Reducing carbon emissions has become a growing concern for policy makers, car manufacturers and building designers alike. Consequently, batteries have taken centre stage in the search for alternative energy and the development of low-cost hybrid electric vehicles.

Rechargeable batteries – their evolution and beyond: Part I

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Breakthroughs in renewable energy and hybrid electric vehicle research depend on the availability of batteries with high energy density. This article examines how batteries continue to evolve to match the power supply challenges of different sectors ranging from portable electronic equipment to the automotive industry. We review design, operational characteristics and applications of lead acid, nickel-alkaline based, lithium-ion and zebra batteries and discuss the future of these batteries based on their environmental impact, energy density and competition from other technologies such as fuel cells and ultracapacitors.

The introduction of the lithium-ion battery in the early 1990s gave a huge boost to the development of portable computers as this battery's energy density is higher than that of its predecessors, NiCad and Nickel-metal hydride batteries. Batteries also play a major role in the storage of renewable energy.

Although renewable energy is plentiful, it is unpredictable and it is imperative to store the energy when it is generated for use when it is needed. Present developments in the design of renewable energy systems have seen batteries incorporated into both wind and solar PV systems.

Significant developments in battery chemistry, low-cost construction and new recharging methods in the 1990s have made the electric vehicle (EV) a practical alternative.

The nickel-metal hydride battery was considered at one time to be one of the most promising candidates in EV applications because of its (then) relatively high-power capability, long cycle life and no memory effect. However, the nickel-metal hydride system has been supplanted by lithium-ion batteries for this application. Table 1 shows a comparison between a range of rechargeable battery types.

**Lead-acid: the ageing dinosaur**

The lead-acid battery has always been the most important rechargeable electrochemical storage system, maintaining its position unchallenged for more than a century. Its dominance is due to a combination of factors such as low cost, versatility and the excellent reversibility of the electrochemical system.

<table>
<thead>
<tr>
<th>Pb acid (VRLA)</th>
<th>NiFe</th>
<th>NiZn</th>
<th>NiCad (sintered plate)</th>
<th>NiMH</th>
<th>Li-ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy/weight (Wh/kg)</td>
<td>30 – 40</td>
<td>30</td>
<td>60</td>
<td>40 – 60</td>
<td>30 – 80</td>
</tr>
<tr>
<td>Energy/size (Wh/litre)</td>
<td>60 – 75</td>
<td>55</td>
<td>170</td>
<td>50 – 150</td>
<td>140 – 300</td>
</tr>
<tr>
<td>Power/weight (W/kg)</td>
<td>180</td>
<td>100</td>
<td>&gt;900</td>
<td>150</td>
<td>250 – 1000</td>
</tr>
<tr>
<td>Charge/discharge efficiency (%)</td>
<td>70 – 92</td>
<td>65</td>
<td>—</td>
<td>70 – 90</td>
<td>66</td>
</tr>
<tr>
<td>Average self-discharge rate (at 20°C) (%) /month</td>
<td>3 – 20</td>
<td>20 – 40</td>
<td>&lt; 20</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>Calendar life (years)</td>
<td>2 – 8</td>
<td>30 – 50</td>
<td>—</td>
<td>3 – 10</td>
<td>2 – 5</td>
</tr>
<tr>
<td>Nominal cell voltage (V)</td>
<td>2.0</td>
<td>1.2</td>
<td>1.7</td>
<td>1.2</td>
<td>1.2</td>
</tr>
<tr>
<td>Operating temperature(°C)</td>
<td>-40 to 60</td>
<td>-10 to 45</td>
<td>-10 to 50</td>
<td>-40 to 50</td>
<td>-20 to 50</td>
</tr>
</tbody>
</table>

Table 1: Characteristics of the major rechargeable batteries.

Fig. 1: Valve regulated lead-acid (VRLA) batteries.
Lead-acid cells have extensive use both as portable power sources for vehicle service and traction, and in stationary applications ranging from small emergency supplies to load leveling systems. In terms of sales, the lead-acid battery occupies over 50% of the entire primary and secondary market, with an estimated value of R1342-billion per annum before retail mark-up.

The history of the lead-acid battery, more consistently named the "lead-lead oxide cell", commenced in 1859 with the construction by French physicist Gaston Planté of the first practical rechargeable cell consisting of two coiled lead strips separated by a linen cloth. This system forms the basis of the most widely used secondary battery at present. Today, lead-acid batteries (Fig. 1) are manufactured on every continent and in nearly every country. About 300-million lead-acid batteries are made every year. These range in size from 2 to 100 Wh starting, lighting and ignition (SLI) systems, to 40 MWh load leveling modules.

The great success of this system is due in part to its relatively low cost and the availability of the raw materials (lead and sulphur), ease of manufacture, long cycle life and favourable electrochemical characteristics. Its performance has been improved through more than a century of continuous research and development.

The lead-acid cell can be represented schematically as having a negative electrode of porous lead ("lead sponge") and a positive electrode of lead dioxide, electrode of porous lead ("lead sponge") schematically as having a negative electrode of lead oxide, and sulphuric acid as shown by the cell equations:

**Negative:**

\[ \text{Pb} + \text{H}_2\text{SO}_4 \leftrightarrow \text{PbSO}_4 + 2\text{H}^+ 2\text{e}^- \]

**Positive:**

\[ \text{PbO}_2 + \text{H}_2\text{SO}_4 + 2\text{H}^+ + 2\text{e}^- \leftrightarrow \text{PbSO}_4 + 2\text{H}_2\text{O} \]

**Overall:**

\[ \text{Pb} + \text{PbO}_2 + 2\text{H}_2\text{SO}_4 \leftrightarrow 2\text{PbSO}_4 + 2\text{H}_2\text{O} \]

According to the overall cell equation, the discharge reaction is from left to right while the recharge reaction is from right to left.

**Ageing effects in lead-acid batteries**

There are several significant effects associated with ageing lead-acid batteries, both in terms of number of cycles and age. The most commonly observed effects are:

- Loss of active material.
- Loss of electrolyte.
- Increased self-discharge.

**Loss of active material**

Electrode active materials are lost through sulphation and shedding. Sulphation is simply the formation of lead sulphate (PbSO₄) at both the positive electrode (PbO₂) and negative electrode (Pb) due to the chemical reaction between the electrode active materials and the electrolyte (H₂SO₄). This process occurs when the lead acid battery is discharged. The discharge reaction shows that sulphate is absorbed into the electrodes, resulting in the formation of insoluble lead sulphate on both electrodes. When the battery is recharged, however, lead sulphate decomposes into lead, lead dioxide and sulphuric acid according to the recharge reaction. The electrolyte becomes more diluted during discharge due to the active participation of sulphuric acid in the electrode reaction, and is re-concentrated during recharge. Consequently, the acid dilution provides a technique to determine the state of charge with the aid of acid density measurement. Sulphation of the battery plates ultimately reduces battery capacity because sulphate crystals (large or hard sulphate) cannot take part in the cell reactions.

Sulphate crystals may also obscure the surface of the plate, blocking pores and preventing acid from reaching useful active material buried underneath the sulphate, deeper inside the plate. Therefore, a lead-acid cell should never be left in a discharged state, as the active sulphate will become increasingly unrecoverable the longer it is left. It is sometimes possible to recover some of the lost sulphate using specialist recharging systems, but it is far more effective to minimise the likelihood of producing large, unrecoverable sulphate crystals initially.

A scanning electron microscope (SEM) trace of a new battery positive plate is shown in Fig. 2a. The large surface area and spongy texture are clearly visible. By contrast, Fig. 2b shows a heavily sulphated plate, and the large lead sulphate crystals are also clearly visible, obstructing the surface of the plate.

Fig. 3 shows the positive effect of a high current level pulsed recharge on a battery positive plate, which was conventionally charged and was originally sulphated. Compared to the SEM trace of the sulphated battery plate (see Fig. 2b), a remarkable difference in the size and quantity of the crystals on the battery plate can be observed. Upon close inspection, "holes" in the crystals can be seen as the sulphate crystals begin to dissolve and return sulphuric acid to the electrolyte.

Loss of active material also occurs through a process called "shedding". Shedding of active material takes place during overcharging and gassing. The gas evolved from the plate may be at a site deep inside one of the plate’s pores. As the gas forces its way out of the plate it can cause surface material to become detached (due to the rapid expansion experienced in the plate material), and the process is regarded as "shedding".

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Exposing the battery to a physical shock may also loosen the active material, causing it to collect in the sludge space at the bottom of the cell. Excessive corrosion of the support grid, onto which the active material is pasted, may cause pellets of active material to become detached, causing significant and sudden loss of capacity.

**Loss of electrolyte**

Loss of electrolyte, or more correctly loss of the water from the electrolyte (usually due to excessive gassing) leads to increased corrosion and sulphation of the plates and a reduced capacity, as parts of the plates are no longer in contact with the electrolyte. This is much more of a problem with “sealed” or valve regulated lead-acid (VRLA) batteries, as the electrolyte cannot be replaced if the level drops.

**Self-discharge**

Self-discharge is the rate at which battery capacity (charge) is lost when no external load is applied. All battery systems suffer from self-discharge to some extent because the equilibria of the electrode reactions are normally in the discharge direction since, thermodynamically, the discharged state is most stable.

Lead acid batteries naturally have a lower self-discharge rate than NiCad and nickel-metal hydride cells. However, many lead-acid cell plates have a grid sub-structure that is cast from an alloy of lead and antimony, typically 4% to 6% antimony (sometimes as much as 12%).

The purpose of the grid is to hold the active material mechanically and to conduct electricity between the active material and the cell terminals. Antimony is added to improve ductility, stiffness, tensile strength, and casting at lower temperatures.

However, as the positive plate grids corrode, antimony dissolves into solution, and is precipitated on the negative plate. Once deposited on the negative plate, the antimony provides a discharge site for hydrogen gas to be formed, discharging the electrode, and reducing the available capacity of the cell (i.e. self-discharge), as well as generating large quantities of potentially explosive gas resulting in loss of electrolyte.

**Environmental impact**

Surprisingly, lead-acid batteries are the environmental success story of our time because more than 97% of all battery lead is recycled. Compared to 55% of aluminium from soft drink and beer cans, 45% of newspapers, 26% of glass bottles and 26% of tyres, lead-acid batteries top the list as the most highly recycled end-user product.

The lead-acid battery gains its environmental edge from its closed loop life cycle. A typical new lead-acid battery contains 60% to 80% recycled lead and plastic. When a spent battery is collected, it is sent to a permitted recycler where, under strict environmental regulations, the lead and plastic are reclaimed and sent to a new battery manufacturer. The reprocessing cycle goes on indefinitely. This makes lead-acid battery disposal extremely successful from both environmental and cost perspectives.

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