

Storage in PV Systems

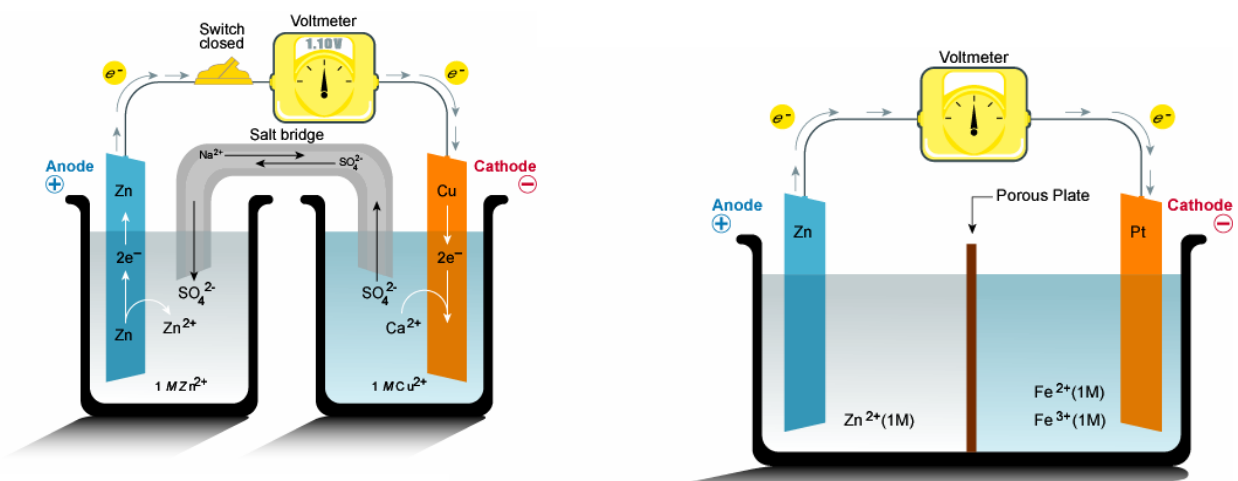
A fundamental characteristic of a photovoltaic system is that power is produced only while sunlight is available. For systems in which the photovoltaics is the sole generation source, an exact match between available sunlight and the load is limited to a few types of systems - for example powering a cooling fan – and therefore storage is typically required. Even in hybrid or grid-connected systems, where batteries are not inherently required, they may be beneficially included for load matching or power conditioning. By far the most common type of storage is chemical storage in the form of a battery. However, in some cases other forms of storage can be used. For example, for small, short term storage a flywheel or capacitor can be used for storage, or for specific, single-purpose photovoltaic systems such as water pumping or refrigeration, the storage can be in the form of water or ice.

In any photovoltaic system that includes batteries, the batteries have a major effect on the system, impacting performance, cost, maintenance requirements, reliability, and design of the photovoltaic system. The cost of the batteries in a stand-alone system is similar to the cost of the photovoltaic modules. Because of large impact of batteries in a stand-alone photovoltaic system, understanding the properties of batteries is critical in understanding the operation of photovoltaic systems. The important battery parameters are the battery capacity and voltage (and how these change and interact with other system parameters), battery maintenance requirements, lifetime of the battery. These are controlled not only by the initial choice of the battery but also by how it is used in the system, particularly how it is charged and discharged and its temperature.

Battery Basics

A battery converts energy stored in the chemical bonds of a material into electrical energy via a set of oxidation/reduction (redox) reactions. Redox reactions are chemical reactions in which an electron is either required or produced. For primary batteries, this is a one-way process – the chemical energy is converted to electrical energy, but the process is not reversible and electrical energy cannot be converted to chemical energy. This means that a primary battery cannot be recharged. For a secondary battery, the conversion process between electrical and chemical energy is reversible, – chemical energy is converted to electrical energy, and electrical energy can be converted to chemical energy, allowing the battery to be recharged. For photovoltaic systems, batteries should be rechargeable or secondary batteries.

The key aspect of a battery which differentiates it from other oxidation/reduction reactions is that the two reactions are physically separated, which allows the insertion of a load between the two reactions. The electrochemical potential between the two sides of the battery is the voltage which drives the load, and the movement of electrons from the oxidation to the reduction reaction provides the current. The components of a battery are shown in the figure below and are: an anode and cathode (together called the electrodes), an electrolyte, provision for electron transport between the anode and cathode (usually a wire), and provision for ion transport between the anode and cathode, either a salt bridge if the electrolyte for the anode and cathode are different or simply one chemical bath if they are the same. If both the anode and the cathode have the same electrolyte, then a porous plate is often inserted between the anode and cathode to keep them from physically touching each other and shorting out the battery. The components are described in more detail below.



Schematic of a battery in which (a) the electrolyte of the reduction and oxidation reaction are different and (b) the electrolyte is the same for both reactions.

The components which differentiate one battery type from another are the materials of the electrode and electrolyte for both the oxidation and reduction reactions. The electrode/electrolyte interface is the physical location where the core of the redox reaction – the transfer of electrons – takes place. In many battery systems, including lead acid and alkaline batteries, the electrode also consists of the material being oxidized or reduced in the chemical reactions, while in some battery systems (for example fuel cells) the electrode itself is inert and is only the site for the electron transfer from one reactant to another. For a discharging battery, the electrode at which the oxidation reaction occurs is called the anode and is at a positive voltage, and the electrode at which the reduction reaction occurs is the cathode and is at a negative voltage. (Note that during charging, the sites of the oxidation and reduction reaction switch, but by convention the terms anode and cathode refer to the reactions when discharging.) The electrolyte contains other reactant species needed to complete the oxidation and reduction reaction. For example, in lead acid batteries, the sulfate ion from the sulfuric acid in the electrolyte is essential in the formation of lead sulfate.

The current in the battery arises from the transfer of electrons from one electrode to the other. During discharging, the oxidation reaction at the anode generates electrons and reduction reaction at the cathode uses these electrons; therefore during discharging, electrons flow from the anode to the cathode. The electrons generated or used in the redox reaction can easily be transported between the electrodes via a conventional electrical connection, such as a wire attached to the anode and cathode. However, unlike a conventional electrical circuit, electrons are not the only charge carrier in the circuit. Electrons travel from the anode to the cathode, but do not return from the cathode to the anode (unless the battery is charging, in which case the electrons also only travel in one direction, but flow the opposite way). Instead, electrical neutrality is maintained by the movement of ions in the electrolyte. If each redox reaction has a different electrolyte, a salt bridge joins the two electrolyte solutions to allow the ion to move from one system to the other, but to keep the electrolyte solutions otherwise separate. The direction of the ion movement acts to prevent a charge build-up at either the anode or the cathode. In most practical battery systems, the electrolyte is the same for both the anode and the cathode, and ion transport can take place via the electrolyte itself, eliminating the need for a salt bridge. In this case, a separator is also inserted between the anode and the cathode which prevents the anode and cathode from physically touching each other since they are usually in very close physical proximity to one another. If they were to touch, it would short out the battery as the electrons can be transferred directly without flowing through the external circuit and load.

The redox reactions which comprise a particular battery system define many fundamental parameters about the battery system, including the maximum battery voltage, specific power or energy, and the impact of parameters such as temperatures, low state of discharge, etc. Other key battery properties, including as battery capacity, charging/discharging performance and other practical considerations are also influenced by the physical configuration of the battery, for example the amount of material in the battery or the geometry of the electrodes. The following pages describe how battery characteristics – voltage behavior, battery efficiency, battery non-idealities (self-discharge, degradation of battery capacity, etc) – are dependant on the redox reactions and the battery configuration.

Oxidation/Reduction Reactions

Reduction/oxidation (redox) reactions are an important class of chemical reactions since they are the driving force behind a vast range of process, both desirable (for example breathing in mammals) and undesirable (for example rusting of iron). A redox reaction is characterized by the fact that electrons are produced (in an oxidation reaction) or are used by the reaction (in a reduction reaction). An oxidation reaction must be paired with a reduction reaction, as the oxidation reaction produces the electrons required by the reduction reaction.

The electrons transferred in a redox reaction arise from the change of the valence state of materials in the redox reaction. If a material gives up or loses an electron, then its valence state becomes more positive (since an electron has a negative charge) and the reaction is called an oxidation reaction. Since an oxidation reaction gives up electrons, it will always have electrons as one of its products. By definition, the oxidation reaction occurs at the anode. The chemical reaction shown below is an oxidation reaction where zinc metal (with a neutral valence state or valence charge = 0) is oxidized to give a zinc ion, which has a 2+ valence charge. The two electrons lost by the zinc metal are products of the oxidation reaction. The zinc ion exists most readily as a dissolved salt in a solution, and the (aq) after the zinc ion indicates that it is aqueous.

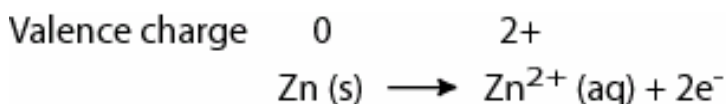


Figure 2: Oxidation reaction (the valence state of the reactant increases) of zinc metal to a zinc ion. The (s) after the zinc indicates that it is in solid form. The zinc ion has (aq) after to indicate that it is aqueous, (ie in solution).

If a material gains an electron then its valence state decreases or reduces due to the negative charge of the electrons and the reaction is a reduction reaction. The reaction below is a reduction reaction in which a copper ion with a valence state of 2+ is reduced to copper metal, with a valence state of zero. Since a reduction reaction requires electrons, it will always have electrons as one of the reactants. The reduction reaction occurs at the cathode.

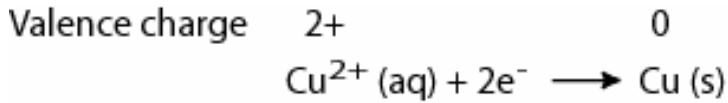
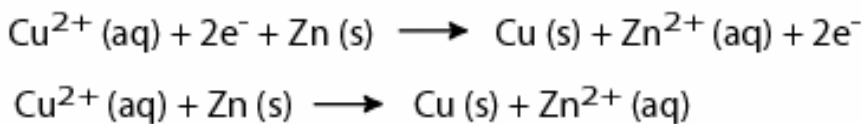


Figure 3: Reduction reaction of Cu ions to form copper metal. The valence state of copper is reduced from 2+ to 0.

The total redox reaction consists of both of the two reactions together. For the example of copper and zinc above, the total reaction is shown below. Since the reaction with zinc metal (ie the reactant of the oxidation reaction) is providing the electron required to reduce the copper, the zinc is the reducing agent and the zinc itself is oxidized. Copper ions in this case are the oxidizing agent - they oxidize the zinc and are themselves reduced. Note that since the electrons appear on both sides of the chemical equation, they may be omitted when writing the redox reaction. Further note that for redox reaction, it is important to balance not only the elements in the chemical reactions, but also the electrons.



Mnemonic Devices: Remembering which reaction occurs where and does what

There are several mnemonic devices to assist in remembering the terms in a battery. The first method is just based on the words describing reduction. In a reduction reaction, the valence state is reduced, meaning that it gains a negative charge, ie an electron, and therefore the electron must be a reactant in a reduction reaction. Thus the word itself – reduction – identifies the process that occurs there. An imaginative mnemonic to remember which reaction is the oxidation and the reduction is "LEO (the Lion goes) GER (grrr)" in which LEO is short for "Loss of Electrons - Oxidation" and GER is short for "Gain of Electrons - Reduction". Another way is to remember the difference between oxidation and reduction reactions, (which is not quite the spirit of renewable energy), is "OIL RIG": Oxidation Involves Loss of electrons, Reduction Involves Gain of electrons."

There are also a few mnemonics to help remember which reaction occurs at the anode (the oxidation) and which at the cathode (the reduction). "The RED CAT and AN OX", groups the abbreviations for REDuction and CAThode together and also the abbreviations for ANode and OXidation. Another way to remember which reactions occur at the anode and cathode is to note that the letter "O" (for oxidation) occurs before the letter "R" (for reduction) and similarly that the letter "A" (for anode) occurs before the letter "C" (for cathode). Thus, the oxidation occurs at the anode and the reduction occurs at the cathode. Finally, you may also remember that both "anode" and "oxidation" begin with vowels and both "cathode" and "reduction" begins with consonants.

A final piece of information to remember is that the anode is negative and the cathode positive. The mnemonic for this is similar to that of the anode and cathode. The anode is negative, the cathode is positive, "A" comes before "C" and "N" comes before "P". In a battery the situation is slightly more complex, as the physical location of the oxidation and reduction reaction changes between when the battery is charging and discharging. By convention, the terms anode and cathode are defined according to conventional rules when the battery is discharging and retain the same names when the battery is being charged.

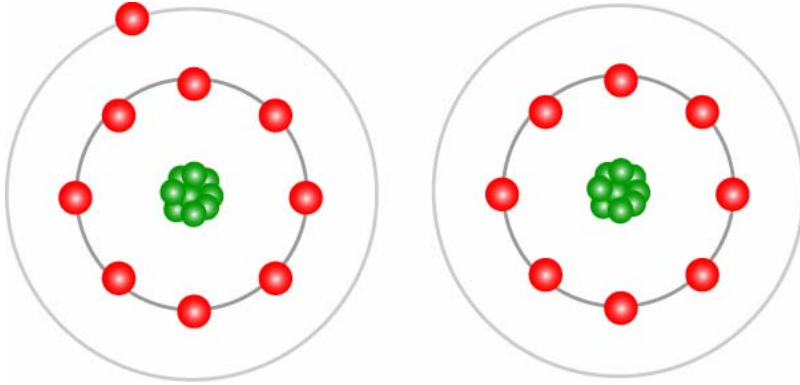
Electrochemical Potential

The voltage or potential difference between an oxidation and reduction reaction arises from the different electrochemical potentials of the reduction and oxidation reactions in the battery. The electrochemical potential is a measure of the difference between the average energy of the outer most electrons of the molecule or element in its two valence states. (For those familiar with semiconductor theory, the electrochemical potential difference between an oxidation and reduction reaction is analogous to the Fermi level difference between two sides of a diode). As the electrochemical potential is a measure of the energy of the outer most electrons, examination of the electronic configuration of the outer shell of the material will give an indication of the magnitude and sign of the electrochemical potential between the reactants and products of a reduction or oxidation reaction. The lowest energy configuration for materials is for their outer shell to be

fully occupied by electrons. Hence, an element (say lithium, Li) with one electron in its outer shell will have a higher energy than the element with the electron removed. Thus in the reaction

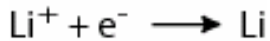


lithium metal has a higher energy than Li^+ . The oxidation reaction has a large positive electrochemical potential, with a value of 3.04V, since the positive sign is defined such that the reaction proceeds spontaneously (assuming that there is another reaction which will accept the electron).



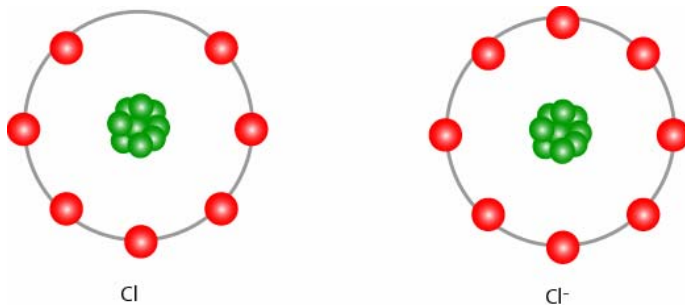
Outer electron configuration showing an element with one electron in its outer shell. When it loses its electrons, the outer shell has eight electrons, and hence is a stable, low energy configuration. The core electrons are not shown.

By convention half reactions (a half reaction is either the oxidation or reduction reaction of a oxidation/reduction reaction, i.e. half of the overall redox reaction) are written as reduction reactions, and hence the above reaction is typically tabulated as:



which has a *negative* standard potential. For all half reactions, changing the direction of the reaction changes the sign of the standard potential, such that the reduction reaction of lithium above has a standard potential of $E^0 = -3.04 \text{ V}$.

If an element has 7 electrons in its outer shell (say chlorine), the spontaneous condition (assuming that there is another reaction which will provide the electron) is that the element will accept an electron.



Therefore, given that the spontaneous reaction is defined as positive, in the reaction



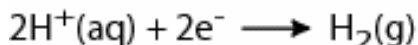
the chlorine ion Cl^- has a lower energy than the neutral Cl , and the reduction reaction has a large positive electrochemical potential of 1.36V.

Standard Potential

The overall energy of the outer electrons for a material depends on the temperature of the systems and also, for a material that is not a pure solid, also depends on the concentration of the reacting species. Thus, in measuring the electrochemical potentials, both the temperature and the concentration must be specified. The standard potential, given the symbol E^0 , is the

electrochemical potential at 25 °C, with gasses having a pressure of 1 atm and solutions a concentration of 1 Molar (1 M or 1 mol/liter).

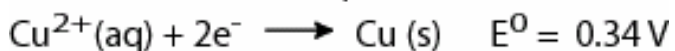
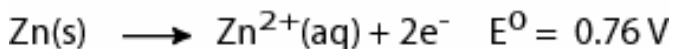
When measuring standard potentials, as with all voltages, only a difference in potential or voltage can be measured, and hence only a potential between an oxidation and reduction reaction can be measured. To determine the potential of a single oxidation or reduction reaction, the potential of one reaction is measured compared to the oxidation of hydrogen, which is by definition set to zero.



The standard potential of the reduction/oxidation reaction pair is the sum of the standard potentials for the half reactions (to avoid continually having to say the oxidation and reduction reaction, they are more generally termed a half reactions, since they make up half of the overall redox reaction). The values of common half reactions are listed in Tables of Standard Potentials. The standard potential of a redox reaction is used to determine if a redox reaction will occur spontaneously (ie if it will generate a voltage between the reduction and oxidation reaction). If the difference between the standard potentials is positive, then the reaction will proceed spontaneously. If the standard potential is negative, a voltage needs to be applied in order for the reaction to proceed. For example, for the copper/zinc redox reaction described previously, the standard potential of the Cu reduction reaction is 0.34 V and of the zinc is -0.76V as shown below:



The zinc under goes an oxidation reaction (since the reduction reaction has a negative standard potential), so the direction of the reaction and the sign of the standard potential must be reversed. The overall the oxidation/reduction reaction is:



and the standard potential for the reaction is $(0.76 + 0.34) = 1.1\text{V}$.

Nernst Equation

The standard electrochemical potential defines the voltage between a redox reaction under standard conditions (1 molar for aqueous solutions, 1 atmosphere for gases). The voltage also depends on the concentration (for liquids) or pressure (for gaseous reactants) of the components in the redox reaction since the average energy of the components will be altered by changes in concentration or pressure. The voltage under conditions other than 1 M for solutions and 1 atm for gasses is given by the Nernst equation.

$$E = E^0 - \frac{RT}{nF} \ln Q$$

where R is the universal gas constant (8.3145 J/mol K), T is temperature, and F is Faraday's constant (96,484.6 C mol⁻¹), and n is the number of moles of electrons exchanged between the redox and oxidation reaction. Q is the reaction coefficient. Q can be found for a reaction of the form

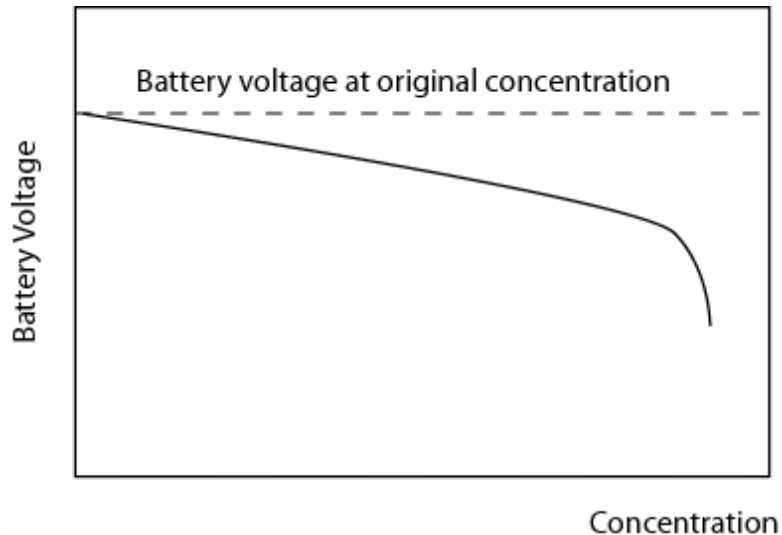


by:

$$Q = \frac{[\text{D}]^d [\text{C}]^c}{[\text{B}]^b [\text{A}]^a}$$

where [X] refers to the concentration or pressure of the material X (ie [D] is the concentration of the compound D in the reaction). For a solid, the concentration is 1, which means that for a battery in which all the components of the redox

reactions are solids and hence do not change their concentration, their ideal battery voltage calculated from equilibrium conditions is constant. For battery systems in which the concentrations of the components change as the battery discharges (in practice, this is a large number of batteries), a key implication of the Nernst equation is that the voltage of a battery is not constant, but varies as it is charged or discharged as the concentration of the components change. This is shown below for a lead acid battery.



Ideal battery capacity

The battery capacity is a measure of the amount of charge or energy (by including the electrochemical potential) stored in the battery. As such, a fundamental unit of battery capacity is coulombs (C), although a more common and useful unit is Amp-hrs (Ah) (amps = C/time, so Ah = C/time(sec) x time (hrs)). The Amp-hour unit is more convenient since it can be viewed as the number of hours a battery can provide a given current, which tends to be more physically intuitive and Coulombs. The battery capacity can be ideally calculated from the weight/volume or number of moles of materials of the electrode and/or electrolyte (the electrolyte only plays a part if it is an active component in the redox reactions) in the battery. The ideal battery capacity under equilibrium conditions (which can differ substantially from the “real” battery capacity under load) is calculated by from the moles of available reactants. From the chemical reaction of the battery, the number of moles of electrons transferred from the anode to the cathode, given by n and also used in the Nernst Equation, is determined. Using Faraday’s constant, which gives the number of Coulombs for a mole of electrons ($F = 96,484.56 \text{ C/mol}$), the total available coulombs (charge) can be determined for the battery. The battery capacity in coulombs is simply the moles of electrons multiplied by Faraday’s constant or $\text{Capacity (coulombs)} = n \times F$. However, since the battery capacity is more typically specified in units of Ah, the battery capacity can be determined by the equation:

$$\text{Capacity (Ah)} = n \times F \times \frac{1 \text{ hour}}{3600 \text{ sec}}$$

Since the primary function of a battery is to store electrical *energy* rather than electrical *charge*, the energy storage of a battery is also an essential parameter. A simple way to determine the energy storage capacity of the battery is to multiply the Ah capacity by the nominal battery voltage, such that:

$$\text{Energy Capacity} = \text{Ah} \times \text{Battery Voltage}$$

It practice, the battery voltage is not constant, and this and several other factors contribute to substantially different battery parameters when a battery is measured or used under load conditions.

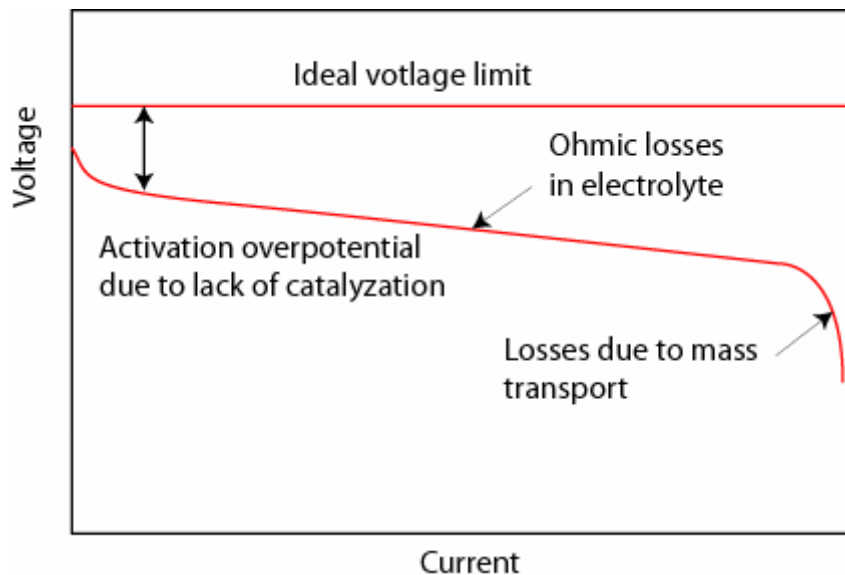
Battery voltage and capacity in non-equilibrium

The battery voltage described by the Nernst Equation and the ideal battery capacity assume that the battery is in equilibrium. Since a battery under load is not in equilibrium, the measured voltage and battery capacity may differ significantly from the equilibrium values, and the further from equilibrium (i.e. the higher the charge or discharge currents),

the larger the deviation between the equilibrium battery voltage and capacity and the realistic battery voltage and capacity may be.

The difference between the voltage under equilibrium and that with a current flow is termed polarization. Polarization effects have a significant impact on battery operation, both beneficial and detrimental. For example, polarization effects mean that under normal operation of lead acid batteries the electrolysis of water proceeds much more slowly. Since the standard potential for the electrolysis of water is -1.23V , this would imply that electrolysis of water would dominate the charging reactions for any battery with voltage > 1.23 and using water as a component in the electrolyte. However, the polarization effects mean that electrolysis typically occurs at over 2V . Polarization effects also have detrimental effects on performance, for example reducing efficiency and making the battery sensitive to charging and discharging conditions.

The polarization is comprised of three basic mechanisms. These mechanisms include resistive drops in the battery, and to two effects relating to the rates at which a reaction can proceed. The overvoltage causes a deviation of the voltage and capacity from the equilibrium values calculated earlier. As shown below, during discharging, the battery voltage is lower than that in equilibrium, while during charging, a higher voltage than the Nernst voltage is required.



Cell potential from equilibrium and including polarization effects.

Reaction Rates

The equilibrium electrochemical potentials only take into account the initial and final potentials of the materials in the reaction, without considering the rates or kinetics of the reactions themselves. The chemical reaction rates play an important role in determining the operation of a battery and in the processes that control battery behavior. For example, if multiple reactions can occur, then a reaction with a reaction rate significantly lower than all other reaction rates will not proceed to a significant extent and may potentially be ignored.

A chemical reaction is typically composed of multiple steps, and each of these steps has a particular rate. The reaction is controlled by two processes. First, in order for the reaction to proceed, all the reactants must be physically present in one location, which for a battery is the electrode. The steps are: all the reactants must be present in their appropriate form (ie in solution or as a solid), those in solution must diffuse to the site of the reaction, the reactant species must adsorb on the surface of the electrode, and finally the electron transfer must occur. The processes which involve the transport of the reactants to the site of the chemical reaction are called mass transport or concentration overpotential.

In addition to the transport of the reactant species to the site of the reaction, a second possible rate limiting step for the reaction is the rate at which the chemical reaction proceeds due to the kinetics of the chemical reaction. In many chemical reactions, the reacting species form short-lived intermediate products, and then these intermediate products react to form the final products. If the rate of formation of the intermediate species is slower than the remaining steps, then these intermediate steps control the reaction rate. The rate of the intermediate steps may be slower since the energy required to form these intermediate products may be higher than the average energy of the reactants. The reactants have a distribution of kinetic energy, and only those with higher energy can form the intermediate products. In this case, only a fraction of the initial reactants have sufficient energy to allow the reaction to proceed, thus limiting the reaction rate. The higher energy of the

intermediate species gives rise to an activation energy. In order for the reaction to proceed at a rapid rate, the reactants must be given energy greater than the activation energy.

The activation energy may be reduced for some reactions by the use of a catalyst. In some chemical reactions, the reactant atoms must interact or collide in a particular way, such that a new material forms. The interaction may require that the reactants be physically oriented in a particular way. For such reactions, species that tend to orient the molecules in a specific direction increase the probability of the reaction proceeding. Materials that have such an effect are called catalysts. This effect makes reaction rates sensitive to the presence of small number of other species, which do not appear in the formula of the chemical reaction. While the effect of a catalyst may be beneficial, it may also reduce the activation energy of an unwanted, side reaction in the battery, for example the electrolysis of water.

For battery systems, the two key ways to give the reactant species additional energy is by increasing the temperature or by giving the species potential energy (usually by the presence of a voltage) to overcome the activation energy, and either of these two effects may change the relative rates of the reactions in the battery.

Activation Overvoltage

The kinetic or activation overvoltage of the reduction and oxidation reactions of the battery should be as small as possible, since during charging the voltage required is equal to the equilibrium voltage plus activation overvoltage. The difference in the charging voltage and the discharging voltage (i.e., the overvoltage) reduces the battery efficiency.

If there are secondary or additional, unwanted reactions in the battery, then the kinetic overpotential has different effects between charging and discharging. During discharging, the battery voltage is lower, and therefore there is less possibility that the voltage is sufficient to overcome the activation energy of secondary battery reactions. During charging, the battery voltage is higher, and hence there is the possibility that additional reactions can occur.

Mass Transport Overvoltage

The mass transport overvoltage has a significant impact on batteries, particularly at high rates of charge and discharge. As the battery discharges, it depletes the region around the electrode of some of the reactants. The concentration gradient between the region surrounding the electrode and further away in the electrolyte causes reactants to diffuse towards the electrode. However, if the discharge rate of the battery causes the reactants to be used at a greater rate than they can diffuse towards electrode, then the concentration near the electrode will continue to drop as the battery discharges. This drop in concentration is greater than that expected voltage drop if the reactants were uniformly distributed through the electrolyte and therefore, according to the Nernst equation, the battery voltage decreases more rapidly than that calculated by equilibrium. The more rapidly a battery is discharged, the more rapid the fall in voltage compared to that from equilibrium. Rapid discharging affects not only the battery voltage, but also battery capacity. Since some of the reactants are not used in the reaction before the voltage drops below the minimum voltage, then the available battery capacity is also reduced. During charging, a similar process occurs, except that charging increases the concentration surrounding the electrode. Consequently, a higher voltage is required to charge the battery than expected by equilibrium calculations.

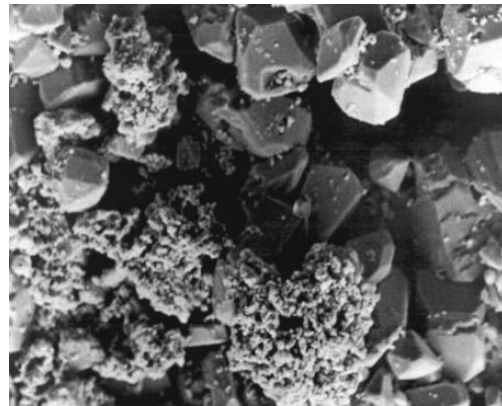
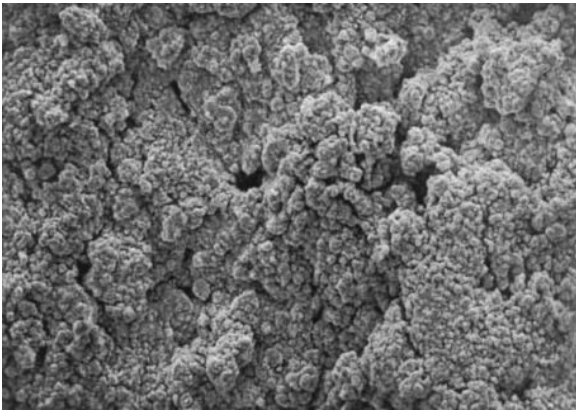
Resistive Drops in Batteries

A final contribution to the overvoltage in a battery is the resistive drops that occur in a battery. There are several components of the total battery resistance. Part of the overall resistance is due to resistance of the components in the path of the electron flow, including the electrode and the connections between the two electrodes. Other components of the resistive polarization include the surface of the electrodes. For example, in a lead acid battery, as the discharge reaction proceeds, lead sulfate builds up on the surface of the electrode. Since lead sulfate is non-conductive, if a uniform coating of lead sulfate were to form, there would be an insulating layer, and hence a high resistance. Because of these or similar effects, the resistive polarization may not be linear with applied voltage, or constant with charge/discharge. The resistive overpolarization has several practical impacts on battery performance and operation. Similar to the concentration polarization, it reduces the efficiency and places limits on how much the battery can be charged or discharged.

Physical State of the Electrodes

The physical state of the electrodes plays an important part in the practical operation of a battery. The key characteristic of a battery electrode is that its surface area should be large. This lowers the series resistance, increases the area over which the chemical reaction can take place, and ensures that the reactants are not completely covered by the products of the chemical reaction, which would prevent the reactions from continuing. A large surface area is typically achieved by using porous materials.

During charging and discharging, several processes occur that change the structure or shape of the electrode. In many battery reactions, the electrode materials undergo a physical change during the discharge/charge cycle. For example, in lead acid batteries, lead sulfate, lead oxide and lead reform during each charge/discharge cycle. These changes to the electrode give rise to numerous non-idealities. For example, the reactant products seldom have the identical density as the reactants, and hence the electrode undergoes physical changes in its size and as the electrode material is re-formed during charging, the electrode may change. This means that upon repeated cycling, the electrodes may distort, or material may “shed” and drop to the bottom of the battery (where it can not longer participate in the desired redox reaction since the electrons are not transferred from one electrode to the other). In lead acid batteries, this is circumvented by the fact that the solubility of the lead ion Pb^{2+} is very low, and hence Pb^{2+} is rapidly converted to Pb in the close physical proximity to where it was dissolved, thus preventing significant changes of shape of the electrode. Alternately, either the products during discharging or the original battery material during charging may form so as isolate regions from charging or discharging, thus permanently reducing battery capacity. An additional effect that may alter the porous structure of the original electrode is the formation of larger crystals rather than the fine-grained porous material of the original battery. For example, in lead acid batteries, larger lead-sulfate crystals may form, which are difficult to convert back into lead or lead oxide.



Terminal Characteristics of Batteries

The most critical battery characteristics for photovoltaic systems include the battery voltage and capacity, how it responds to charging and discharging, lifetime of the battery, maintenance requirements, and efficiency.

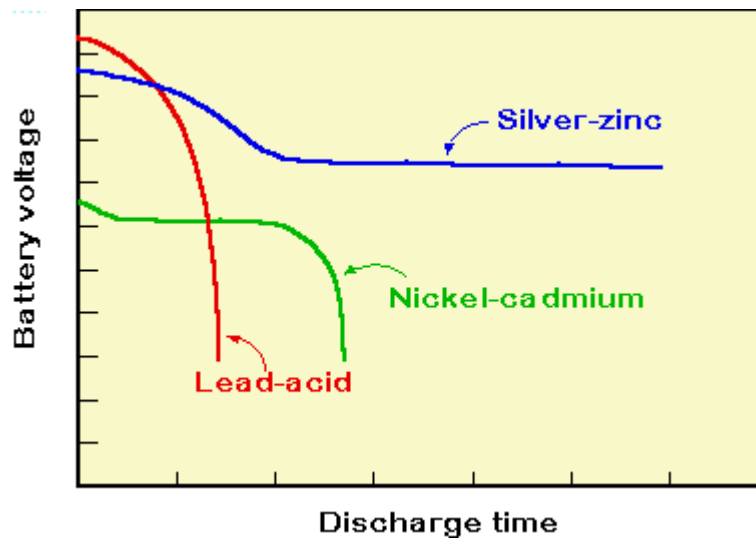
Battery Voltage

The voltage of a battery is a fundamental characteristic of a battery, which is determined by the chemical reactions in the battery, the concentrations of the battery components, and the polarization of the battery. The voltage calculated from equilibrium conditions is typically known as the nominal battery voltage. In practice the nominal battery voltage cannot be readily measured, but for practical battery systems (in which the overvoltages and non-ideal effects are low) the open circuit voltage is a good approximation to the nominal battery voltage.

Since the electric potential (voltage) from most chemical reactions is on the order of 2V while the voltage required by loads is typically larger, in most batteries, numerous individual battery cells are connected in series. For example, in lead acid batteries, each cell has a voltage of about 2V. Six cells are connected to form a typical 12V lead acid battery.

Voltage Variation with Discharging

Due to the polarization effects, the battery voltage under current flow may differ substantially from the equilibrium or open circuit voltage. A key characteristic of a battery technology is how the battery voltage changes due under discharge conditions, both due to equilibrium concentration effects and due polarization. Battery discharge and charging curves are shown below for several different battery systems. The discharge and charge curves are not necessarily symmetric due to the presence of additional reactions that may be present at the higher voltages encountered in charging.



Variation of voltage with state of charge for several different types of batteries.

Cut-Off Voltage

In many battery types, including lead acid batteries, the battery cannot be discharged below a certain level or permanent damage may be done to the battery. This voltage is called the "cut-off voltage" and depends on the type of battery, its temperature and the battery's rate of discharge.

Measuring State of Charge Based on Voltage

While the reduction of battery voltage with discharge is a negative aspect of batteries which reduces their efficiency, one practical aspect of such a reduction, if it is approximately linear, is that at a given temperature, the battery voltage may be used to approximate the state of charge of the battery. In systems where the battery voltage is not linear over some range of BSOC or in which there are rapid variations in the voltage with the BSOC will be more difficult to determine the BSOC and therefore will be more difficult to charge. However, a battery system that maintains a more constant voltage with discharge rate will have a high voltage efficiency and will be more easily used to drive voltage sensitive loads.

Effect of Temperature on Voltage

Battery voltage will increase with the temperature of the system.

Battery Charging and Discharging Parameters

The key function of a battery in a PV system is to provide power when other generating sources are unavailable, and hence batteries in PV systems will experience continual charging and discharging cycles. All battery parameters are affected by battery charging and recharging cycle.

Battery State of Charge (BSOC)

A key parameter of a battery in use in a PV system is the battery state of charge (BSOC). The BSOC is defined as the fraction of the total energy or battery capacity that has been used over the total available from the battery.

Battery state of charge (BSOC or SOC) gives the ratio of the amount of energy presently stored in the battery to the nominal rated capacity. For example, for a battery at 80% SOC and with a 500 Ah capacity, the energy stored in the battery is 400 Ah. A common way to measure the BSOC is to measure the voltage of the battery and compare this to the voltage of a fully charged battery. However, as the battery voltage depends on temperature as well the state of charge of the battery, this measurement provides only a rough idea of battery state of charge.

Depth of Discharge

In many types of batteries, the full energy stored in the battery cannot be withdrawn (in other words, the battery cannot be fully discharged) without causing serious, and often irreparable damage to the battery. The Depth of Discharge (DOD) of a

battery determines the fraction of power that can be withdrawn from the battery. For example, if the DOD of a battery is given by the manufacturer as 25%, then only 25% of the battery capacity can be used by the load.

Nearly all batteries, particularly for renewable energy applications, are rated in terms of their capacity. However, the actual energy that can be extracted from the battery is often (particularly for lead acid batteries) significantly less than the rated capacity. This occurs since, particularly for lead acid batteries, extracting the full battery capacity from the battery dramatically reduced battery lifetime. The depth of discharge (DOD) is the fraction of battery capacity that can be used from the battery and will be specified by the manufacturer. For example, a battery 500 Ah with a DOD of 20% can only provide $500\text{Ah} \times .2 = 100 \text{ Ah}$.

Daily Depth of Discharge

In addition to specifying the overall depth of discharge, a battery manufacturer will also typically specify a daily depth of discharge. The daily depth of discharge determined the maximum amount of energy that can be extracted from the battery in a 24 hour period. Typically in a larger scale PV system (such as that for a remote house), the battery bank is inherently sized such that the daily depth of discharge is not an additional constraint. However, in smaller systems that have relatively few days storage, the daily depth of discharge may need to be calculated.

Charging and Discharging Rates

The charging rate, in Amps, is given in the amount of charge added the battery per unit time (i.e., Coulombs/sec, which is the unit of Amps). The charging/discharge rate maybe specified directly by giving the current - for example, a battery may be charged/discharged at 10 A. However, it is more common to specify the charging/discharging rate by determining the amount of time it takes to fully discharge the battery. Note that the battery is only "theoretically" discharged to its maximum level as most practical batteries cannot be fully discharged without either damaging the battery or reducing its lifetime. The notation to specify battery capacity in this way is written as C_x , where x is the time in hours that it takes to discharge the battery. For example, $C_{10} = xxx$ (also written as $C10 = xxx$) means that the battery capacity is xxx when the battery is discharged in 10 hours. When the discharging rate is halved (and the time it takes to discharge the battery is doubled to 20 hours), the battery capacity rises. The discharge rate when discharging the battery in 10 hours is found by dividing the capacity by the time. Therefore, $C/10$ is the charge rate. This may also be written (confusingly) as $0.1C$. Such relatively complicated notations may result when higher or lower charging rates are used for short periods of time.

Charging and Discharging Regimes

Each battery type has a particular set of restraints and conditions related to its charging and discharging regime, and many types of batteries require specific charging regimes or charge controllers. For example, nickel cadmium batteries should be nearly completely discharged before charging, while lead acid batteries should never be fully discharged. Furthermore, the voltage and current during the charge cycle will be different for each type of battery. Typically, a battery charger or charge controller designed for one type of battery cannot be used with another type.

Battery Capacity

"Battery capacity" is a measure (typically in Amp-hr) of the charge stored by the battery, and is determined by the mass of active material contained in the battery. The battery capacity represents the maximum amount of energy that can be extracted from the battery under certain specified conditions. However, the actual energy storage capabilities of the battery can vary significantly from the "nominal" rated capacity, as the battery capacity depends strongly on the age and past history of the battery, the charging or discharging regimes of the battery and the temperature.

Units of Battery Capacity: Ampere Hours

The energy stored in a battery, called the battery capacity, is measured in either watt-hours (Wh), kilowatt-hours (kWh), or ampere-hours (Ahr). The most common measure of battery capacity is Ah, defined as the number of hours for which a battery can provide a current equal to the discharge rate at the nominal voltage of the battery. The unit of Ah is commonly used when working with battery systems as the battery voltage will vary throughout the charging or discharging cycle. The Wh capacity can be approximated from the Ahr capacity by multiplying the AH capacity by the nominal (or, if known, time average) battery voltage. A more accurate approach takes into account the variation of voltage by integrating the AH capacity $\times V(t)$ over the time of the charging cycle. For example, a 12 volt battery with a capacity of 500 Ah battery allows energy storage of approximately $100 \text{ Ah} \times 12 \text{ V} = 1,200 \text{ Wh}$ or 1.2 kWh. However, because of the large impact from charging rates or temperatures, for practical or accurate analysis, additional information about the variation of battery capacity are also provided by battery manufacturers.

Depth of Discharge

In many types of batteries, the full energy stored in the battery cannot be withdrawn (in other words, the battery cannot be fully discharged) without causing serious, and often irreparable damage to the battery. The Depth of Discharge (DOD) of a battery determines the fraction of power that can be withdrawn from the battery. For example, if the DOD of a battery is given by the manufacturer as 25%, then only 25% of the battery capacity can be used by the load.

In addition to an overall DOD below which the battery should not be discharged, many battery manufacturers will specify a daily DOD, which determines that maximum power that can be withdrawn from a battery in a single day.

Impact of Charging and Discharging Rate

The charging/discharging rate affects the rated battery capacity. If the battery is being discharged very quickly (i.e., the discharge current is high), then the amount of energy that can be extracted from the battery is reduced and the battery capacity is lower. This is due to the fact the necessary components for the reaction to occur do not necessarily have enough time to either move to their necessary positions. The only a fraction of the total reactants are converted to other forms, and therefore the energy available is reduced. Alternately, if the battery is discharged at a very slow rate using a low current, more energy can be extracted from the battery and the battery capacity is higher.

Temperature

The temperature of a battery will also affect the energy that can be extracted from it. At higher temperatures, the battery capacity is typically higher than at lower temperatures. However, intentionally elevating battery temperature is not an effective method to increase battery capacity as this also decreases battery lifetime.

Specification of Battery Capacity

Because of the strong variation of battery capacity with charge/discharge rate, manufacturers must specify the capacity as a function of discharge rate and temperature (although it is common to give battery capacity only at a single temperature).

Age and history of battery

The age and history of the battery have a major impact on the capacity of a battery. Even when following manufacturers specifications on DOD, the battery capacity will stay at or close to its rated capacity for a limited number of charge/discharge cycles. The history of the battery has an additional impact on capacity in that if the battery has been taken below its maximum DOD, then battery capacity may be prematurely reduced and the rated number of charge/discharge cycles may not be available.

Battery Efficiency

As with any other component in a PV system, efficiency is an important issue in component selection due to the relatively high cost of power generated by PV modules. The overall battery efficiency is specified by two efficiencies: the coulombic efficiency and the voltage efficiency.

Coulombic Efficiency

The coulombic efficiency of battery is the ratio of the number of charges that enter the battery during charging compared to the number that can be extracted from the battery during discharging. The losses that reduce coulombic efficiency are primarily due to the loss in charge due to secondary reaction, such as the electrolysis of water or other redox reactions in the battery. In general, the coulombic efficiency may be high, in excess of 95%.

Voltage Efficiency

The voltage efficiency is determined largely by the voltage difference between the charging voltage and voltage of the battery during discharging. The dependence of the battery voltage on SOC will therefore impact voltage efficiency. Other factors being equal, a battery in which the voltage varies linearly with SOC will have a lower efficiency than one in which the voltage is essentially constant with SOC.

Energy, Volumetric and Power Density

Specific and Volumetric Energy Density

Energy density is a parameter used chiefly to compare one type of battery system to another. The energy density of a battery is the capacity of the battery divided by either the weight of the battery, which gives the gravimetric energy density in Wh/kg, or by the volume, which gives a volumetric energy density in Wh/dm³ (or Wh/litre³). A battery with a higher energy density will be lighter than a similar capacity battery with a lower energy density. In portable systems, the energy density is a critical parameter but in conventional PV systems which provide power for a stationary object, the energy density may be less important. Nevertheless, the costs of transporting batteries to remote locations are considerably high, so a high energy density battery is typically an advantage.

Power Density

The power density of a battery is related to its energy density, as well as the ability of the battery to discharge quickly. While the power density is important in some applications, particularly transport, it is typically not critical in photovoltaic systems.

Other Electrical Battery Parameters

Internal Series Resistance

The internal series resistance of a battery determines the maximum discharge current of the battery. Consequently, for applications in which the batteries are required to provide high instantaneous power, the internal series resistance should be low. In addition, the series resistance will effect the battery's efficiency but may change as the battery ages.

Self-Discharge

Self-discharge refers to the fact that even in the absence of a connected load, the discharge reaction will proceed to a limited extent and the battery will therefore discharge itself over time. The rate of self-discharge depends primarily on the materials involved in the chemical reaction (i.e., the type of battery system) and on the temperature of the battery.

Cold Cranking Current

The maximum amount of current a battery can provide for a short period of time is called the cranking current. This parameter is often specified for transport applications, in which the battery must provide enough current to start a large engine. However, it is typically not an important parameter in PV systems.

Temperature effects

The temperature sensitivity and temperature range over which batteries can be operated depend on the type of battery and the state of charge of the battery. All batteries lose capacity as the temperature is reduced. Some types of batteries are sensitive to freezing and suffer irreversible damage if they are frozen.

Battery Lifetime and Maintenance

Battery Lifetime

Since batteries inherently involve chemical reactions that are reactive, the materials used in batteries are susceptible to alternate reactions that degrade battery performance. While certain catastrophic battery failure mechanisms are possible, battery lifetime is typically controlled by the gradual degradation in battery capacity which accompanies charge/discharge cycles. Consequently, battery lifetime is typically given as the number of charge/discharge cycles which it can undergo and still maintain its original capacity. However, in systems which do not frequently experience charge/discharge cycles (such as in uninterruptible power supplies), battery lifetime is more appropriately specified in years. Improper use of the battery can greatly accelerate battery aging and further decrease the number of cycles over which a battery can be used.

Battery life is defines either in years (if it remains fully charged or in # of cycles under a given set of conditions (including temperature and DOD).

Maintenance Requirements

The type of battery used will also have an important impact on the maintenance requirements of the battery. Some types of battery reactions evolve gasses and other products which change the volume of the components in the battery. In cases in which the volume of a battery changes, it is more difficult to seal the battery, and the battery will need to have certain chemical components (usually simply water) added to compensate for the evolution of gasses. A hermetically sealed battery does not exchange any materials with its surrounding environment. Such a battery will have lower maintenance requirements than a battery in which the various battery elements interact with the surroundings. Nearly all small common primary batteries are hermetically sealed and require no maintenance, but many secondary batteries, particularly lead acid batteries, require a strict maintenance schedule.

Failure Modes

A battery can degrade or can fail catastrophically. Modes are: shorts, degradation of electrode material, freezing, increases in resistance.

Battery Safety and Disposal

Safety

Most battery systems, including those used in renewable energy systems, contain corrosive or dangerous chemicals. For example, the evolution of hydrogen during charging a lead acid battery can lead to an explosive build-up of hydrogen if the system is not properly vented. Other battery hazards include electric hazards due to the possibility of high voltage and/or high current driving capabilities.

Battery Disposal

Batteries should not be thrown away as most batteries contain toxic and/or corrosive material.

Batteries for Photovoltaic Systems

The use of batteries in photovoltaic systems differs from the use of batteries in other common battery applications since PV batteries experience both deep cycling and being left at low states of charge for extended periods of time as part of expected operation. For example, in batteries for starting cars or other engines, the battery experiences a large, short current drain, but is at full charge for most of its life. Similarly, batteries in uninterruptible power supplies are kept at full charge for most of their life. While a large number of application exist where batteries experience regular deep discharge, they are typically fully charged at the end of their discharge cycle and are not left at reduced charge for long periods of time.

Lead Acid Batteries

Lead acid batteries are the most commonly used type of battery in photovoltaic systems. Although lead acid batteries have a low energy density, only moderate efficiency and high maintenance requirements, they also have a long lifetime and low costs compared to other battery types. One of the singular advantages of lead acid batteries is that they are the most commonly used form of battery for most rechargeable battery applications (for example, in starting car engines), and therefore have a well-established established, mature technology base.



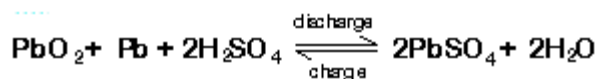
Lead acid battery bank.

Operation of Lead Acid Batteries

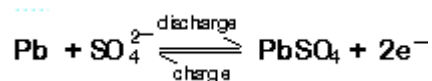
Operation of Lead Acid Batteries

A lead acid battery consists of a negative electrode made of spongy or porous lead. The lead is porous to facilitate the formation and dissolution of lead. The positive electrode consists of lead oxide. Both electrodes are immersed in an electrolytic solution of sulfuric acid and water. In case the electrodes come into contact with each other through physical movement of the battery or through changes in thickness of the electrodes, an electrically insulating, but chemically permeable membrane separates the two electrodes. This membrane also prevents electrical shorting through the electrolyte. Lead acid batteries store energy by the reversible chemical reaction shown below.

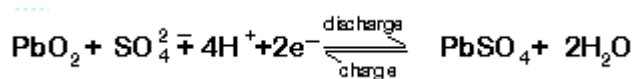
The overall chemical reaction is:



At the negative terminal the charge and discharge reactions are:

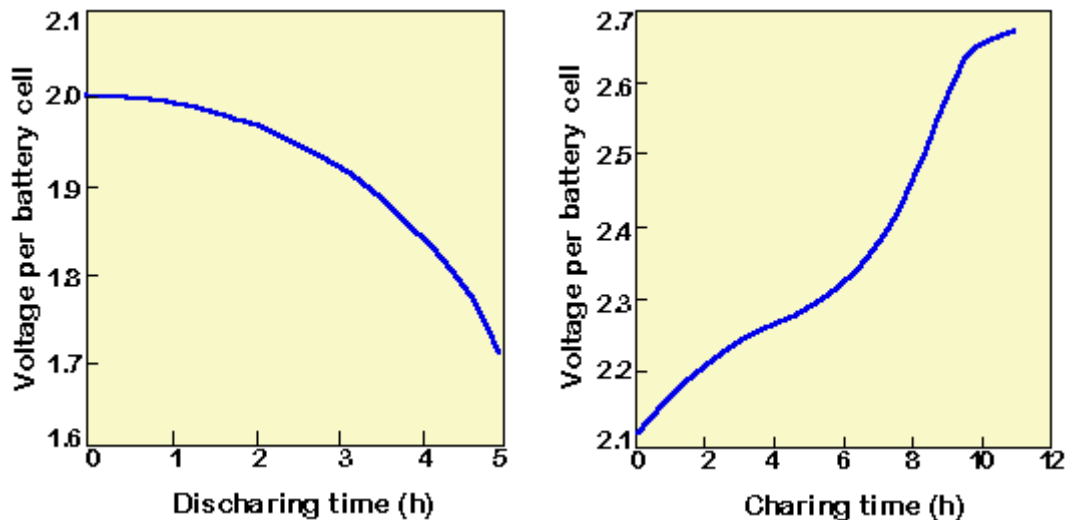


At the positive terminal the charge and discharge reactions are:



As the above equations show, discharging a battery causes the formation of lead sulfate crystals at both the negative and positive terminals, as well as the release of electrons due to the change in valence charge of the lead. The formation of this lead sulfate uses sulfate from the sulfuric acid electrolyte surrounding the battery. As a result the electrolyte becomes less concentrated. Full discharge would result in both electrodes being covered with lead sulfate and water rather than sulfuric acid surrounding the electrodes. At full discharge the two electrodes are the same material, and there is no chemical potential or voltage between the two electrodes. In practice, however, discharging stops at the cutoff voltage, long before this point. The battery should not therefore be discharged below this voltage.

In between the fully discharged and charged states, a lead acid battery will experience a gradual reduction in the voltage. Voltage level is commonly used to indicate a battery's state of charge. The dependence of the battery on the battery state of charge is shown in the figure below. If the battery is left at low states of charge for extended periods of time, large lead sulfate crystals can grow, which permanently reduces battery capacity. These larger crystals are unlike the typical porous structure of the lead electrode, and are difficult to convert back into lead.



Voltage of lead acid battery upon charging.

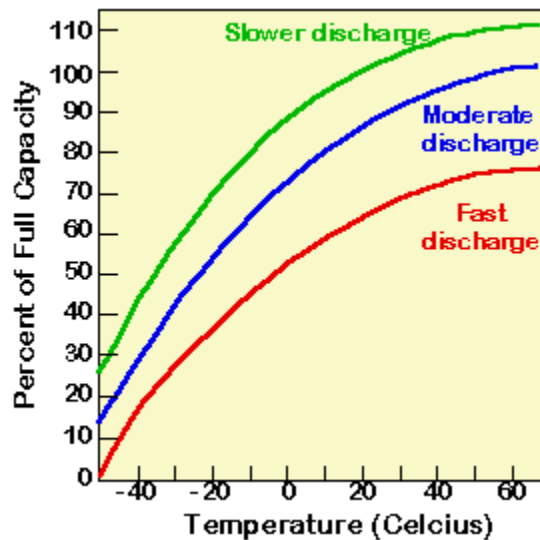
The charging reaction converts the lead sulfate at the negative electrode to lead. At the positive terminal the reaction converts the lead to lead oxide. As a by-product of this reaction, hydrogen is evolved. During the first part of the charging cycle, the conversion of lead sulfate to lead and lead oxide is the dominant reaction. However, as charging proceeds and most of the lead sulfate is converted to either lead or lead dioxide, the charging current electrolyzes the water from the electrolyte and both hydrogen and oxygen gas are evolved, a process known as the "gassing" of the battery. If current is being provided to the battery faster than lead sulfate can be converted, then gassing begins before all the lead sulfate is converted, that is, before the battery is fully charged. Gassing introduces several problems into a lead acid battery. Not only does the gassing of the battery raise safety concerns, due to the explosive nature of the hydrogen produced, but gassing also reduces the water in the battery, which must be manually replaced, introducing a maintenance component into the system. In addition, gassing may cause the shedding of active material from the electrolyte, thereby permanently reducing battery capacity. For these reasons, the battery should not regularly be charged above the voltage which causes gassing. Lead sulphate is an insulator, and therefore the way in which lead sulfate forms on the electrodes determined how easily the battery can be discharged.

Characteristics of Lead Acid Batteries

Depth of Discharge and Battery Capacity

The depth of discharge in conjunction with the battery capacity is a fundamental parameter in the design of a battery bank for a PV system, as the energy which can be extracted from the battery is found by multiplying the battery capacity by the depth of discharge. Batteries are rated either as deep-cycle or shallow-cycle batteries. A deep-cycle battery will have depth of discharge greater than 50%, and may go as high as 80%. To achieve the same useable capacity, a shallow-cycle battery bank must have a larger capacity than a deep-cycle battery bank.

In addition to the depth of discharge and rated battery capacity, the instantaneous or available battery capacity is strongly affected by the discharge rate of the battery and the operating temperature of the battery. Battery capacity falls by about 1% per degree below about 20°C. However, high temperatures are not ideal for batteries either as these accelerate aging, self-discharge and electrolyte usage. The graph below shows the impact of battery temperature and discharge rate on the capacity of the battery.



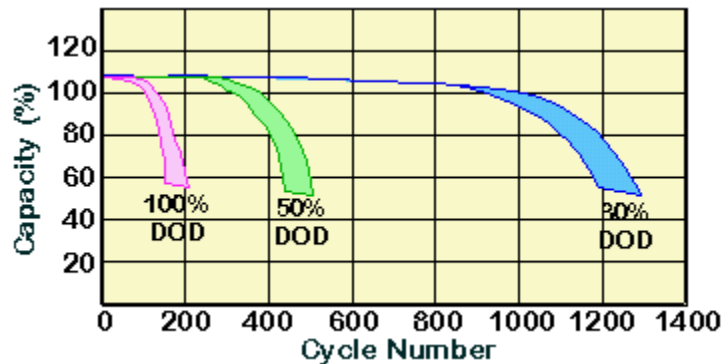
Relationship between battery capacity, temperature and discharge rate.

Battery Lifetime

Over time, battery capacity degrades due to sulfation of the battery and shedding of active material. The degradation of battery capacity depends most strongly on the interrelationship between the following parameters:

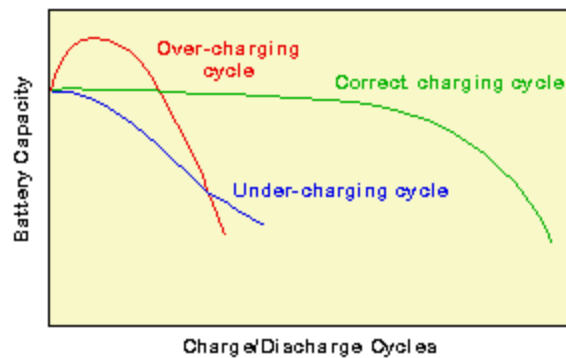
- * the charging/discharging regime which the battery has experienced;
- * the DOD of the battery over its life;
- * its exposure to prolonged periods of low discharge; and
- * the average temperature of the battery over its lifetime.

The following graph shows the evolution of battery function as number of cycles and depth of discharge for a shallow-cycle lead acid battery. A deep-cycle lead acid battery should be able to maintain a cycle life of more than 1,000 even at DOD over 50%.



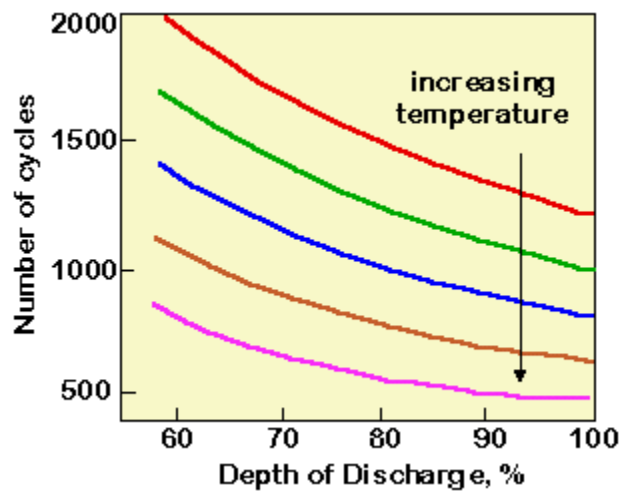
Relationship between battery capacity, depth of discharge and cycle life for a shallow-cycle battery.

In addition to the DOD, the charging regime also plays an important part in determining battery lifetime. Overcharging or undercharging the battery results in either the shedding of active material or the sulfation of the battery, thus greatly reducing battery life.



Impact of charging regime of battery capacity.

The final impact on battery charging relates to the temperature of the battery. Although the capacity of a lead acid battery is reduced at low temperature operation, high temperature operation increases the aging rate of the battery.



Relationship between battery capacity, temperature and lifetime for a deep-cycle battery.

Maintenance Requirements

The production and escape of hydrogen and oxygen gas from a battery causes water loss and water must be regularly replaced in lead acid batteries. Other components of a battery system do not require maintenance as regularly, so water loss can be a significant problem. If the system is in a remote location, checking water loss can add to costs. Maintenance-free batteries limit the need for regular attention by preventing or reducing the amount of gas which escapes the battery. However, due to the corrosive nature the electrolyte, all batteries to some extent introduce an additional maintenance component into a PV system.

Battery Efficiency

Lead acid batteries typically have coulombic efficiencies of 85% and energy efficiencies in the order of 70%.

Potential Problems with Lead Acid Batteries

A lead acid battery consists of electrodes of lead oxide and lead are immersed in a solution of weak sulfuric acid. Potential problems encountered in lead acid batteries include:

- * **Gassing: Evolution of hydrogen and oxygen gas.** Gassing of the battery leads to safety problems and to water loss from the electrolyte. The water loss increases the maintenance requirements of the battery since the water must periodically be checked and replaced.

- * **Damage to the electrodes.** The lead at the negative electrode is soft and easily damaged, particularly in applications in which the battery may experience continuous or vigorous movement.
- * **Stratification of the electrolyte.** Sulfuric acid is a heavy, viscous liquid. As the battery discharges, the concentration of the sulfuric acid in the electrolyte is reduced, while during charging the sulfuric acid concentration increases. This cycling of sulfuric acid concentration may lead to stratification of the electrolyte, where the heavier sulfuric acid remains at the bottom of the battery, while the less concentrated solution, water, remains near the top. The close proximity of the electrode plates within the battery means that physical shaking does not mix the sulfuric acid and water. However, controlled gassing of the electrolyte encourages water and sulfuric acid to mix, but must be carefully controlled to avoid problems of safety and water loss. Periodic but infrequent gassing of the battery to prevent or reverse electrolyte stratification is required in most lead acid batteries in a process referred to as "boost" charging.
- * **Sulfation of the battery.** At low states of charge, large lead sulfate crystals may grow on the lead electrode as opposed to the finely grained material which is normally produced on the electrodes. Lead sulfate is an insulating material, and as well as "removing" the material tied up in lead sulfate from contributing to energy storage, it also increases the resistance of the battery.
- * **Spillage of the sulfuric acid.** If sulfuric acid leaks from the battery housing it poses a serious safety risk. Gelling or immobilizing the liquid sulfuric acid reduces the possibility of sulfuric acid spills.
- * **Freezing of the battery at low discharge levels.** If the battery is at a low discharge level following the conversion of the whole electrolyte to water, then the freezing point of the electrolyte also drops.
- * **Loss of active material from the electrodes.** The loss of active material from the electrodes can occur via several processes. One process that can cause a permanent loss of capacity is the flaking off of the active material due to volumetric changes between the different form of lead at the electrodes. In addition, improper charging conditions and gassing can cause shedding of active material from the electrodes, leading to a permanent loss in capacity.

Lead Acid Battery Configurations

Depending on which one of the above problems is of most concern for a particular application, appropriate modifications to the basic lead acid battery configuration improve battery performance. For renewable energy applications, the most significant problems are the depth of discharge, the battery lifetime and the maintenance requirements. The changes to the battery typically involve modification in one of the three basic areas:

- changes to the electrode composition and geometry;
- changes to the electrolyte solution; and
- modifications to the battery housing or terminals to prevent or reduce the escape of generated hydrogen gas.

Electrode Materials and Configuration

The materials from which the electrodes are made have a major affect on the battery chemistry, and hence affect the battery voltage and its charging and discharging characteristics. The geometry of the electrode determines the internal series resistance and the charging and discharging rate.

Plate Material

The basic anode and cathode materials in a lead acid battery are lead and lead dioxide (PbO₂). The lead electrode is in the form of sponge lead. Sponge lead is desirable as it is very porous, and therefore the surface area between the lead and the sulfuric acid electrolyte is large. In many cases, the electrode also contains small amounts of other materials, in order to increase its hardness, reduce sulfation, and reduce gassing. The main types of electrodes used are lead/antimony (using several percent antimony), lead/calcium alloys, and lead/antimony/calcium alloys.

Antimony lead alloy batteries have several advantages over pure lead electrodes. These advantages include: the lower cost of lead/antimony; the increased strength of the lead/antimony electrode; and the ability to be deeply discharged for short period of time. However, lead/antimony alloys are prone to sulfation and should not be left at low states of charge for extended periods of time. In addition, lead/antimony alloys increase the gassing of the battery during charging leading to high levels of water loss. Since the water must be added to these batteries, they have higher maintenance. Furthermore, lead/antimony batteries have a high discharge rate and a short lifetime.

Lead calcium batteries are an intermediate cost technology. Like antimony, calcium also adds strength to the lead of the negative electrode, but unlike antimony, the addition of calcium reduces the gassing of the battery and also produces a lower self-discharge rate. However, lead calcium batteries should not be deeply discharged. Consequently, these types of batteries

may be considered "maintenance-free", but are only shallow cycle batteries. Adding both antimony and calcium to the electrodes provides some of the advantages of both antimony and lead, making them suitable to deep discharge, but at an increased cost. Deep discharge batteries such as these can also have a high lifetime. Furthermore, trace amounts of other materials can be added to the electrodes to increase battery performance.

Electrode Configuration

In addition to the material used to make the electrode plates, the physical configuration of the electrodes also has an impact on the charging and discharging rates and on the lifetime. Thin plates will allow faster charging and discharging, but are less robust and more prone to shedding of material from the plates. As high charging or discharging currents are not typically a required feature of batteries for renewable energy systems, thicker plates can be used, which have lower charge and discharge times, but also have longer lifetimes.

Modifications to the electrolyte

A standard "flooded" lead acid battery has the electrodes immersed in liquid sulfuric acid. Several modifications to the electrolyte are used to improve battery performance in one of several areas. The key parameters of the electrolyte which control the performance of the battery are the volume and concentration of the electrolyte and forming a 'captive' electrolyte.

Electrolyte Volume and Concentration

Changes in the volume of the electrolyte can be used to improve the robustness of a battery. Increasing the volume of an electrolyte makes the battery less sensitive to water losses, and hence makes regular maintenance less critical. Adding to the volume of the battery will also increase its weight and reduce the energy density of the battery.

Captive Electrolyte Lead Acid Batteries

In 'captive' electrolyte batteries, the sulfuric acid is immobilized by either 'gelling' the sulfuric acid or by using an 'absorptive glass mat'. Both have lower gassing compared to a flooded lead acid battery and are consequently often found in "maintenance-free" sealed lead acid batteries. Gelled or AGM lead acid batteries (which are typically sealed or valve regulated) have several potential advantages, including that they can be deep cycled while retaining battery life, that they do not require boost charging, that they have lower maintenance. However, these batteries typically require a more precise and lower voltage charging regime. The lower voltage charging regime is due to the use of lead-calcium electrodes to minimize gassing, and a more precise charging regime is also required to minimize gassing from the battery. In addition, these batteries may be more sensitive to temperature variations, particularly if the charging regime does not compensate for temperature or is not designed for these types of batteries.

- **Gelling.** In a "gelled" lead acid battery, the electrolyte may be immobilized by gelling the sulfuric acid using silica gel. The gelled electrolyte has an advantage in that gassing is reduced, and consequently the batteries are low-maintenance. In addition, stratification of the electrolyte does not occur with gelled batteries and therefore boost charging is not required, and because the electrolyte is gelled, the chances of spilling sulfuric acid are also reduced. However, in order to further reduce gassing, these "gell-cell" batteries also typically use lead calcium plates, making them unsuited to deep discharge applications. A further drawback is that the charging conditions of a gelled lead acid battery must be more carefully controlled to prevent overcharging and damage to the battery.
- **Absorptive Glass Matting.** A second technology which can be used to immobilize the sulfuric acid is "absorptive glass mat" or AGM batteries. In an AGM battery, the sulfuric acid is absorbed in a fiberglass mat which is placed between the electrode plates. AGM batteries have numerous advantages including the ability to be deeply discharged without affecting lifetime, allowing high rates of charge/discharge and an extended temperature range for operation. The key disadvantage with these batteries is their need for more carefully controlled charging regimes and their higher initial cost.

Battery Housing

In an open, flooded battery, any gas which is generated can escape to the atmosphere, causing both safety and maintenance problems. A sealed lead acid (SLA), valve-regulated lead acid (VRLA) or recombining lead acid battery prevent the loss of water from the electrolyte by preventing or minimizing the escape of hydrogen gas from the battery. In a sealed lead acid (SLA) battery, the hydrogen does not escape into the atmosphere but rather moves or migrates to the other electrode where it recombines (possibly assisted by a catalytic conversion process) to form water. Rather than being completely sealed, these batteries include a pressure vent to prevent the build-up of excess pressure in the battery. Sealed batteries require stringent

charging controls to prevent the build-up of hydrogen faster than it can recombine, but they require less maintenance than open batteries.

Valve regulated lead acid (VRLA) batteries are similar in concept to sealed lead acid (SLA) batteries except that the valves are expected to release some hydrogen near full charge. SLA or VRLA batteries typically have additional design features such as the use of gelled electrolytes and the use of lead calcium plates to keep the evolution of hydrogen gas to a minimum.

Special Considerations for Flooded Lead Acid Batteries

Flooded lead acid batteries are characterized by deep cycles and long lifetimes. However, flooded batteries require periodic maintenance. Not only must the level of water in the electrolyte be regularly monitored by measuring its specific gravity, but these batteries also require "boost charging".

Boost Charging

Boost or equalization charging involves short periodic overcharging, which releases gas and mixes the electrolyte, thus preventing stratification of the electrolyte in the battery. In addition, boost charging also assists in keeping all batteries at the same capacity. For example, if one battery develops a higher internal series resistance than other batteries, then the lower SR battery will consistently be undercharged during a normal charging regime due to the voltage drop across the series resistance. However, if the batteries are charged at a higher voltage, then this allows all batteries to become fully charged.

Specific Gravity (SG)

A flooded battery is subject to water loss from the electrolyte due to the evolution of hydrogen and oxygen gas. The specific gravity of the electrolyte, which can be measured with a hydrometer, will indicate the need to add water to the batteries if the batteries are fully charged. Alternately, a hydrometer will accurately indicate the SOC of the battery if it is known that the water level is correct. SG is periodically measured after boost charging to insure that the battery has sufficient water in the electrolyte. The SG of the battery should be provided by the manufacturer.

The battery for a PV system will be rated as a certain number of cycles at a particular DOD, charging regime and temperature. However, batteries may experience either a premature loss in capacity or a sudden failure for a variety of reasons. Sudden failure may be caused by the battery internally short-circuiting due to the failure of the electrical separator within the battery. A short circuit in the battery will reduce the voltage and capacity from the overall battery bank, particularly if sections of the battery are connected in parallel, and will also lead to other potential problems such as overcharging of the remaining batteries. The battery may also fail as an open circuit (that is, there may be a gradual increase in the internal series resistance), and any batteries connected in series with this battery will also be affected. Freezing the battery, depending on the type of lead acid battery used, may also cause irreversible failure of the battery.

The gradual decline in capacity may be worsened by inappropriate operation, particularly by degrading the DOD. However, the operation of one part of the battery bank under different conditions to another will also lead to a reduction in overall capacity and an increase in the likelihood of battery failure. Batteries may be unintentionally operated under different regimes due either to temperature variations or to the failure of a battery in one battery string leading to unequal charging and discharging in the string.

Battery installation should be conducted in accordance with the relevant standard in the country in which they are being installed. At present there are Australian standards AS3011 & AS2676 for battery installation. There is also a draft standard for batteries for RAPS applications which will eventually become an Australian standard.

Among other factors to be considered in the installation of a battery system are the ventilation required for a particular type of battery bank, the grounding conditions on which the battery bank is to be placed, and provisions taken to insure the safety of those who may have access to the battery bank. In addition, when installing the battery bank care must be taken to ensure that the battery temperature will fall within the allowable operating conditions of the battery and that the temperature of the batteries in a larger battery bank are at the same temperatures. Batteries in very cold conditions are subject to freezing at low states of charge, so that the battery will be more likely to be in a low state of charge in winter. To prevent this, the battery bank may be buried underground. Batteries regularly exposed to high operating temperatures may also suffer a reduced lifetime.

Safety

Batteries are potentially very dangerous and users should be aware of three main hazards:

- **The sulfuric acid in the electrolyte is corrosive.** Protective clothing in addition to foot and eye protection are essential when working with batteries.
- **Batteries have a high current generating capability.** If a metal object is accidentally placed across the terminals of a battery, high currents can flow through this object. The presence of unnecessary metal objects (e.g. jewellery) should be minimised when working with batteries and tools should have insulated handles.
- **Explosion hazards due to evolution of hydrogen and oxygen gas.** During charging, particularly overcharging, some batteries, including most batteries used in PV systems, may evolve a potentially explosive mixture of hydrogen and oxygen gas. To reduce the risk of explosion, ventilation is used to prevent the buildup of these gasses and potential ignition sources (i.e. circuits which may generate sparks or arcs) are eliminated from the battery enclosure.

Batteries introduce a periodic maintenance component into a PV system. All batteries, including "maintenance free" batteries require a maintenance schedule which should ensure that:

Flooded batteries require extra and more frequent maintenance. For flooded batteries, the level of electrolyte and the specific gravity of the electrolyte for each battery needs to be checked regularly. Checking the specific gravity of a battery by using a hydrometer should be carried out at least 15 minutes after an equalisation or boost charge. Only distilled water should be added to batteries. Tap water contains minerals which may damage the battery electrodes.

Battery Disposal and Recycling

The lead in a lead acid battery presents an environmental hazard if it is not properly disposed of. Lead acid batteries should be recycled so that the lead can be recovered without causing environmental damage.

Types of Lead Acid Batteries

Types of Lead Acid Batteries

Despite the range in battery types and applications, the characteristics particularly important in PV applications are the maintenance requirements of the battery and the ability to deep charge a battery while maintaining a long lifetime. To promote long cycle life with deep discharge, deep cycle batteries may be either of the open-flooded type with an excess of electrolytic solution and thick plates, or of the immobilized electrolytic type. Sealed gelled batteries may be rated as deep cycle batteries, but they will usually withstand fewer cycles and lower discharges than the specially designed flooded plate or AGM batteries. Shallow-cycle batteries typically use thinner plates made from lead calcium alloys and do not typically have a depth of discharge above 25%.

Batteries for PV or remote area power supplies (RAPS)

The stringent requirements for batteries used in photovoltaic systems have prompted several manufacturers to make batteries specifically designed for PV or other remote power systems. The batteries most commonly used in stand-alone photovoltaic systems are either deep-cycle lead acid types, or shallower cycle maintenance-free batteries. Deep-cycle batteries may be open flooded batteries (which are not maintenance-free) or captive electrolyte AGM batteries which are maintenance-free (but which do require care in regulator selection). Special shallow-cycle maintenance-free batteries that withstand infrequent discharging may also be used in PV applications, and provided that the battery bank is appropriately designed, never require a DOD of more than 25%. A long-life battery in an appropriately designed PV system with correct maintenance can last up to 15 years, but the use of batteries which are not designed for long service life, or conditions in a PV system, or are part of a poor system design can lead to a battery bank which fails after only a few years.

Several other types of specific purpose batteries are available and these are described below.

- **Starting, lighting ignition batteries (SLI).** These batteries are used in automotive applications and have high discharge and charge rates. Most often they use electrode plates strengthened with either lead antimony in a flooded configuration, or lead calcium in a sealed configuration. These batteries have a good life under shallow-cycle conditions, but have very poor lifetime under deep cycling. SLI batteries should not be used in a PV system since their characteristics are not optimized for use in a renewable energy system because lifetime in a PV system is so low.

- **Traction or motive power batteries.** Traction or motive batteries are used to provide electric power for small transport vehicles such as golf carts. Compared to SLI batteries, they are designed to have a greater ability to be deep-cycled while still maintaining a long lifetime. Although this feature makes them more suited to a PV system than one which uses SLI batteries, motive power batteries should not be used in any PV systems since their self discharge rate is very high due to the use of lead antimony electrodes. A high self discharge rate will effectively cause high power losses from the battery and make the overall PV system inefficient unless the batteries experience large DOD on a daily basis. The ability of these batteries to withstand deep cycling is also far below that of a true deep-cycle battery. Therefore, these batteries are not suited to PV systems.
- **RV or marine batteries.** These batteries are typically a compromise between SLI batteries, traction batteries and true deep-cycle batteries. Although they are not recommended, both motive and marine batteries are used in some small PV systems. The lifetime of such batteries will be restricted to a few years at best, so that the economics of battery replacement mean that such batteries are typically not a long-term cost effective option.
- **Stationary batteries.** Stationary batteries are often used for emergency power or uninterruptable power supply applications. They are shallow-cycle batteries intended to remain close to fully charged for the majority of their lifetime with only occasional deep discharges. They may be used in PV systems if the battery bank is sized so that it never falls below a DOD of between 10% and 25%.
- **Deep-cycle Batteries.** Deep-cycle batteries should be able to maintain a cycle life of several thousand cycles under high DOD (80% or more). Wide differences in cycle performance may be experienced with two types of deep cycle batteries and therefore the cycle life and DOD of various deep-cycle batteries should be compared.