

Common and Alternative Battery Chemistries

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FLOW BATTERIES

A flow battery is a rechargeable battery in which electrolytes flow through one or more electrochemical cells from one or more tanks. For simple flow batteries, it is a straightforward process to increase the energy storage capacity by increasing the quantity of electrolytes stored in the tanks. Electrochemical cells can be electrically connected in series or parallel, thus determining the power of the flow battery system. This decoupling of energy rating and power rating is an important feature of flow battery systems.

The interconversion of energy between electrical and stored chemical energy occurs in the electrochemical cell. This consists of two half-cells separated by a porous or an ion exchange membrane. As well as permitting ionic conduction, the separator minimizes the loss of the generated electroactive species in the half-cells and so maintains high coulombic efficiency. The redox reactions during charge and discharge take place at the electrodes of the half-cells. In its simplest form the electrodes themselves, usually carbon felt, are not altered by these electrochemical reactions. Cell voltage is calculated as the difference between the negative electrode reaction and that at the positive electrode. During charging, electrons released at the positive electrode through oxidation of the electroactive species in that half-cell are pushed round the circuit to the negative electrode where reduction of electroactive species in that half-cell takes place. These processes are reversed during discharge. The electroactive materials are known as redox pairs (i.e., chemical compounds that can reversibly undergo reduction and oxidation).

LEAD-ACID (PB) BATTERIES

Lead-acid batteries (LAB) consist of a lead dioxide positive electrode active material, a sponge metallic lead negative electrode active material, a separator between cathode and anode that prevents short circuits while allowing the flow of ions between the electrodes. The most common LAB format is "flooded" with the electrode submerged under free-flowing electrolyte. The gases are freely vented to the atmosphere which requires the battery to be continuously maintained in an upright configuration. There are valve regulated lead-acid (VRLA) versions of LABs in both absorbent glass mat (AGM) and gel in which the electrolyte is immobilized (no free acid under most conditions). The valves prevent air from entering but enable venting if more than a small positive pressure is exceeded. Both AGM and gel batteries utilize an oxygen recombination cycle to preserve water and minimize outgassing. Since they emit much less gas than flooded batteries under equivalent conditions, they are excellent choices for applications inside the car or passenger cabin as well as office or computer room installations and places where acid leakage could cause problems.

The fully charged cell voltage for an LAB is nominally around 2.08 to 2.18 volts, which depends on the electrolyte specific gravity value and ambient temperature for different applications. For automotive applications, lead batteries are primarily used as starter batteries for internal combustion engine (ICE) vehicles. They are also used as auxiliary batteries for purposes such as maintaining voltage levels while the main battery is restarting the engine. A low-voltage battery is also required for electric vehicle (EV) use because the traction battery may need to be taken offline under certain conditions. Because lead is used for both active materials and conducting components, these batteries may have lower specific energy compared to other chemistries. The nominal voltage is 2.0 volts per cell.

Lead-acid is the dominant chemistry for engine starting because of its robust design and low cost. It has excellent highrate performance over a wide temperature range and a low self-discharge rate. In starting service, lead-acid batteries can provide many thousands of shallow cycles.

For applications requiring deep cycling capability, specially designed lead-acid batteries are required. There are also specially designed lead-acid batteries for standby power and energy storage applications.

Like most other batteries, lead-acid batteries contain toxic and corrosive materials. Improper disposal would be hazardous to the environment. However, lead-acid batteries are easily and inexpensively recycled through a well-established infrastructure.

Lead-acid Variants

The introduction of vehicles equipped with start-stop functionality required that lead-acid batteries have improved charge acceptance and function at lower states of charge and with increased "micro" cycling or warm restarts. This challenge was met with enhanced flooded battery (EFB) and modified AGM designs. These enhancements may include paste additives, paste retention materials, lead alloys and new separators to provide over 10 times the number of engine starts, improve partial state of charge operation, and improve dynamic charge acceptance to support vehicle loads while the engine is shut off at traffic stops.

LITHIUM-ION BATTERIES

Lithium-ion is a large family of batteries. Several practical positive electrode active materials exist such as NMC — lithiumnickel-manganese-cobalt (NMC) (which itself comes in several varieties), lithium iron phosphate (LFP), and several others. They are often paired with a negative electrode of graphite or other forms of carbon as the negative electrode. Lithium titanate (LTO) can be used as a negative electrode for a low-energy, high-power version. Designs using silicon as a highcapacity negative electrode must deal with large volume changes during cycling. Solid-state designs may use lithium metal as the negative electrode instead of a substance capable of intercalating lithium ions into its structure. Electrolyte typically consists of a lithium salt dissolved in a solvent that is a flammable mixture of organic chemicals. Nominal cell voltage varies with electrode selection from about 2.2 up to about 3.7 volts per cell.

Some lithium-ion batteries, because of their low weight and high voltage, can provide over three times the energy density of traditional rechargeable batteries. The technology, however, is still advancing with extensive research to increase energy density, high-rate capability, cycle life, increased charging rates, safety, and cost reduction. With its higher energy density than other battery systems, it is most suited for EVs, plug-in hybrid electric vehicles (PHEVs), and hybrid electric vehicles (HEVs). Driving range for EVs can be somewhat limited, especially in colder weather. Although advancements are occurring on a regular basis.

Whereas the lead-acid battery consists of 55 to 60% lead and no other metals at a significant level, the lithium-ion battery contains less than 20% lithium. Copper, aluminum and graphite make up a large percentage of the battery content. The cathode can consist of a variety of metal compounds such as cobalt, manganese, nickel and/or iron, each with different characteristics and electrochemical performance.

The energy density of the battery is limited by the specific capacity of the electrodes and the associated nominal voltage. Much investment and research has therefore been devoted to alternative cathode materials.

Cells are manufactured in various form factors such as cylindrical, prismatic, and pouch. Many contain cell-level safety features such as special separators or current interrupt devices. When assembled into batteries (or modules that are part of a larger battery) a battery management system (BMS) is nearly always required to ensure the string voltage is balanced between the cells and usually includes a means to disconnect the battery from the circuit in the event of an internal fault or if external conditions are outside of allowable operating limits. A BMS may also communicate status information to other systems.

The cost of the lithium systems is still high and recycling of spent batteries is just starting to be taken seriously.

Lithium Variants

Lithium Cobalt Oxide (LiCoO₂) or (LCO)

This was the original lithium-ion battery. While lithium cobalt oxide has been the most widely used cathode material in lithium batteries for computers and cell phones to date, it has several drawbacks compared to the newer chemistries. While it provides moderate cycle life (approximately 500 cycles) and energy density, it is less thermally stable than other transition metal oxide or phosphate chemistries making it highly combustible under extreme abuse conditions.

Lithium Iron Phosphate (LiFePO,) or (LFP) and Lithium Manganese Iron Phosphate (LMFP)

Due to the ability to not release oxygen during abusive conditions, phosphate-based cathodes have superior thermal stability compared to other lithium-ion technologies. They have lower operating voltage than other cathode chemistries, thereby giving a lower specific energy and energy density. Lithium iron phosphate batteries offer a longer cycle life and can support higher currents and thus greater power density. They are a significant improvement over lithium cobalt oxide cells in terms of cost, safety and toxicity; however, they still contain a combustible electrolyte that can ignite if boiled and vented from the battery. Adding manganese increases the operating voltage of the phosphate system compared with iron alone.

Lithium Manganese Oxide Spinel (LiMn, O,) or (LMO)

In comparison with cobalt-based cathodes, lithium manganese oxide spinel provides a higher cell voltage and is more thermally stable. Manganese, unlike cobalt, is also a safe and more environmentally benign cathode material. Other benefits include lower cost and higher temperature performance. It does however suffer from a lower energy density.

Lithium Nickel Cobalt Manganese (LiNi, Mn, Co, O,) or (NMC)

Using a mixed metal content of nickel, manganese, and cobalt in the cathode gives energy density superior to $LiCoO_2$ and $LiFePO_4$. Power density performance is better than $LiCoO_2$ but not as high as $LiFePO_4$. This chemistry is itself a family with several practical ratios of nickel (Ni), manganese (Mn), and cobalt (Co).

Lithium Titanate Oxide (Li₄Ti₅O₁₂) or (LTO)

Lithium titanate can replace the graphite anode and work with various cathode materials. This anode is compatible with any of the cathodes discussed earlier in this paper but is generally used with high voltage manganese-based systems. They display superior high-rate capability and power density over a wide operating temperature range and are also safer than the graphite anode. Unlike graphite, they do not form a passivating layer with the electrolyte, thus increasing cycle life. However, lithium titanate batteries tend to have slightly lower energy density than graphite-based systems. This tends to make them more expensive when energy content is the critical design parameter.

Main Lithium Variants	Energy Density (Wh/kg)	Energy Density (Wh/l)	Cycle Life (100% DOD)	Price (\$/Wh)	Power	Thermal Runaway Onset Temperature °C	Voltage	Temperature Range °C
LiCoO ₂	170-185	450-490	500	0.31-0.46	1C	170	3.6	-20 to 60
LiFe PO ₄ (EV/PHEV)	90-125	130-300	2000	0.3-0.6	5C cont. 10C pulse	270	3.2	-20 to 60
LiFe PO ₄ (HEV)	80-108	200-240	>1000	0.8-1.2	30C cont. 50C pulse	270	3.2	-20 to 60
NCM (HEV)	150	270-290	1500	0.5-0.58	20C cont. 40C pulse	215	3.7	-20 to 60
NCM (EV/PHEV)	155-190	330-365	1500	0.5-0.58	1C cont. 5C pulse	215	3.7	-20 to 60
Titanate vs NCM/LMO	65-100	118-200	12000	1-1.7	10C cont. 20C pulse	Not susceptible	2.5	-50 to 75
Manganese Spinel (EV/PHEV)	90-110	280	>1000	0.45-0.55	3-5C cont.	255	3.8	-20 to 50

Lithium Chemistry Performance

NICKEL BATTERIES

Nickel Cadmium (NiCd)

Nickel Cadmium batteries use nickel oxide hydroxide NiO(OH)₂ positive electrode active material, metallic cadmium (Cd) as the negative electrode active material and an alkaline solution of sodium or potassium hydroxide (NaOH or KOH) for the electrolyte. An oxygen recombination cycle may allow them to be sealed for portable applications or flooded for stationary use.

NiCd batteries have been used for storing electrical energy in a wide variety of applications. They have a long cycle life and good high-rate performance over a wide temperature range with rapid recharge capability. The batteries can suffer from memory effect and high self-discharge at high temperatures. Cost is higher than lead-acid. The nominal voltage is 1.2 volts per cell.

Because cadmium metal is highly toxic and yields soluble compounds, its use in batteries is restricted or banned in many countries.

Nickel Metal Hydride (NiMH)

NiMH batteries replace the negative active material of a NiCd with hydrogen. The hydrogen is adsorbed into an appropriate metal mixture (alloy) that may include rare earth elements (lanthanum, cerium, neodymium, and/or praseodymium) and more common elements (nickel, cobalt, manganese, and/or aluminum). Higher capacity cells may use titanium or vanadium with zirconium or nickel that also includes smaller amounts of chromium, cobalt, iron, or manganese.

NiMH batteries have higher energy density than NiCd. They can be recharged rapidly but their high-rate performance is less than that of NiCd. They also suffer because of poor charge retention and higher cost anodes. They have been used successfully in hybrid electric vehicles, computers, cell phones, and other consumer electronic applications where they provide a safer operation than many lithium-ion variations. Cost is much higher than lead acid, but they usually have longer life. The nominal voltage is 1.2 volts per cell.

Nickel Zinc (NiZn)

The nickel zinc battery replaces the negative active material of the NiCd or NiMH battery with zinc. The system reduces the problem of a cadmium anode and gives good high rate and cycle performance and has relatively cheap materials. The nominal voltage is typically designated as 1.65 volts per cell. This battery has in the past suffered from the formation of dendrites and electrode reshaping, but this has been reduced through materials stabilizers and electrolyte additives giving cycle life similar to NiCd batteries.

SODIUM BATTERIES

Sodium-ion (Na+)

The sodium-ion battery, a secondary (rechargeable) battery that works mainly by exchanging sodium ions between the positive and negative poles, works in a similar way to lithium-ion batteries. The sodium salt, which is richer and cheaper than lithium salt, is the main component of the electrode material for sodium-ion batteries.

Zebra – Sodium Nickel Chloride (Na-NiCl₂)

The zebra battery is a molten salt battery that operates at 270 to 350° C — typically 300° C. The positive electrode active material is nickel chloride. The negative electrode active material is molten sodium. Molten sodium aluminum chloride (NaAlCl₄), which has a melting point of approximately 157°C, is used as the electrolyte. Separators are made from betaalumina ceramic.

The zebra battery has an attractive specific energy and good cycle life but is somewhat limited in power (90 Wh/kg and 150 W/kg). Its cost is higher than lead acid. The nominal voltage is 2.4 volts per cell.

When not in use, zebra batteries typically are required to be kept hot to be ready for use when needed. If shut down, the reheating process lasts 24 hours, and then a normal charge process of 6 to 8 hours is required for a full charge. This is a major issue for EV customers who may not use their vehicle every day or forget to put the vehicle on charge. It is also inefficient as it consumes energy when not in use.

RELATIVE ENERGY DENSITY OF SOME COMMON SECONDARY CELL CHEMISTRIES



EXEMPLAR OF SIDE-BY-SIDE COMPARISON OF BATTERY CHEMISTRIES

Chemistry	Energy Density (Wh/kg)	Energy Density (Wh/l)	Power Density (W/kg)	Power Density (W/l)	Voltage	Cycle Life	Temperature Range	Self- discharge	Environmental
Lead Acid	30-45	50-100	300-700	600-1400	2.1	low-med	-40 to +80	Low	Good (recycled)
Nickel Cadmium	40-60	100-160	140-160	250-300	1.2	very good	-20 to +50	High	Poor (cadmium)
Nickel Metal Hydride	60-90	200-280	200-250	550-700	1.2	good	-20 to +60	High	ОК
Lithium Ion	100-160	270-350	250-350	600-850	2.3-4.0	good	-20 to +60	Low	ОК
Lithium Polymer	130-200	250-350	260-450	600-800	3.7	OK-good	-20 to +60	Low- medium	ОК
Sodium Nickel Chloride	80-100	130-170	80-120	180-220	2.6	ОК	Molten salt	High	ОК

Chemistry	Cost	Strengths	Weaknesses	Applications
Lead Acid	Low (1X)	Low cost, robust, mature, wide tempera- ture, recycling, power	Weight, life, sulfation	SLI, motive power, standby, HEV (lower voltage)
Nickel Cadmium	Medium (2X)	Robust, cycle life, high charge rate, power	Cadmium, memory effect, weight, low voltage, cost	SLI, motive power, small power
Nickel Metal Hydride	Medium (3-4X)	Robust, cycle life, high charge rate	Self-discharge, weight, over discharge, low voltage, cost	HEV, small power
Lithium Ion	Medium (4-10X)	High voltage, light weight, cycle life	Safety, cost, life, multiple chemistries, cost, temperature	Small power, EV, PHEV, HEV
Lithium Polymer	High (6-10X)	High voltage, light weight, cycle life	Safety, cost, life, cost, temperature	Small power, EV, PHEV, HEV
Sodium Nickel Chloride	Medium (3X)	Robust, safety, operating condition	Power, restricted to large capacity, maintaining molten salt	Large motive power, large HEV

CHEMISTRY DEVELOPMENT

There is considerable room for the development of new materials for electrode chemistries that would offer the possibility of increasing the energy density of cells, thus making them more attractive for automotive traction applications. Some potential replacement cell chemistries are outlined below.

Transition Metal Oxide (TMO)/Silicon Alloy

Silicon-alloy materials are particularly attractive as replacements for a graphite anode, as they offer higher energy density than graphite (up to three times as much) and would be potentially much cheaper to manufacture than both soft, hard, and semi-graphitized carbons.

When used in conjunction with an advanced transition metal oxide (TMO) or even silicate-based cathodes, cells using these anode and cathode combinations have a theoretical energy rating of over 300Wh/kg, depending on the exact materials used.

Zinc-air Cells

Discharge is powered by the oxidation of zinc with oxygen from the air. Using a free external source of energy (oxygen) makes the energy density very attractive. Rechargeable cells use a catalyst to allow the reverse process of discharge to occur and make the cell rechargeable.

Although they offer high energy density, the downside is slow discharge rates and low power density; in other words, the energy cannot be accessed quickly.

Lithium-sulfur Cells

These have a high capacity, but many years of development have not solved the main problems — poor cycle life and high self-discharge. Work is ongoing.

Lithium-air Cells

Lithium-air cells potentially offer 5 to 10 times the energy density of existing lithium-ion cells.

A porous composite carbon and catalyst-positive electrode is used to achieve recharge with selective membranes that allow selective oxygen transfer but no water and electrolyte. Cells in development have demonstrated only limited cycling capability.



Learn more at BatteryCouncil.org