



19CH101– ENGINEERING CHEMISTRY

Unit-5 ENERGY SOURCES AND STORAGE DEVICES

SECONDARY BATTERY

A rechargeable battery, storage battery, or secondary cell (formally a type of energy accumulator), is a type of electrical battery which can be charged, discharged into a load, and recharged many times, as opposed to a disposable or primary battery, which is supplied fully charged and discarded after use. It is composed of one or more electrochemical cells. The term "accumulator" is used as it accumulates and stores energy through a reversible electrochemical reaction. Rechargeable batteries are produced in many different shapes and sizes, ranging from button cells to megawatt systems connected to stabilize an electrical distribution network. Several different combinations of electrode materials and electrolytes are used, including lead–acid, zinc–air, nickel–cadmium (NiCd), nickel–metal hydride (NiMH), lithium-ion (Li-ion), lithium iron phosphate (LiFePO₄), and lithium-ion polymer (Li-ion polymer).

Rechargeable batteries typically initially cost more than disposable batteries, but have a much lower total cost of ownership and environmental impact, as they can be recharged inexpensively many times before they need replacing. Some rechargeable battery types are available in the same sizes and voltages as disposable types, and can be used interchangeably with them.

Billions of dollars in research are being invested around the world for improving batteries and industry also focuses on building better batteries.

LEAD ACID BATTERY

The lead-acid battery is a type of rechargeable battery first invented in 1859 by French physicist Gaston Planté. It is the first type of rechargeable battery ever created. Compared to modern rechargeable batteries, lead-acid batteries have relatively low energy density. Despite this, their ability to supply high surge currents means that the cells have a relatively large power-to-weight ratio. These features, along with their low cost, make them attractive for use in motor vehicles to provide the high current required by starter motors.

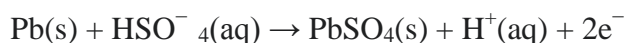
In the charged state, the chemical energy of the battery is stored in the potential difference between the pure lead at the negative side and the PbO₂ on the positive side, plus the aqueous sulfuric acid. The electrical energy produced by a discharging lead–acid battery can be attributed to the energy released when the strong chemical bonds of water (H₂O) molecules are formed from H⁺ ions of the acid and O²⁻ ions of PbO₂.^[9] Conversely, during charging, the battery acts as a water-splitting device.



Discharge

In the discharged state both the positive and negative plates become lead(II) sulfate (PbSO_4), and the electrolyte loses much of its dissolved sulfuric acid and becomes primarily water. The discharge process is driven by the pronounced reduction in energy when $2\text{H}^+(\text{aq})$ (hydrated protons) of the acid react with O^{2-} ions of PbO_2 to form the strong O-H bonds in H_2O (ca. -880 kJ per 18 g of water).^[9] This highly exergonic process also compensates for the energetically unfavorable formation of $\text{Pb}^{2+}(\text{aq})$ ions or lead sulfate ($\text{PbSO}_4(\text{s})$).

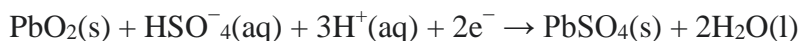
Negative plate reaction



The release of two conducting electrons gives the lead electrode a negative charge.

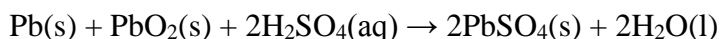
As electrons accumulate they create an electric field which attracts hydrogen ions and repels sulfate ions, leading to a double-layer near the surface. The hydrogen ions screen the charged electrode from the solution which limits further reaction unless charge is allowed to flow out of the electrode.

Positive plate reaction



taking advantage of the metallic conductivity of PbO_2 -

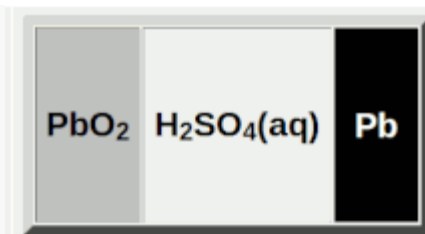
The total reaction can be written as



The net energy released per mol (207 g) of $\text{Pb}(\text{s})$ converted to $\text{PbSO}_4(\text{s})$, is ca. 400 kJ, corresponding to the formation of 36 g of water. The sum of the molecular masses of the reactants is 642.6 g/mol, so theoretically a cell can produce two faradays of charge (192,971 coulombs) from 642.6 g of reactants, or 83.4 ampere hours per kilogram (or 13.9-ampere hours per kilogram for a 12-volt battery) for a 2-volt cell. This comes to 167 watt-hours per kilogram of reactants, but in practice, a lead-acid cell gives only 30–40 watt-hours per kilogram of battery, due to the mass of the water and other constituent parts.



Charging



In the fully charged state, the negative plate consists of lead, and the positive plate is lead dioxide. The electrolyte solution has a higher concentration of aqueous sulfuric acid, which stores most of the chemical energy.

Overcharging with high charging voltages generates oxygen and hydrogen gas by electrolysis of water, which bubbles out and is lost. The design of some types of lead-acid battery allows the electrolyte level to be inspected and topped up with pure water to replace any that has been lost this way.

APPLICATIONS

Traction (propulsion) batteries are used in golf carts and other battery electric vehicles. Large lead-acid batteries are also used to power the electric motors in diesel-electric (conventional) submarines when submerged, and are used as emergency power on nuclear submarines as well. Valve-regulated lead-acid batteries cannot spill their electrolyte. They are used in back-up power supplies for alarm and smaller computer systems (particularly in uninterruptible power supplies; UPS) and for electric scooters, electric wheelchairs, electrified bicycles, marine applications, battery electric vehicles or micro hybrid vehicles, and motorcycles. Many electric forklifts use lead-acid batteries, where the weight is used as part of a counterweight.

LITHIUM ION BATTERY

A lithium-ion battery or Li-ion battery is a type of rechargeable battery composed of cells in which lithium ions move from the negative electrode through an electrolyte to the positive electrode during discharge and back when charging. Li-ion cells use an intercalated lithium compound as the material at the positive electrode and typically graphite at the negative electrode.



Charging and discharging

During discharge, lithium ions (Li^+) carry the current within the battery cell from the negative to the positive electrode, through the non-aqueous electrolyte and separator diaphragm.

During charging, an external electrical power source (the charging circuit) applies an over-voltage (a higher voltage than the battery produces, of the same polarity), forcing a charging current to flow **within each cell** from the positive to the negative electrode, i.e., in the reverse direction of a discharge current under normal conditions. The lithium ions then migrate from the positive to the negative electrode, where they become embedded in the porous electrode material in a process known as intercalation.

Energy losses arising from electrical contact resistance at interfaces between electrode layers and at contacts with current collectors can be as high as 20% of the entire energy flow of batteries under typical operating conditions.

The charging procedures for single Li-ion cells, and complete Li-ion batteries, are slightly different:

- A single Li-ion cell is charged in two stages:^{[64][65][unreliable source?]}
 1. Constant current (CC).
 2. Constant voltage (CV).
- A Li-ion battery (a set of Li-ion cells in series) is charged in three stages:
 1. Constant current.
 2. Balance (not required once a battery is balanced).
 3. Constant voltage.

During the *constant current* phase, the charger applies a constant current to the battery at a steadily increasing voltage, until the voltage limit per cell is reached.

During the *balance* phase, the charger reduces the charging current (or cycles the charging on and off to reduce the average current) while the state of charge of individual cells is brought to the same level by a balancing circuit, until the battery is balanced. Some fast chargers skip this stage. Some chargers accomplish the balance by charging each cell independently.

During the *constant voltage* phase, the charger applies a voltage equal to the maximum cell voltage times the number of cells in series to the battery, as the current gradually declines towards 0, until the current is below a set threshold of about 3% of initial constant charge current.



Periodic topping charge about once per 500 hours. Top charging is recommended to be initiated when voltage goes below 4.05 V/cell.^[dubious - discuss]

Failure to follow current and voltage limitations can result in an explosion.^{[66][67]}

Charging temperature limits for Li-ion are stricter than the operating limits. Lithium-ion chemistry performs well at elevated temperatures but prolonged exposure to heat reduces battery life. Li-ion batteries offer good charging performance at cooler temperatures and may even allow 'fast-charging' within a temperature range of 5 to 45 °C (41 to 113 °F). Charging should be performed within this temperature range. At temperatures from 0 to 5 °C charging is possible, but the charge current should be reduced. During a low-temperature charge, the slight temperature rise above ambient due to the internal cell resistance is beneficial. High temperatures during charging may lead to battery degradation and charging at temperatures above 45 °C will degrade battery performance, whereas at lower temperatures the internal resistance of the battery may increase, resulting in slower charging and thus longer charging times. Consumer-grade lithium-ion batteries should not be charged at temperatures below 0 °C (32 °F). Although a battery pack^[69] may appear to be charging normally, electroplating of metallic lithium can occur at the negative electrode during a subfreezing charge, and may not be removable even by repeated cycling. Most devices equipped with Li-ion batteries do not allow charging outside of 0–45 °C for safety reasons, except for mobile phones that may allow some degree of charging when they detect an emergency call in progress.^[70]



A lithium-ion battery from a laptop computer (176 kJ)

Batteries gradually self-discharge even if not connected and delivering current. Li-ion rechargeable batteries have a self-discharge rate typically stated by manufacturers to be 1.5–2% per month.

The rate increases with temperature and state of charge. A 2004 study found that for most cycling conditions self-discharge was primarily time-dependent; however, after several months of stand on open circuit or float charge, state-of-charge dependent losses became significant. The self-discharge rate did not increase monotonically with state-of-charge, but dropped somewhat at intermediate states of charge. Self-discharge rates may increase as batteries age. In 1999, self-discharge per month was measured at 8% at 21 °C, 15% at 40 °C, 31% at 60 °C. By 2007, monthly self-discharge rate was estimated at 2% to 3%.



USES AND APPLICATIONS

The vast majority of commercial Li-ion batteries are used in consumer electronics and electric vehicles. Such devices include:

- **Portable devices:** these include mobile phones and smartphones, laptops and tablets, digital cameras and camcorders, electronic cigarettes, handheld game consoles and torches (flashlights).
- **Power tools:** Li-ion batteries are used in tools such as cordless drills, sanders, saws, and a variety of garden equipment including whipper-snippers and hedge trimmers.
- **Electric vehicles:** electric vehicle batteries are used in electric cars, hybrid vehicles, electric motorcycles and scooters, electric bicycles, personal transporters and advanced electric wheelchairs. Also radio-controlled models, model aircraft, aircraft, and the Mars Curiosity rover.