battery is continued to be discharged for another 2 h at the same current. What is the c_{15} capacity of the battery? Compute the SoC and DoD at 6 h and at 20 h.

Solution Since the battery reaches the cut-off voltage after 20 h, its c_{15} capacity is $20 \times 15 = 300$ Ah. That the battery is discharged for another 2 h is irrelevant to the calculation. The SoC and DoD at 6 h are found using (8.29) and (8.30):

$$SoC = 100 \times \frac{c_x - \int_0^{T_{\text{use}}} i_{\text{B}}(t)\,\mathrm{d}t}{c_x} = 100 \times \frac{300 - 6 \times 15}{300} = 70\%$$

$$DoD = 100 \times \frac{\int_0^{T_{\text{use}}} i_{\text{B}}(t)\,\mathrm{d}t}{c_x} = DoD = 100 \times \frac{6 \times 15}{300} = 30\%.$$

A similar approach shows that after 20 h, the SoC is 0% and the DoD is 100%.

8.5.3.4 Charge Rate (C-Rate)

To have meaning, the charge capacity c_x of a battery must be referenced to a specific discharge current x. In addition to expressing the current directly in amps, the *charge rate* (C-rate) is used. The C-rate standardizes the current in terms of the cell capacity. The C-rate τ is defined as

$$\tau = \frac{\text{discharge current (A)}}{\text{capacity when discharged at } x \text{ amps (Ah)}} = \frac{x}{c_x}. \tag{8.32}$$

The units of C-rate are therefore h^{-1} but are frequently dropped. Rather, the letter C is used to indicate that the value is a C-rate. For example, it is common to write C-rates as 0.05C, 0.1C, 1C, and so on rather than 0.05/h, 0.1/h, and 1/h. A C-rate of τ indicates that the capacity is referenced to an amount of current that will discharge the battery in $1/\tau$ h. Equivalently, the C-rate tells us what portion of the charge capacity is discharged (or charged) each hour. For example, when a battery is discharged at 0.25C, it loses 25% of its charge each hour and therefore will only be able to do so for 4 h. As another example, if the battery is discharged at a C-rate of 2C, then the battery will discharge 200% of its charge per hour, and so it can only discharge at this rate for 30 min (half an hour).

The numerical value of the discharge or charge current is found by multiplying the C-rate by the stated capacity, per (8.32). For example, a battery rated at 2 Ah at a C-rate of 0.20C means the battery is capable of supplying $0.20 \times 2 = 0.4$A continuously for 5 h until its terminal voltage falls to the cut-off voltage. The inverse of the C-rate $1/\tau$ is known as the *hour rate*. The hour rate has units of time (hours) and is also commonly used to describe the discharge conditions in which a capacity is referenced to. A battery rated 2 Ah at a C-rate of 0.20C could equivalently be described as having a capacity of 2 Ah at the *5-hour rate*. If a battery is rated at 220 Ah at 0.05C, then the proper interpretation is that “the battery can supply 11 A (220 × 0.05) continuously for 20 h (1/0.05) until the terminal voltage drops below the manufacturer prescribed cut-off voltage.”

Example 8.5 A wind energy conversion system is used to charge a battery. The battery supplies electricity to a school. The battery is discharged at 50 A for 10.5 h before the terminal voltage drops below the cut-off voltage of 1.75 V/cell. Compute the capacity, in amphours, of the battery. What C-rate does this capacity correspond to? What is the hour rate?

Solution The capacity of the battery when discharged at 50 A is

$$c_{50} = 50 \times 10.5 = 525 \text{ Ah}$$

The C-rate is $\tau = 50/525 = 0.0952$/hr (an hour rate of 10.5 h).

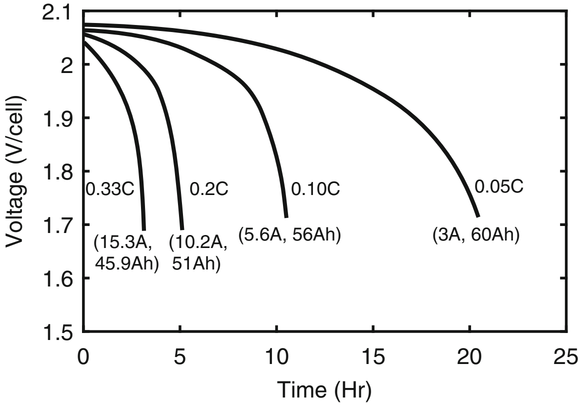

Fig. 8.14 Capacity curves of a battery at different discharge rates for a 60 Ah (at 0.05C) lead–acid battery

Manufacturers will sometimes provide the capacity of a battery without explicit presentation of the C-rate or hour rate. For example, you might encounter a battery rated at 100 Ah. Without more information, you cannot confidently know if, for example, this battery can supply 100 A for 1 h or 1 A for 100 h. While this adds confusion, the C-rate to which the capacity is referenced is implied by its application or chemistry. For example, the rating of a AA-cell battery is given assuming a C-rate of 1; lead–acid batteries in mini-grids use a C-rate of 0.05 (20 h); batteries used in forklifts might use a C-rate of 0.16C (6 h). If unsure, the battery vendor should be consulted. The remainder of this book assumes lead–acid batteries are referenced to a C-rate of 0.05C (20 h) unless otherwise noted. This is also the capacity which the SoC and DoD are referenced to.

8.5.3.5 Capacity Curves

Manufacturers often provide a battery's "capacity curves." Capacity curves are a family of plots of voltage versus discharge time for different C-rates. An example is shown in Fig. 8.14. As we expect, at higher C-rates, the battery voltage drops sooner and more rapidly. The total amphours provided is found by multiplying the current corresponding to the C-rate by the time until the cut-off voltage is reached, as in (8.27). As the C-rate increases, the rated capacity decreases. For example, if the battery in Fig. 8.14 is discharged at 3 A, it will last 20 h (60 Ah). But if it is discharged at 10.2 A, it will only last 5 h (51 Ah). Note that the cut-off voltage for the lower C-rates is somewhat higher.

From Fig 8.14, we can deduce that a battery's capacity is inversely related to the discharge current. Thus, no single value can describe the capacity of battery; it must always be referenced to a discharge rate. The dependence of capacity on discharge current is largely due to the cut-off voltage being reached more quickly at higher current. This is because the voltage drop across R_B increases, not only because the current is greater, but also because R_B itself increases with current.

Table 8.2 Charge capacity of a 2V, 1000 Ah flooded lead–acid battery. The battery's capacity is in reference to its 0.05C discharge characteristics, shown in bold

C-rate (h^{-1})	Hour rate (h)	Current (A)	Capacity (Ah)
0.01C	100	14.10	1410
0.02C	50	24.60	1230
0.05C	**20**	**50.00**	**1000**
0.10C	10	83.00	830
0.5C	2	240	480
1.0C	1	340	340

The capacity of a battery at different discharge rates is often provided by the manufacturer in a tabular format. An example of a 1000 Ah (at 0.05C) flooded lead–acid battery is shown in Table 8.2.

Example 8.6 Consider the battery whose discharge curve is plotted in Fig. 8.13. Estimate the charge capacity if a cut-off voltage of 1.33 V/cell is used.

Solution The battery has a nominal voltage of 12 V, so there are six cells. The cut-off voltage therefore is $6 \times 1.33 \approx 8$ V. Approximately 260 min (4.33 h) have elapsed when the terminal voltage reaches 8 V. Since the battery is discharged at a constant current of 8 A, the corresponding capacity would be $4.33 \times 8 = 34.67$ Ah.

8.5.3.6 Peukert's Equation

The relationship between capacity and discharge current can be approximated using Peukert's equation.[5] It relates the known capacity at a discharge rate of c_{x_r} at current x_r to the capacity c_x if the battery is discharged at some other constant rate x:

$$c_x = c_{x_r} \left(\frac{x_r}{x} \right)^{k-1} \tag{8.33}$$

where k is the experimentally determined and battery-specific Peukert exponent.[6] The Peukert exponent typically is between 1.0 and 1.3. Larger values of k are less desirable as they indicate that the battery capacity is more severely reduced by high discharge rates. This effect is seen in Fig. 8.15 for a hypothetical battery whose rating is 65 Ah at 1 A (0.0154C). If the battery's Peukert coefficient is 1.15, then the capacity at C-rate of 0.05C (20-h discharge time) is approximately 55.7 Ah

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[5] Peukert's equation is sometimes known as "Peukert's law," but this is a misnomer.

[6] Peukert's exponent is often, but erroneously, referred to as "Peukert's coefficient."

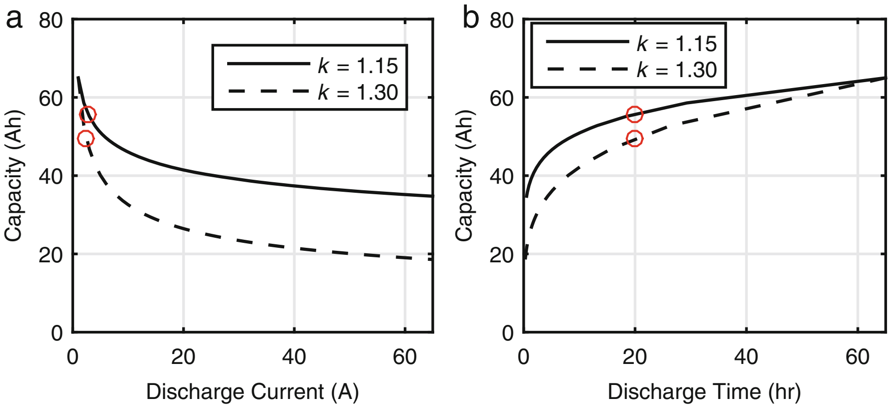


Fig. 8.15 The effect of discharge current and time on battery capacity for batteries with different Peukert exponents

(2.875 A × 20). If the Peukert coefficient is 1.30, then the capacity at a 0.05C is reduced to 49.5 Ah (2.475A × 20). These points are shown as the circles in Fig. 8.15. We must apply Peukert's equation with care. If the battery discharge current varies during the discharge or the temperature changes, then the capacity suggested by Peukert's equation will not be accurate.

Example 8.7 A battery in an off-grid system is rated at 105 Ah when discharged at 5.25 A. What is the capacity when discharged at 11.7 A? What is the corresponding C-rate? Let $k = 1.18$.

Solution Setting $x = 11.7\text{A}$, $c_{x_\mathrm{r}} = 105$ Ah and $x_\mathrm{r} = 5.25$ A and using (8.33):

$$c_{11.7} = c_{x_\mathrm{r}} \left(\frac{x_\mathrm{r}}{x}\right)^{k-1} = 105 \left(\frac{5.25}{11.7}\right)^{1.18-1} = 90.90 \text{ Ah}.$$

The C-rate is found by dividing the discharge current by the corresponding capacity $c_{11.7}$: $11.7/90.90 = 0.129\text{C}$. The battery can supply a current of 11.7 A for 1/0.129 = 7.77 h.

Example 8.8 A hypothetical battery has a capacity of 5 Ah at 1C and $k = 1.0$. How many hours will the battery be able to supply a current of 15 A? What C-rate does this discharge current correspond to?

(continued)

Solution The Peukert exponent is 1.0, which means there is no "penalty" for fast discharge. Therefore, the capacity is 5 Ah regardless of the discharge current. From (8.32), the battery can supply 15 A for 5/15 = 0.333 h. The corresponding C-rate is 1/0.333 = 3C.

8.5.3.7 Energy Capacity

Another way of expressing the capacity of a battery is by its energy. Unlike the charge capacity, the energy capacity considers the voltage that the charge is supplied at. Determining the energy capacity therefore requires simultaneously monitoring voltage and current during discharge. The energy capacity e_x of a battery when discharged at a constant current of x is expressed in watthours or kilowatthours and is calculated as

$$e_x = x \int_0^{T_{\mathrm{d},x}} v_{\mathrm{B}}(t)\mathrm{d}t. \tag{8.34}$$

The terminal voltage $v_{\mathrm{B}}(t)$ will vary with time, and so for the discharge current x to be constant, the discharge resistance will need to be varied with time. The discharge time ends when the terminal voltage drops below a specified cut-off voltage, just like for the charge capacity. The energy capacity will depend on the discharge rate, with less energy capacity associated with higher discharge. Energy capacity values are rarely provided by the manufacturer. Instead, it is common to approximate the energy capacity by multiplying the charge capacity by the battery's nominal voltage V_{nom}

$$\hat{e}_x = c_x \times V_{\mathrm{nom}}. \tag{8.35}$$

The energy capacity of a battery is useful because its units are watthours. Many loads are rated in watts, and so the duration that a battery can supply a given load is found by dividing its energy capacity by the power of the load.

Example 8.9 Consider the 12 V battery discharged at 8 A whose voltage is shown in Fig. 8.13. The voltage can be modeled as a piecewise linear function:

$$v_{\mathrm{B}}(t) = \begin{cases} -0.006088t + 12.39 : 0 \le t \le 180 \\ -0.02769t + 16.11 \quad : 180 < t \le 213.5 \end{cases}$$

(continued)

where t is the time in minutes. Compute the energy capacity of the battery if the cut-off voltage is 10.2 V. Compare this to the energy capacity estimated by the battery's nominal voltage.

Solution We know the battery has been discharged at a constant current of x =8 A. From (8.34), to compute the energy capacity, we need to integrate the battery voltage.

$$\begin{aligned} e_x &= 8\int_0^{180} (-0.006088t + 12.39)\,\mathrm{d}t + 8\int_{180}^{213.5} (-0.02769t + 16.11)\,dt \\ &= 8 \times (2131.6 - 0) + 8 \times (2808.4 - 2451.2) = 19,910.0 \text{ wattminutes} \end{aligned}$$

Converting to watthours: 19,910.0/60 = 331.84 Wh. The energy capacity when estimated from the nominal is $12 \times (8 \times 213.5/60) = 341.6$ Wh. The two values are fairly close.

8.5.4 *Efficiency*

Just as with energy conversion technologies, no form of energy storage is 100% efficient. The efficiency of a battery is found by dividing the energy that can be meaningfully output by the energy that is input:

$$\eta_\mathrm{B} = \frac{\int_0^{T_\mathrm{B,D}} i_\mathrm{B,D}(t) v_\mathrm{B,D}(t)\mathrm{d}t}{\int_{T_\mathrm{D}}^{T_\mathrm{C}+T_\mathrm{D}} i_\mathrm{B,C}(t) v_\mathrm{B,C}(t)\mathrm{d}t} \tag{8.36}$$

where the subscripts C and D denote whether the battery is being charged or discharged, we have assumed that charging immediately follows discharging, and the current is not necessarily constant.

For most charge and discharge scenarios, the efficiency can be approximated by

$$\eta_\mathrm{B} \approx \frac{\bar{V}_\mathrm{B,D} \int_0^{T_\mathrm{D}} i_\mathrm{B,D}(t)\mathrm{d}t}{\bar{V}_\mathrm{B,C} \int_{T_\mathrm{D}}^{T_\mathrm{C}+T_\mathrm{D}} i_\mathrm{B,C}(t)\mathrm{d}t} \tag{8.37}$$

were $\bar{V}_\mathrm{B,D}$ and $\bar{V}_\mathrm{B,C}$ are the average terminal voltage during discharge and charge, respectively.

The energy efficiency can then be split into two parts: the voltage efficiency η_{V} and the coulombic efficiency η_{C}. Thus, the battery efficiency can be approximated as

$$\eta_{\mathrm{B}} \approx \eta_{\mathrm{V}} \times \eta_{\mathrm{C}}. \tag{8.38}$$

The energy efficiency is often expressed as a percent.

8.5.4.1 Voltage Efficiency

The voltage efficiency is the ratio of the average voltage during discharge to the average voltage during charge:

$$\eta_{\mathrm{V}} = \frac{\bar{V}_{\mathrm{B,D}}}{\bar{V}_{\mathrm{B,C}}}. \tag{8.39}$$

The voltage efficiency is often expressed as a percentage. The average voltage of a discharge period T_{D} is computed as any other average:

$$\bar{V}_{\mathrm{B,D}} = \frac{1}{T_{\mathrm{D}}} \int_{t}^{t+T_{\mathrm{D}}} v_{\mathrm{B}}(t)\mathrm{d}t. \tag{8.40}$$

The average voltage during a charge period is computed in a similar fashion. The average discharge voltage is always less than the average charging voltage due to the battery resistance R_{B}. The voltage efficiency will therefore be less than 100%. The voltage efficiency depends upon the charge and discharge rate, as well as the other factors that influence battery resistance in general. Voltage efficiencies generally range between 80 and 90%.

8.5.4.2 Coulombic Efficiency

The coulombic efficiency or "Faraday efficiency" of a battery is the ratio of charge input to the battery during charging to the charge that is output from the battery during discharge

$$\eta_{\mathrm{C}} = \frac{\int_{0}^{T_{\mathrm{D}}} i_{\mathrm{B,D}}(t)\mathrm{d}t}{\int_{T_{\mathrm{D}}}^{T_{\mathrm{C}}+T_{\mathrm{D}}} i_{\mathrm{B,C}}(t)\mathrm{d}t}. \tag{8.41}$$

The coulombic efficiency is also often expressed as a percent. The coulombic efficiency tends to be high, between 90 and 95%. A coulombic efficiency less than 100% might seem strange—what happens to the electrons that enter the battery but never leave? These electrons are consumed in "side reactions" inside the battery, for example, producing hydrogen and oxygen gases in a lead–acid battery. The "loss" of electrons primarily occurs during charging when voltages tend to be higher and in particular when a battery is nearly fully charged [6].

8.5.4.3 Energy Efficiency

The energy efficiency η_{B} of the battery is typically in the range of 70% to 85%. Lower efficiencies are associated with rapid charging and discharging and in general any condition that increases R_{B} or side reactions. A practical consequence of this is that to supply 1 kWh of energy, the battery might require 1.4 kWh of input energy. It is sometimes convenient to define a charging efficiency η_{C} and a discharging efficiency η_{D} of the battery, so that

$$\eta_{\mathrm{B}} = \eta_{\mathrm{C}} \times \eta_{\mathrm{D}} \tag{8.42}$$

This is useful in simulations. It is common to set the charging and discharging efficiencies equal to each other, so that

$$\eta_{B} = \sqrt{\eta_{\mathrm{C}}} = \sqrt{\eta_{\mathrm{D}}} \tag{8.43}$$

This is a simplification, again in part to dependency of charging efficiency on SoC. The battery efficiency must be accounted for in designing an off-grid system, which we discuss in Chap. 12.

8.5.5 Cycle Life

The rated charge or energy capacity of a battery assumes the battery is in new condition. Unfortunately, as a battery degrades over time and with use, its capacity diminishes. The cycle life of a battery is the number of charge and discharge cycles the battery can experience before its capacity drops below a certain value—typically 60 or 80% of the initial rated value. In other words, if a battery is rated at 100 Ah at 0.05C, after a certain number of charge and discharge cycles, its effective rating will only be 80 Ah at the same C-rate. At this point, the battery is said to have reached its end of life. The battery is still functional and so it does not necessarily need to be immediately replaced, but its capacity has been appreciably diminished.

Figure 8.16 shows the typical cycle life of flooded and AGM batteries with respect to the DoD of each cycle. The number of cycles decreases as the DoD increases. Each cycle causes some irreversible damage to the cell's electrode, which reduces the amount of active material that can be used in the chemical reactions. Some battery types, like lithium iron phosphate ($\mathrm{LiFePO_4}$) batteries, have a cycle life far exceeding lead–acid. The cycle life is also dependent on the calendar age of the battery. The active materials will corrode over time, leading to a decrease in capacity. This effect is accelerated with temperature.

This is an important concern. To prolong battery life, many systems limit the DoD to 40 to 60%. Each cycle can be taken as a day so that most lead–acid batteries will last between 4 and 6 years if the DoD is limited. However, other factors, primarily elevated temperature, can shorten the cycle life.

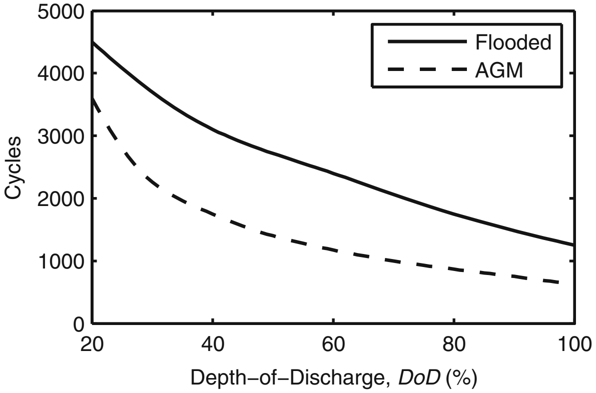


Fig. 8.16 Cycle life of lead–acid batteries decreases with the depth-of-discharge

Example 8.10 A 220 Ah flooded lead–acid battery is discharged at a constant rate of 11.0A for 8 h each day. Estimate the number of days the battery will last before it reaches the end of its cycle life. Use the curve in Fig. 8.16 to estimate the cycle life.

Solution To use the curve in Fig. 8.16, we must know the depth-of-discharge. The battery capacity is given as 220 Ah, which we assume is the 20-h (0.05C) rate. The corresponding current is $220/20 = 11$ A, which conveniently matches the discharge rate. The charge supplied by the battery each day is:

$$8 \text{ h} \times 11 \text{ A} = 88 \text{ Ah}.$$

Using (8.30), this corresponds to 40% DoD. Consulting Fig. 8.16, 40% DoD corresponds to approximately 3000 cycles, or $3000/365 = 8.2$ years.

8.5.6 Self-Discharge

A battery that is not connected to an external circuit will discharge internally, causing it to lose a portion of the energy it stores over time. The self-discharge is not caused by internal current; rather, it is caused by chemical "side" reactions. A typical self-discharge rate is 2.5% to 5% per month for lead–acid batteries designed for off-grid applications. The rate is lower for lithium–ion batteries. However, many lithium–ion batteries are packaged with integrated protection circuits, which might also consume another 1 to 2% per month. Self-discharge is accelerated at high temperatures, approximately doubling for every 10°C increase in temperature.

Depending on the discharge rate, it is advisable to periodically charge batteries, for example, every 3 months, when not in use. Batteries can be stored at lower temperatures to minimize self-discharge.

8.5.7 Temperature Dependence

The performance and characteristics of all batteries depend on the temperature of operation, which is often near the ambient temperature. Qualitatively, the following effects are observed for lead–acid batteries as temperature increases past about 25°C.

- Decreased internal impedance
- Increased capacity
- Increased open-circuit voltage
- Increased self-discharge
- Decreased cycle life

In many mini-grids, the batteries will not be in temperature-controlled environments, and thus the influence of temperature should be considered in the design phase. While the first three effects can be considered beneficial, they are typically outweighed by the last two—the decreased cycle life in particular.

The voltage of a fully charged lead–acid cell will increase by approximately 0.2 mV/cell/°C. But this rate depends on the SoC, as seen in Fig. 8.17. Thus at a very low or negative SoC, an increase in temperature leads to a *decrease* in voltage. The voltage increases because temperature increases the rate of all chemical reactions, including those in the battery. The battery capacity is effectively increased with temperature, as shown in Fig. 8.18. At very high temperatures, the battery capacity increases by perhaps 10%, and at very low temperatures, it is perhaps just 60% of its rated value.

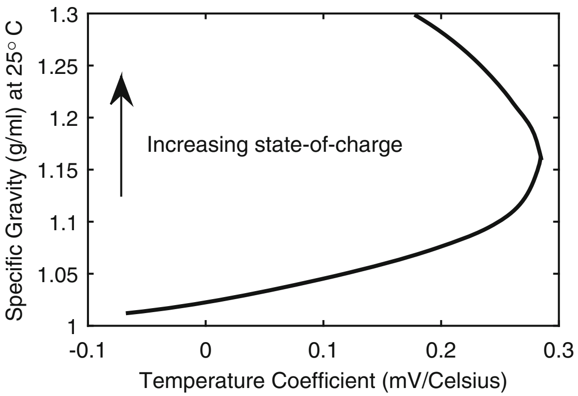


Fig. 8.17 The temperature coefficient of a lead–acid battery depends on the specific gravity of the electrolyte [10]

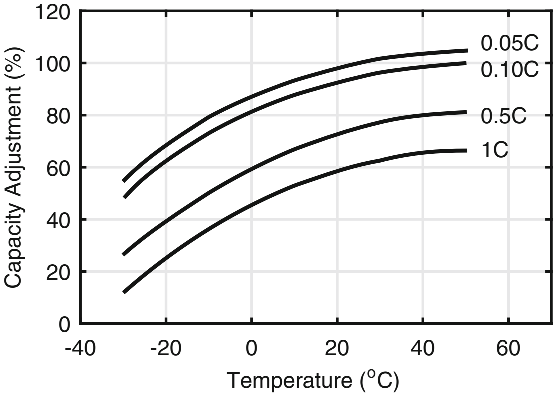


Fig. 8.18 The effect of temperature on maximum capacity at various discharge rates

High temperature also promotes the unwanted side reactions and self-discharge in a battery. The rate approximately doubles for every 10°C increase in temperature. Gassing can also increase, and the voltage that the battery is charged at should be reduced. This will be discussed in more detail in Chap. 10.

8.6 Lithium–Ion Batteries

Lithium–ion (LI) batteries are a relatively new technology, only becoming commercially available since the 1990s. They generally offer higher energy density, longer cycle life, a flatter I–V curve, less severe high-discharge penalty (Peukert exponent close to 1.0), and slower self-discharge rate than lead–acid batteries. Balancing these benefits are higher cost and some safety concerns. We will cover the fundamentals of LI batteries; other resources may be consulted for additional information [3, 11, 13].

There are two general types of LI battery chemistries: lithium iron phosphate ($LiFePO_4$) and those using lithium nickel, cobalt, or manganese. LI batteries operate by transferring positive lithium ions between electrodes through the electrolyte while electrons pass through an external circuit. The anode is typically a graphite carbon and the cathode one of several lithium metal oxide materials. The electrodes also incorporate copper or other materials to improve their conductivity.

In a completely discharged state, all the lithium is in the cathode. When the cell is charging, lithium ions travel through the electrolyte to the anode; the ions are shuttled back to the cathode when discharging. The electrolyte is usually a lithium salt dissolved in an organic solvent such as $LiPF_6$ or $LiBF_4$. The electrolyte facilitates the flow of the ions but is not part of the active material as in a lead–acid battery. The anode and cathode are physically separated by an electrically insulating microporous polymer membrane. The ions can pass through the membrane, but the electrodes are prevented from touching each other, as this would cause a damaging short-circuit.

The anode must have a physical structure that allows lithium ions to be inserted and extracted (to electrochemists this is known as "intercalation" and "de-intercalation"). The more lithium ions that can be inserted into the anode, the greater the charge capacity of the cell. The most common anode material is graphite carbon. Its layered molecular structure has space for one lithium ion for every six carbon atoms. As the cell becomes charged, the anode evolves from C_6 to Li_yC_6 where $0 \leq y \leq 1$. Li_yC_6 is expressed as an empirical formula, which is different from the structural molecular formula most often used in introductory chemistry classes. An empirical chemical formula expresses the ratio of the elements in a compound, and so the subscripts need not be whole numbers. For our purposes, we should be comfortable with the concept that as y increases, the proportion of lithium in the anode increases, and consequentially the SoC of the battery increases. We can write a similar empirical formula for the cathode in which the portion of lithium decreases as the SoC increases.

The basic reaction for an LI cell using a lithium cobalt oxide ($LiCoO_2$) cathode as an example during charging (insertion of the lithium–ion) is, for the anode:

$$y\mathrm{Li}^+ + \mathrm{C}_6 + y\mathrm{e}^- \rightarrow \mathrm{Li}_y\mathrm{C}_6 \tag{8.44}$$

and for the cathode

$$\mathrm{LiCoO}_2 \rightarrow \mathrm{Li}_{1-z}\mathrm{CoO}_2 + y\mathrm{Li}^+ + y\mathrm{e}^-. \tag{8.45}$$

The reactions are reversed during discharge. Most $LiCoO_2$ cells are charged so that $y = 1$ and $z \approx 0.5$; the overall reaction can be expressed as

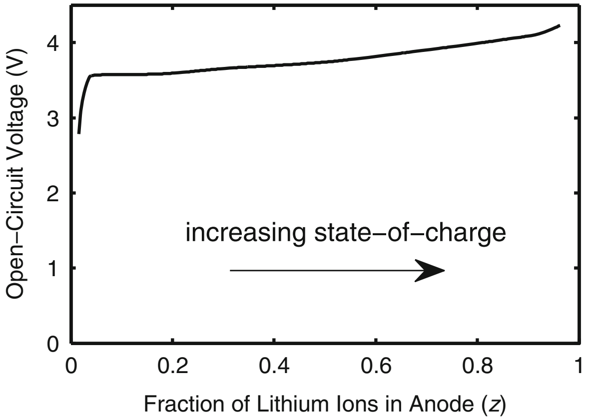
$$2\mathrm{LiCoO}_2 + \mathrm{C}_6 \leftrightarrow 2\mathrm{Li}_{0.5}\mathrm{CoO}_2 + \mathrm{LiC}_6. \tag{8.46}$$

8.6.1 Open-Circuit Voltage

The open-circuit voltage for a $LiCoO_2$ battery is shown in Fig. 8.19. In this figure, the horizontal axis is the fraction of lithium ions in the anode z. The right side of the figure is when all of the lithium ions have left the cathode and are in the anode (fully charged). The left side of the figure is when there are no lithium–ions in the anode and they are in the cathode (fully discharged). As with lead–acid batteries, the voltage developed depends on the chemical composition of the electrodes, and so this varies with the amount of lithium in the anode or cathode. The amount of lithium directly relates to the SoC, and so the horizontal axis can also be thought of as a SoC of sorts.

An important aspect of LI batteries is what happens near either end of the curves. When z approaches 1.0, the energy stored in the cell is the highest. The voltage is also at its highest level, in excess of 4.40 V. The voltage is so high in fact that the

Fig. 8.19 Cell potential of a lithium–ion cobalt oxide ($LiCoO_2$) battery



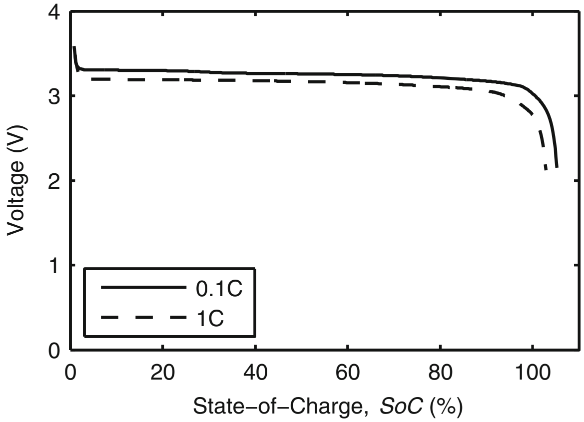
electrolyte begins to irreversibly degrade. The lithium becomes plated on the surface on the anode. Remember, we want the lithium ions to be inserted into the anode, not plated onto it. The plated lithium can no longer be removed during discharge.

Low voltages are also harmful to the electrodes. The copper conductor at the anode begins to irreversibly dissolve. When the battery is recharged, the copper is precipitated wherever it might be. This can cause an internal short-circuit. The cathode gradually breaks down, which reduces its capacity. If these two harmful extremes are avoided, though, the voltage of an LI battery remains fairly constant over a wide range of lithium–ion concentration.

Just like lead–acid batteries, we define the SoC as being the range of charge or energy that can be meaningfully provide without damaging the battery or the battery voltage becoming too low. The cut-off voltage varies depending on the type of LI battery, but it is often 2.5 to 3.0 V/cell. This roughly corresponds to the steep drop in the cell potential curve. For reasons previously described, the maximum voltage is limited to around 4.0 V/cell. The 100% SoC is in reference to the stored charge at this voltage. Note that the point at which 100% SoC is defined is not necessarily at $z = 1.0$. For example, z is limited to less than 0.5 for $LiCoO_2$ batteries in order to prolong the life of the cathode.

An LI battery can be charged in excess of 4.0 V/cell, in which case the SoC would exceed 100%. The battery lifespan and capacity would be reduced, however due to lithium plating and other reactions. Selecting the charging voltage of an LI battery therefore presents a trade-off—a higher voltage increases the energy that is stored (and consequentially can be extracted) but shortens its lifespan. As a familiar example, if you want your mobile phone battery to last for several years, then you should not fully charge it. By prematurely ending the charging, for example, at 70%, the battery voltage will be lower, and the battery's lifespan will be longer. However, the trade-off is of course that you will need to charge the battery more frequently because it is never full.

Fig. 8.20 Capacity curve of a $LiFePO_4$ battery



We should also expect the voltage to decrease with state of charge. However, the decrease is nonlinear as there are many reactions that are occurring. This will be explored in the capacity curve of the battery.

8.6.2 Capacity Curve

The typical capacity curve for a $LiFePO_4$ battery is shown in Fig. 8.20. Instead of discharge time, the horizontal axis is the SoC referenced to 1.0C. LI batteries are often referenced to 1C instead of 0.05C. Although the capacity of a lead–acid battery is lower at 1.0C than 0.05C, the capacity of an LI battery is less sensitive to the magnitude of the discharge current. In other words, its Peukert exponent is near 1.0. $LiFePO_4$ batteries in particular exhibit flat curves. This is desirable because it means their output voltage is less variable while discharging.

8.6.3 Safety

LI batteries have special safety concerns that must be acknowledged. In particular, a failure mode known as *thermal runaway* can cause LI batteries to ignite [4]. This has led to special handling procedures when LI batteries are transported on aircraft. The risk generally stems from the heat caused when the battery develops an internal short-circuit. The membrane separating the anode and cathode is very thin. If accidentally punctured, the anode and cathode could come into contact. The heat from the resulting short-circuit will cause the battery's internal temperature to rise. This can cause the separator to shrink, exacerbating the problem. At high temperatures, around 80°C, a series of unwanted heat-producing reactions occur. Among them is the decomposition of the cathode, which releases gaseous oxygen.

This accelerates the decomposition of the electrolyte which releases more gas. This is the runaway condition mentioned above. The cell temperature can exceed several hundred degrees Celsius at which point the electrolyte ignites.

8.6.4 Protection

The sensitivity and safety risk associated with over- and undervoltage conditions require LI batteries to include specialized battery protection circuits. The cells in a battery might have different SoC at a given time. This can cause one cell to be overcharged or undercharged, causing failure. To avoid this, a cell balancing circuit is often integrated into the LI battery as well as overcharge and undercharge protection circuits. There are a few ways to balance the cells. Most involve circuits that discharge the cells that have a higher voltage than the rest through a resistor. This, however, is inefficient. More sophisticated designs will transfer this energy to the cells that have a lower charge, thus reducing losses. Pressure release valves are sometimes included.

8.6.5 Cycle Life

LI batteries tend to have a longer cycle life than lead–acid batteries. For $LiCoO_2$, the increase is more modest, perhaps lasting 500 cycles at a DoD of 80%. However, $LiFePO_4$ batteries can withstand several thousand cycles.

8.6.6 Charging

An advantage of LI batteries is that they can be charged more rapidly than lead–acid batteries. The rate varies with the chemistry, but it is usually less than 4 h and for $LiFePO_4$, and for LI manganese batteries as few as 2 h. Of course the charger must be capable of supplying this high rate of charge.

8.6.7 Comparison

The different choices of electrodes and electrolytes change the characteristics of the LI battery. Some general comparisons are shown in Table 8.3. These are approximate only as the performance of any battery depends on many factors. In the context of off-grid systems, $LiFePO_4$ batteries are increasingly common in solar home systems (SHS) and solar lanterns (SL). They offer the highest cycle

Table 8.3 Lithium–ion characteristics

Characteristic	Lead-acid	Lithium cobalt oxide	Lithium nickel manganese cobalt oxide	Lithium iron phosphate
Specific energy (Wh/kg)	40	150–200	150–220	90–120
Nominal voltage/cell (V)	2.04	3.60–3.70	3.60–3.70	3.2
Operating range/cell (V)	1.75–2.50	3.0–4.2	3.0–4.2	2.5–3.65
Cycles (80% DOD)	1000–2000	500–1000	500–1000	2000–5000
Efficiency (%)	70–90	85–95	85–95	85–95
Cost (USD/kWh)	150–500	2000–3000	500–1500	750–1250
Toxicity	High	Low	Low	Low
Self-discharge (%/month)	5–8	2–5	2–5	2–5

life, even up to 10,000 if not deeply discharged or overcharged. They offer good thermal stability and so are less prone to thermal runaway and are more tolerant to overcharging. Their discharge curve is flat and so the voltage regulation is good. However, $LiFePO_4$ have lower nominal voltage, and so their specific energy is lower than other LI batteries.

8.7 Battery Banks

The largest individual batteries used in off-grid applications rarely exceed a few kilowatthours of capacity, and most have a nominal voltage of no more than 12 V (or 12.8 V for $LiFePO_4$). In applications requiring more energy storage or greater voltage, the batteries are connected in series, parallel, or combination thereof to form a battery bank. The battery banks for larger mini-grids can be substantial. A 48 V, 6800 Ah bank is shown in Fig. 8.21. This battery bank fills an entire room. The batteries should be as similar as possible, preferably the same model, with the same parameters, from the same supplier and manufactured at the same time.

As with a PV array, the batteries connected in series are a “string”. The string voltage is equal to the sum of the individual voltages in that string:

$$V_{\mathrm{bank}} = \sum_{i=1}^{N_{\mathrm{series}}} V_{\mathrm{B},i} \tag{8.47}$$

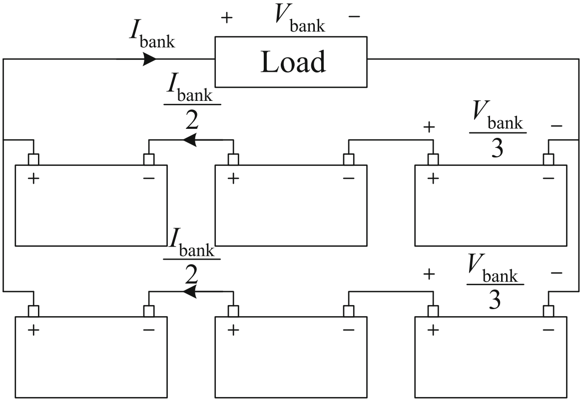
where N_{series} is the number of batteries in the string. During normal operation, the batteries all have the same voltage, V_{B}:

$$V_{\mathrm{bank}} = N_{\mathrm{series}} \times V_{\mathrm{B}}. \tag{8.48}$$

Battery strings can be connected in parallel, so long as the voltage of each string is equal or nearly equal. We expect the battery bank current I_{Bank} to be divided equally by the strings.

Fig. 8.21 Battery bank from a mini-grid in Nigeria; the battery bank has not been connected to the DC bus (courtesy of GVE Projects)

Fig. 8.22 A diagram of a battery bank consisting of two strings each with three batteries



$$I_{\text{string}} = \frac{I_{\text{Bank}}}{N_{\text{string}}}. \tag{8.49}$$

In practice, the number of strings is often limited to about four. The resistance of the cables connecting each string to the DC bus should be kept as uniform as possible. This ensures the batteries are charged and discharged evenly. Should a battery in a string fail, for example, by an internal short circuit, then the other batteries will discharge through the string with the faulty battery. This can cause a catastrophic failure of the entire battery bank.

Figure 8.22 shows a battery bank consisting of two strings of three batteries each. The discharge current is evenly divided among the strings. Similarly, the battery bank voltage is equally divided among the batteries in each string. This is an idealization of course. There will be slight variations in individual batteries. The energy capacity of a battery bank is the sum of the capacities of the individual batteries, which should all be equal

$$E_{\text{bank},x} = N_{\text{string}} \times N_{\text{series}} \times e_{\text{B},x}. \tag{8.50}$$

In other words, the battery bank capacity is independent of how the individual batteries are connected. We must be careful when computing the charge capacity rating of a battery bank. For example, when two, 12V, 100 Ah, are connected in series, the charge capacity remains at 100 Ah (the current through each battery is the same). The voltage, however, has been increased to 24 V and so the energy capacity has doubled.

We often refer to the battery bank as simply the "battery" without providing specific information about how the bank is configured. In this case, V_B and I_B refer to the terminal voltage of and current from the bank, not the individual batteries. The nominal voltage of the battery bank is the sum of the nominal voltages of the series-connected batteries.

The terminals of a battery bank are connected to the positive and negative DC bus. The DC bus voltage therefore is the same as the battery bank voltage.

Example 8.11 The battery bank of a mini-grid consists of 32 lead–acid batteries. Each battery has a nominal voltage of 6 V and a capacity of 375 Ah at the 20-h rate. The nominal voltage of the battery bank is 48 V. Compute the charge capacity of the battery bank, and estimate the energy capacity of each battery at the 20-h rate. According to the manufacturer, the maximum charging current is limited to 18% of the 20-h capacity. What is the maximum charging current that can be supplied to the battery bank without violating this limit?

Solution Each string of the battery bank consists of

$$\frac{\text{battery bank nominal voltage}}{\text{individual battery voltage}} = \frac{48}{6} = 8 \text{ batteries.}$$

Therefore, the battery bank has

$$\frac{\text{total batteries}}{\text{batteries per string}} = \frac{32}{8} = 4 \text{ strings.}$$

Each string has a capacity of 375 Ah, and so the battery bank has a total charge capacity of

$$\text{Ah per string} \times \text{strings} = 375 \times 4 = 1500 \text{ Ah.}$$

The charge capacity is 1500 Ah at the 20-h rate. The energy of each battery is

$$\text{Ah capacity} \times \text{nominal voltage} = 375 \times 6 = 2250 \text{ Wh.}$$

(continued)

Therefore, the energy capacity of the battery bank is $2250 \times 32 = 72.0$kWh. We could also arrive at this value by multiplying the amphour rating of the bank by its nominal voltage: $1500 \times 48 = 72$ kWh.

The maximum charging current per string is 18% of the 20-h capacity: $0.18 \times 375 = 67.5$ A. Since there are four strings, and assuming the current divides equally into each string, the maximum total charging current is $67.5 \times 4 = 270$ A.

8.8 Summary

Electrochemical batteries are an important component in many off-grid systems, particularly those that rely on PV and WECSs. Lead–acid and lithium–ion (LI) batteries are most common in off-grid applications. These, like all batteries, rely on electrochemical reactions to develop a voltage between their terminals and to provide power when connected to a load. The reactions are decidedly nonlinear and temperature sensitive. Because of this complexity, we must be careful in interpreting the ratings and other information provided by battery manufacturers, and when analyzing the operation of a battery-based system. Among the most important to understand is that the battery capacity is based on the charge or energy that can meaningfully extracted without the voltage becoming too low or the battery being damaged. This capacity depends on the rate of discharge, temperature, and the specified cut-off voltage. The battery can be modeled as voltage source V_{SoC} in series with a resistance R_{B}—but both of these are dependent on several factors, and the battery resistance itself represents three polarization affects, only one of which is actually ohmic in nature.

When using a battery, you must be careful not to overcharge or overdischarge it. This is especially true for lithium–ion (LI) batteries as their failure can present a safety hazard. Lead–acid batteries can last for several hundred up to a few thousand cycles. If one assumes a daily charge/discharge cycle, that suggests a battery life of several years. Some LI batteries, $\mathrm{LiFePO_4}$, in particular, can last for several thousand cycles. Limiting the depth-of-discharge and avoiding high operating temperatures promote longer battery life.

The choice between lead–acid and LI depends on the application. LI tend to be used in solar lanterns and solar home system as they are lighter. Lead–acid batteries, flooded, in particular, are less expensive but require regular maintenance in the form of watering.

Problems

8.1 The standard cell voltage for a lead–acid battery is 2.04 V. Compute the corresponding open-circuit voltage of a nominal 48 V battery bank if the concentration of the sulfuric acid in the electrolyte is 2 moles/liter. Assume the temperature is 25°C. Approximate the activity of the sulfuric acid by its concentration. Repeat the calculation with a concentration of 5 moles/liter.

8.2 A flooded 12 V lead–acid battery is charged at a current of 10 A. The terminal voltage is measured to be 11.9 V. The battery resistance is 0.032 Ω. Compute the voltage V_{SoC} and estimate the battery's SoC using Table 8.1.

8.3 A battery is charged in two sequential stages. In the first stage, a constant current of 20 A is applied for 2 h. In the second, the current decreases according to the equation:

$$i_{\mathrm{B}}(t) = 20e^{\frac{-(t-2)}{1.25}}$$

where t is the time since charging began, in hours. The second stage lasts for 4 h. Compute the total charge, in amphours, provided to the battery.

8.4 The capacity of a battery at its 72-h rate is 394 Ah and is 375 Ah at its 20 hour-rate. Compute the current corresponding to the 72- and the 20-h rates. What are the corresponding C-rates?

8.5 A 1100 Ah AGM battery (20-h rate) is used in a mini-grid. The mini-grid supplies a critical load whose current draw is 25 A. Estimate the number of hours the battery can supply this load if the Peukert exponent is 1.046.

8.6 Repeat the previous problem but if a 1100 Ah flooded lead–acid battery with a Peukert exponent of 1.09 is used.

8.7 The capacity of a flooded lead–acid battery at 0.05C is 1547 Ah and at 0.01C is 1990Ah. Compute the Peukert exponent.

8.8 The average voltage of a battery is 13.56 V when charged at 5 A, and the average voltage is 11.46 V when discharged at 5 A. Compute the voltage efficiency of the battery.

8.9 A battery bank consists of three strings of eight 6 V lead–acid batteries. Each battery is rated at 440 Ah. Estimate how long the battery bank can supply a load of 120 A. Assume the Peukert exponent is 1.0. Estimate the energy capacity of the battery bank, in kilowatthours.

8.10 A 48 V battery bank has one string of 2 V lead–acid batteries. Each battery is rated at 1160 Ah. Estimate how long the battery bank can supply a load of 80 A. Assume the Peukert exponent is 1.08. Estimate the energy capacity of the battery bank, in kilowatthours.

8.11 Consider the batteries in the previous problem. Instead of a 48 V battery bank, consider an alternate design where the same number of batteries are arranged in a 24 V battery bank. Since the DC bus voltage has been reduced by one half, the current doubles to 160 A so that the same power to the load is provided. Estimate how long the battery bank can supply the load. Assume the Peukert exponent is 1.08. Estimate the energy capacity of the battery bank, in kilowatthours. Compare the results to the previous problem.

8.12 A 340 Ah battery supplies a constant current load of 17 A for 8 h each day. Compute the battery's state-of-charge and depth-of-discharge at the end of each day.

8.13 Estimate the number of cycles the battery in the previous problem will last if its life cycle characteristic is that of Fig. 8.16. Estimate the number of cycles the battery will last if the load is reduced to 9 A for 8 h each day. Assume the battery is a flooded lead–acid battery.

8.14 A large mini-grid requires its battery to supply 80,000 Wh of energy at 48 V each day. The charge capacity characteristics of the particular 2 V nominal battery type to be used are provided in Table 8.2. Design a battery bank (provide the number of strings and number of batteries per string) to supply this load while discharging the battery no deeper than 60%. Assume the battery is discharged at a constant current over a 10-h period each day.

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