Review of Battery Types

There are two different types of batteries: Primary batteries and Secondary batteries (Rechargeable). Primary batteries, which are also called disposable batteries, often have higher energy densities than the rechargeable ones, and they have a lower self-discharge.

However, as the chemical reactions in these batteries are not reversible and the active materials cannot be restored to their initial forms, these batteries cannot be reliably recharged. The primary batteries are intended to be used once and then discarded, therefore they are not suitable for the energy storage systems.

The other type is rechargeable battery, which is also known as secondary battery because their electrochemical reactions are electrically reversible. There are many different types of rechargeable battery technologies, in which only four of them are leading the world market: *lead-acid*, *nickel-cadmium*, *nickel hydride* and *lithium-ion*.

1. Lead battery

The lead-acid batteries are the oldest type of rechargeable battery with a history of over 140 years, but they are still the most popular battery chemistry for different applications, as there is no cheaper alternative when weight is not a factor. This technology uses lead and lead dioxide as electrodes and an acid electrolyte of sulphuric acid and the advantage of this configuration is that the electrolyte takes part in reactions of both electrodes, and both electrodes turn into lead sulphate when discharging. The lead-acid batteries can be designed for not only deep discharge cycles but high discharge rate, or compromise of the two cycles. They have a lower self-discharge rate compared with the nickel batteries.

The lead acid batteries are widely used in a variety of applications; therefore, different designs are required due to different working environments and duty cycles. Some applications of such batteries are energy storage, emergency power, and powering hybrid vehicles, etc. Because some drawbacks such as: cell reversal, sulfation, storage for long periods, and imbalance of the cell voltage.

Lead-based batteries are currently the only available mass-market technology for SLI applications in conventional vehicles, including those with start-stop and basic micro-hybrid systems, due to their excellent cold cranking performance, reliability and low cost. Starter batteries of 12V are standardized globally.

Advanced lead-based batteries (absorbent glass mat or enhanced flooded batteries) provide start-stop functionality to improve fuel efficiency in all micro- hybrid vehicles currently on the market. In start-stop systems, the internal combustion engine is automatically shut down under braking and rest, reducing fuel consumption by up to 5-10%. In addition, some start-stop systems provide for regenerative braking, in which the vehicle’s kinetic energy is converted to electricity and stored within the lead based battery. Start-stop systems are already commercialized in several mass-market car models, with Pike Research estimating 37 million units for the global micro-hybrid car market by 2020.

In comparison with other battery technologies, lead-based traction batteries are not competitive for use in full hybrid electric vehicles or electric vehicles because of their lower specific energy and higher weight. However, for all electrified powertrains (from micro-hybrid to full electric vehicles), the 12V board-net and electronic component supply are currently provided by auxiliary 12V lead-based batteries (in addition to the larger traction battery). The 12V lead-based battery is also used to maintain the safety management of the larger traction battery. This is expected to continue for the foreseeable future.

All lead-based batteries use the same basic chemistry. In vehicles, three lead-based sub technologies are currently available:

• Flooded SLI batteries

• Enhanced flooded batteries (EFB)

• Absorbent glass mat (AGM) batteries

1.1 Flooded SLI batteries

Because of their lower cost, flooded lead based batteries are used in the vast majority of conventional ICE vehicles to provide starter, lighting and ignition (SLI) functions. Flooded lead-based batteries are characterized by a vented design and an excess of free-flowing electrolyte between and above the electrode stack.

1.2 Advanced lead-based batteries: AGM & EFB

Absorbent glass mat (AGM) and enhanced flooded (EFB) battery technologies have more recently been introduced for use in start-stop and basic micro-hybrid vehicles. These batteries have higher deep-cycle resistance and charge recoverability compared with flooded SLI batteries, in order to handle the more frequent stops and starts, and to provide a continued supply of electrical consumer units during the stop phase. The cranking performance of SLI batteries is carried over.

EFBs feature an improved flooded battery design with increased cyclic durability and increased ability to accept charge current, due to various changes in battery construction.

AGM batteries are valve-regulated lead-based batteries characterized by closed cells and an immobilized electrolyte held permanently in a glass fleece separator. This again allows for increased cyclic durability and improved charge recoverability.

Both EFB and AGM batteries are suitable for use in start-stop and micro-hybrid systems installed to improve fuel efficiency in conventional ICE vehicles. The deep cycling performance of AGM batteries makes them the technology of choice for vehicles with deeper cycling duty.

1.3 Chemistry

Lead-based batteries all use the same basic chemistry. The active material of the positive plate mainly consists of lead dioxide, and the active material of the negative plate is finely dispersed metallic lead. These active materials react with the sulphuric acid electrolyte to form lead sulphate on discharge and the reactions are reversed on recharge. Batteries are constructed with lead grids to support the active materials. Individual cells are connected in series within a single plastic case. The nominal voltage of a cell is 2.0V.

1.4 Components of lead-based batteries

- Lead and lead dioxide: average 60% of the total weight.
- Electrolyte: diluted sulphuric acid: average 30% of the total weight
- Others, like alloying components and polymers (separators PE, battery case PP): average 10% of the total weight.

1.5 Weight and lifecycle of lead-based batteries

The average total weight of a lead-based battery (flooded and EFB/AGM) for a compact passenger car is 18-20kg. The lifetime of an SLI battery heavily depends on usage patterns and the climate in the area of use. It can be estimated to be 5 – 7 years.

Successful efforts have been made to increase the efficiency of the lead-based battery by reducing the amount of lead needed to achieve the required performance. However, the increasing number of electrical components in cars and the additional functions that the

battery is required to cover (e.g. start-stop functionality for improving fuel efficiency) has imposed extra requirements on the automotive battery (i.e. deeper and more frequent discharge), meaning there has not been a corresponding reduction in battery weight for EFB and AGM technologies.

2. Nickel-cadmium (NiCd)

The Nickel-cadmium (NiCd) battery is a kind of rechargeable battery that uses nickel oxide hydroxide and metallic cadmium as electrodes, and an alkaline electrolyte (often potassium hydroxide). NiCd batteries are used in specific industrial applications in which particular performance characteristics are required, including an excellent ability to take mechanical and electrical abuse, an ability to operate at extreme temperatures, and a lower loss of capacity when ageing. Industrial applications include air transportation, train, tram and metro rolling stock, and stand-by uses in extreme weather conditions.

NiCd batteries are no longer used in vehicles, and are only available as spare parts for vehicles put on the market before 2008. The most attractive feature of the nickel-cadmium batteries is that they are more difficult to damage comparing with other batteries during deep discharge cycles. They can also sustain more cycles, and the lower internal resistance can also help achieve a higher maximum discharge rate. A problem preventing the large scale application of this battery technology is that the nickel-cadmium batteries suffers faster self discharge rate than other rechargeable batteries, and the cadmium used as the active material in one of the electrodes is toxic and expensive.

3. Nickel-metal hydride (NiMH)

The nickel-metal hydride (NiMH) battery is a type of rechargeable battery that designed to substitute for the nickel-cadmium cells. They have a similar size and a similar cell voltage but with more advantages. By using hydrogen-absorbing alloy as negative electrode instead of cadmium, this electrochemical technology is considered as "environmental friendly" because of the absence of toxic cadmium. The nickel-metal hydride batteries also have low internal resistance and the high cycle durability as the NiCds, and a NiMH battery can have two to three times the capacity of an equivalent size nickel-cadmium battery. However, the nickel-metal hydride batteries also have a similar high self-discharge rate as the nickel-cadmium batteries, and it also cannot afford complete discharges.

NiMH batteries are primarily used in mild hybrid and full-hybrid vehicles, where they have been the technology of choice over lithium-ion batteries because of their durability and lower cost.

At end of life, and in compliance with the Batteries and ELV Directives, all NiMH batteries from automotive applications are collected and recycled. The metals are used predominantly in the steel industry.

NiMH batteries have been the technology of choice in the HEV market over the last decade, due to their design flexibility, good energy density, high power performance and better environmental compatibility. This was the technology selected by Toyota when the Prius HEV was introduced in 1997. NiMH batteries are still significantly more expensive than lead based batteries, and have not been considered for use in SLI functions because of their inferior cold-cranking performance and other limitations.

3.1 Chemistry

Nickel-metal hydride batteries NiMH batteries comprise nickel hydroxide and hydrogen-absorbing alloys as basic components of the positive and negative active materials. These alloys operate in a concentrated alkaline electrolyte, usually with potassium hydroxide as the main constituent. The nominal voltage of a cell is 1.2V. Under charging, the hydrogen storing alloy (M) in the negative electrode absorbs hydrogen from the electrolyte, thus forming a metal hydride (MH).

NiMH batteries have a very good power performance. However, their low temperature performance and electrochemical stability at elevated temperatures are reduced when compared with NiCd batteries.

3.2 Components of nickel-metal hydride batteries

- Nickel metal in substrate materials and hydrogen storing alloy: 55% weight
- Nickel oxide in cathode materials: 10% weight
- Cobalt additive in cathode & anode: 5% weight
- Rare Earths in NiMH batteries 15% weight
- Others (separator, electrolyte, binders): 10% weight

3.3 Weight and lifecycle of nickel-metal hydride batteries

NiMH batteries have excellent life endurance in terms of capacity turnover. When only a low depth of discharge is required (i.e. 5%), as in hybrid vehicles, 20,000 cycles are possible over battery lifetime.

The high nickel content and the significant amount of cobalt makes the product of interest for recycling and reuse. Nickel is among the most highly recycled metals in the world today, with most nickel from batteries ending up in the manufacture of stainless steel.

4. **Lithium-ion (Li-ion)**

The lithium-ion (Li-ion) batteries are almost the perfect cell chemistry and are currently used a wide range of consumer electronics products including cameras, cell phones, laptops, etc.

Lithium-ion rechargeable battery systems entered the mass market of small-sized consumer applications in the early 1990s. Their up-front cost is at present significantly higher than corresponding battery technologies based on other chemistries. Therefore, larger-sized lithium-ion batteries are currently found in segments such as military and space applications, where their high energy and power density as well as their superior cycling ability create value. The high capacity of the active materials and a single cell voltage of up to 4.2V (depending on active material used) give lithium-ion the highest energy density of all rechargeable systems operating at room temperature.

They have many attractive performance advantages which make them also ideal for higher power applications such as automotive and standby power. First of all, the lithium-ion batteries have the highest energy density in all the rechargeable batteries now, which is about 4 times better than lead-acid. They are also capable for deep discharge and high discharge rate, with a relatively slow self discharge. There is no liquid electrolyte in the lithium-ion batteries, which means they are immune from leaking. However, just opposite to the lead-acid batteries, the most serious problem that discourages the lithium-ion batteries is the low economic efficiency comparing with the lead acid batteries .

In automotive applications, they are the product of choice for plug-in HEVs and full EVs, in which both these criteria are important. For hybrid vehicles, lithium-ion systems have started to compete with NiMH batteries and are now used at an industrial level in several hybrid cars on the market.

For use in SLI, start-stop and micro-hybrid applications, lithium-ion batteries still require improvements in cold-cranking ability and economic packaging (including cost level) to be considered a viable mass-market alternative to lead-based batteries. Lithium-ion batteries are used in hybrid and electric vehicles due to their high energy density and because their relatively greater expense is less of a barrier in these higher-end vehicles. Lithium-ion batteries are also being investigated for use in dual battery applications alongside a lead-based battery.

At end-of-life, all lithium-ion batteries from vehicles are collected. Industrial zero-waste recycling processes at present mainly target the recovery of nickel, cobalt and copper. The recycling of lithium is technically and industrially feasible, but as only a small quantity is used in each battery (between 1 to 2% of their total weight), and because only a small number of large-format lithium-ion batteries have reached end of life, this has not yet become economically viable.

4.1 Chemistry

There are several active materials used in lithium-ion rechargeable batteries. Systems using metallic lithium as a negative active material are called lithium-metal batteries, while systems based on carbon or lithium titanate as the negative active material are called lithium-ion. The positive active material is a lithiated metal oxide or a mixture of those components. The electrolyte is composed of fluorine-based lithium salts (such as LiPF6) dissolved in organic carbonate liquid mixtures. Non-aqueous solutions have to be used, as lithium reacts to water. A moisture-proof casing is essential to avoid moisture ingress and evaporation of the organic solvent.

While the battery is being charged, the lithium atoms from the positive electrode migrate as ions through the electrolyte toward the negative electrode, where they are deposited between carbon layers. This process is reversed during discharge. Lithium-based batteries are also available as lithium polymer batteries, which can, for example, use a lithium-metal alloy electrode in conjunction with a solid or gel-type electrolyte.

Different lithiated metal oxides are used by battery manufacturers in the battery's cathode or anode, each with unique performance characteristics.

4.2 Components of lithium-ion batteries

- Various metal oxide-based materials for cathode
- Carbon based materials for anode
- Lithium salts
- Copper for negative substrate and collectors
- Aluminium or steel for positive substrate and cell case
- Others (separator, electrolyte, binders)

4.3 Weight and life cycle of lithium-ion batteries

Most available lithium-ion battery systems provide excellent calendar life and life cycle endurance, with performance depending on the specific operational mode and temperature.

Recharge at low temperatures is restricted in order to avoid lithium-metal plating and early deterioration. With low depth of discharge (DoD), e.g. 2% to 5%, turnover figures of more than 20,000 nominal capacity throughput can be achieved. Under high DoD (e.g. 80%) more than 3000 cycles are feasible.

Various novel chemistries for the electrodes and the electrolyte are the subject of projects currently in the laboratory stage, with targets for first industrial applications to be established beyond 2025.

Summary of battery characteristics

Specifications	Lead Acid	NiCd	NiMH	Li-ion		
				Cobalt	Manganese	Phosphate
Specific energy density (Wh/kg)	30–50	45–80	60–120	150–190	100–135	90–120
Internal resistance[1] (mΩ)	<100 12V pack	100–200 6V pack	200–300 6V pack	150–300 7.2V	25–75[2] per cell	25–50[2] per cell
Cycle life[4] (80% discharge)	200–300	1000[3]	300–500[3]	500–1,000	500–1,000	1,000–2,000
Fast-charge time	8–16h	1h typical	2–4h	2–4h	1h or less	1h or less
Overcharge tolerance	High	Moderate	Low	Low. Cannot tolerate trickle charge		
Self-discharge/ month (room temp)	5%	20%[5]	30%[5]	<10%[6]		
Cell voltage (nominal)	2V	1.2V[7]	1.2V[7]	3.6V[8]	3.8V[8]	3.3V
Charge cutoff voltage (V/cell)	2.40 Float 2.25	Full charge detection by voltage signature		4.20		3.60
Discharge cutoff voltage (V/cell, 1C)	1.75	1.00		2.50 – 3.00		2.80
Peak load current Best result	5C[9] 0.2C	20C 1C	5C 0.5C	>3C <1C	>30C <10C	>30C <10C
Charge temperature	–20 to 50°C	0 to 45°C		0 to 45°C[10]		
Discharge temperature	–20 to 50°C	–20 to 65°C		–20 to 60°C		
Maintenance requirement	3–6 months[11] (topping chg.)	30–60 days (discharge)	60–90 days (discharge)	Not required		
Safety requirements	Thermally stable	Thermally stable, fuse protection common		Protection circuit mandatory[12]		
In use since	Late 1800s	1950	1990	1991	1996	1999